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Synthesis, characterization and mixed micellization study of benzene sulphonate based

gemini surfactant with sodium dodecyl sulphate

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Abstract:

"Herein, we have shown the mixed micelle formation between anionic benzene sulphonate (viz.,sodium4,4'-(16,25-dioxo-15,17,24,26-tetraaza-hexatriacontane15,26-diyl)

dibenzenesulphonate [BSC14-C6-14CSB] and sodium 4,4'-(18,27-dioxo-17,19,26,28dibenzenesulphonate tetraaza-tetracontane15,26-diyl) [BSC16-C6-16CSB]) with conventional anionic surfactant (sodium dodecyl sulphate [SDS]) by conductivity and fluorometry methods. The conductivity measurements were done over a range of mole fractions of SDS at different temperatures to study the mixed micellization and thermodynamic parameters, while fluorescence measurements were performed over entire range of mole fraction of SDS in order to observe the aggregation and micro-polarity. The conductometric study confirms the synergism in all mole fractions of SDS with [BSC14-C6-14CSB] and [BSC16-C6-16CSB] at all temperatures. The Rubinghs regular solution theory (RST) was employed to evaluate micellar mole fraction, X_{i} , ideal micellar mole fraction, X^{ideal} , interaction parameter (β), activity coefficients (f_1 , and f_2) for both mixed micelles systems and Gibbs excess free energy (G^E) . The G^E values are negative for entire mole fraction range suggesting the formation of stable mixed micelles. In addition to this, other thermodynamic parameters like Gibbs free energy change of micellization (ΔG_{mic}), enthalpy change of micellization (ΔH_{mic}) and entropy change of micellization (ΔS_{mic}) were evaluated. Also, the aggregation number (N_{agg}) in micelles was calculated using pyrene probe fluorescence measurement. The binding constant, dielectric constant and micropolarity of mixed systems of SDS+ [BSC14-C6-14CSB] and SDS+ [BSC16-C6-16CSB] binary mixtures were obtained from the ratio of peak strength (I_1/I_3) from the pyrene probe fluorescence emission spectra.

Keywords: Gemini Surfactants; SDS; Fluorescence; Mixed micelles; Synergism; Aggregation number

1. Introduction

Amphiphiles having a polar hydrophilic head group and a stretchy hydrophobic hydrocarbon chain which on impulse forms aggregates in aqueous solution results in a supra-molecular assemblies simply known as micelles at a definite concentration called critical micelle concentration (cmc)[1, 2]. This amphiphilic nature of such molecules is accountable for their distinctive properties like self-aggregation, adsorption at the interfaces and dissolving of hydrophobic molecules that are responsible for their extensive utilize in the food. pharmaceutical, petrochemical, agrochemical, textile, paint and coating industries as wetting and foaming agents, emulsifying and suspension stabilizers[3]. The amphiphilic compounds have a unique feature of self-aggregation forming micelles that result due to the hydrophobic attraction by hydrocarbon chains of tail and electrostatic repulsion of hydrophilic groups[2, 4-7]. They have a unique property such as cmc, a necessary criteria for micelle formation to be used in drug delivery systems. The surfactants are usual amphiphiles having two core parts i.e., the hydrophilic part providing a highly polarized environment and other is the hydrophobic part that provides a low polarity environment[8]. These two regions are able to encapsulate drugs by improving their solubility, bioavailability and also shields them from harsh factors on parenteral administration[9]. Some physicochemical properties of gemini surfactants such as high surface activity, low cmc, better wetting and foaming ability, and high solubility are much better than conventional surfactants[10]. The two head groups and two hydrophobic hydrocarbon tails are joined by a rigid or flexible spacer [11, 12] have attracted great attention due to their unique dimeric structural design that renders their properties, especially higher effectiveness in reducing surface tension and low cmc values compared to their monomeric counterparts[13-23]. They can be used as templates for nanoparticles and biomembrane model systems as capable drug delivery as well as transfecting agents [12, 24-26]. In recent times, the examination and synthesis of numerous

new classes of gemini surfactant (cationic/anionic surfactants) has been reported like imidazolium[27-29], pyridinium[30, 31], pyrrolidinium[32], piperidinium[33], amino acid based[34], benzene sulphonate based[35] etc. These surfactants were able to interact with biological (macro) molecules, like serum albumin proteins, membrane lipids and macro cyclic oligosaccharides [36-45]. Great work has been reported on mixed micellization of anionic gemini surfactants with different additives like Kazuyuki *et al* has observed the interaction between two anionic gemini surfactants having N,N-dialkylamide and carboxylate groups in the molecule with anionic surfactants in 0.1 M NaCl at pH 5.0 [46]. Luis *et al*. has observed the mixed micellization between anionic amino acid based surfactants and bile salts [47]. Siddiqui *et al*. studied the mixed micellization of G5 gemini surfactants with conventional surfactants like SDS, CTAB and Brij35[48].

In this work, we report the synthesis and characterization of two anionic gemini surfactants, [BSC14-C6-14CSB] and [BSC16-C6-16CSB] having benzene sulphonate head groups with different chain lengths. Further, this paper highlights the mixed micellization of these gemini surfactants with conventional surfactant SDS in aqueous solution. The mixed micellization was studied by employing conductivity measurements and were further supported by fluorescence studies. The purpose of this study is to get an insight into the relative interaction of the synthesized gemini surfactants having dissimilar hydrophobic moiety but has same electrical charged head group with SDS.

2. Materials and Methods

2.1. Materials.

Lauric acid (>99.1% purity) Sigma Aldrich USA, chlorosulphonic acid (>98% purity, AR) Sigma Aldrich USA, thionyl chloride (>99% purity, AR), aniline (>97.5% purity, AR), lithium aluminium hydride (\geq 96% purity were purchased from Merck India, 1, 6hexamethylene diisocyanate (\geq 99% purity, GC) Sigma Aldrich USA and SDS (\geq 99% purity,

AR) Sigma Aldrich USA. All other reagents were used without additional purification. Milli Q water having specific conductivity $< 1.4 \ \mu\text{S cm}^{-1}$ was used in all experiments.

2.2. Synthesis of anionic gemini surfactants

Step I. Synthesis of N-phenyl myristamide

Myristic acid (0.10mol, 22.8g) was added to 100ml of thionyl chloride. The solution was stirred at 323.15 K for about 40 minutes and then at 363.15 K for another 3 hours. The excess thionyl chloride was removed by distillation to give myristoyl chloride (0.07mol, 17.2g). Aniline (0.04mol, 3.7ml) and triethylamine (24 ml) were dissolved in DCM (120ml), the stirred solution was cooled to 273.15 K in an ice bath and myristoyl chloride (0.07mol, 17g) was added in drop wise manner to the stirred solution under nitrogen environment. The reaction was continued for 48 hours at room temperature. Then the reaction mixture was transferred to a separating funnel followed by washing with water (200ml) and water layer was extracted twice with DCM. Finally, product was washed with brine and then dried with sodium sulphate anhydrous. The compound was checked by running column chromatography and crude product was purifying via recrystallization in hexane to give white solid as N-phenyl myristamide (yield 85%).

Step II. Synthesis of N- tetradecyl aniline

To a stirred solution of lithium aluminium hydride (0.04 mol, 1.51g) in tetrahydrofuran anhydrous (35 ml), N- phenyl myristamide (0.02mol, 6.06g) separately dissolved in tetrahydrofuran (35 ml) were added drop wise under nitrogen environment. The mixture was heated at reflux for 8 hours followed by cooling to 273.15K. Water was added to quench the reaction and the mixture was stirred for another 1 hour. The white precipitate was removed by filtration and filtrate was dried sodium sulphate anhydrous and then filtered and concentrated. The crude product was purified by running the column chromatography with n-

hexane ethyl acetate (10:2) as an eluent. The N-tetradecyl aniline was obtained as pale white solid (yield 78%).

Step III. Synthesis of precursor (hexane1, 6 diyl- bis 3, 3 tetradecyl phenyl urea)

Hexamethylene diisocyanate (0.01mol, 1.68ml) was added to stirred solution of N-tetradecylaniline (0.017mol, 5.05g) in 25ml DCM. The mixture was stirred over night at room temperature. After the evaporation of the solvent, the crude product was purified by running column chromatography with petroleum ether, ethyl acetate as an eluent. The product was further purified by recrystallization in ether to give greenish white powder (yield 82%).

Step IV. Synthesis of the surfactant I [BSC14-C6-14CSB]

The precursor (0.003mol, 2.24g) was cooled to 0 °C. under nitrogen environment and chlorosulphonic acid (0.0125mol, 1.45ml) was added and mixture was kept undisturbed for 3 hours. Then the mixture was poured in to 25ml ice cold water and pH of solution was maintained at 7.0 by adding sodium hydroxide (1M). After the solvent evaporation a pale-yellow residue was desalted in methanol. Finally, the product was purifying through column chromatography with DCM, methanol (4:1) as an eluent. The Surfactant I was obtained as a white solid (with yield 81%) shown in schame1.



sodium4,4'-(16,25-dioxo-15,17,24,26-tetraaza-hexatriacontane15,26-diyl) dibenzenesulphonate Scheme: 1 Synthesis of [BSC14-C6-14CSB]

(Synthesis of surfactant II was same but palmic acid is taken in place of myristic acid)

2.3. Methods

2.3.1. Conductivity measurements

Eutech Con 700 conductometer with a cell constant $1.002 \pm 0.001 \ \mu \text{Scm}^{-1}$ was utilized to monitor the specific conductance of the surfactant solutions after appropriate mixing. 13 mL of water (milli Q) was taken in a glass tube in which cell is immersed and glass tube is immersed in a thermostatic water bath Grant GD120 with temperature constancy of $\pm 0.01 \ \text{°C}$ to maintain the temperature. The specific conductivity of milli Q water is 1.80 μ S/cm measured at 25 °C. The reading was noted after every adding of pure anionic gemini surfactant, and its binary solution with SDS in the mole fractions of 0.1 to 0.9 mol/kg solution at various temperatures and plots of specific conductivity versus molar concentration were drawn in origin.

2.3.2. Fluorescence

Cary Eclipse fluorescence spectrometer (Agilent Technologies) with 1cm quartz cuvette path length has been used to perform fluorescence measurements. The instrument is equipped with xenon lamp 150W. The excitation wavelength was set at 335nm, and emission wavelength range was selected from 345 to 600 nm with a slit width of 5nm respectively. The pyrene was used as external probe and benzoquinone as quencher. Throughout measurements, the pyrene concentration was constant at 1μ M.[49]

3. RESULTS AND DISCUSSION

3.1. Characterization

The two anionic gemini surfactants, i.e. [BSC14-C6-14CSB] and [BSC16-C6-16CSB] were characterized by FT-IR, ¹H NMR and mass spectroscopy (see Figures: S_1 - S_3). The spectral results are given below

1.Sodium4,4'-(16,25-dioxo-15,17,24,26-tetraaza-hexatriacontane15,26-diyl)dibenzenesulphonate [BSC14-C6-14CSB].

(i) FT-IR (4000-600cm⁻¹ATR tablet) 3341cm⁻¹ [ν (N-H)], 2907cm⁻¹ [ν (CH₃)], 2848cm⁻¹ [ν (CH₂)], 1626cm⁻¹[ν (C=O)], 1567cm⁻¹ [ν (N-H bending)], 1442cm⁻¹[ν (C-N bending)], 1397cm⁻¹ [ν (C-C bending)], 1238cm⁻¹ [ν _{As} (SO₂)], 1093cm⁻¹[ν _S (SO₂)], and 602 cm⁻¹ [ν (C-H in plane bending)].

(ii) ¹HNMR Bruker Avance II 400 MHz (DMSO) δ= 0.87ppm (t, 6H), 1.25ppm (m, 48H),
2.58ppm (m, 8H), 3ppm (t, 2H attached to nitrogen), 7.6ppm (s, for aromatic hydrogen's).

(iii) ESI-MS (HP1100LC-MSD): $[C_{48}H_{80}N_4O_8S_2Na]^+$: calcd: 944, found 939.8, $[C_{35}H_{53}N_4O_8S_2Na]$: calcd: 767, observed 770, $[C_{37}H_{38}N_2O_4SNa]^+$: calcd: 435, observed: 441, $[C_9H_8N_2O_4SNa]^+$: calcd: 252, observed: 257, $[C_7H_4NO_4SNa]$: calcd: 222, observed: 227.3, $[C_{13}H_{27}]$: calcd: 181, observed: 179.1.

2. Sodium 4,4'-(18,27-dioxo-17,19,26,28-tetraaza-tetracontane15,26-diyl) dibenzenesulphonate [BSC16-C6-16CSB].

(i) FT-IR (4000-600cm⁻¹ATR tablet) 3334cm⁻¹ [ν (N-H)], 2907cm⁻¹ [ν (CH₃)], 2853cm⁻¹ [ν (CH₂)], 1619cm⁻¹[ν (C=O)], 1573cm⁻¹ [ν (N-H bending)], 1476cm⁻¹[ν (C-N bending)], 1370cm⁻¹ [ν (C-C bending)], 1252cm⁻¹[ν _A (SO₂)], 1100cm⁻¹ [ν _S (SO₂)], and 608cm⁻¹ [ν (in plane C-H bending)].

(ii) ¹HNMR Bruker Avance II 400 MHz (DMSO) δ = 0.91ppm (t, 6H), 1.25ppm (m, 52H), 2.59ppm (m, 8H), 2.61ppm (s, 2H attached to nitrogen), 7.39ppm (s, for aromatic hydrogen's).

(iii) ESI-MS (HP1100LC-MSD): $[C_{50}H_{84}N_4O_8S_2Na]^+$: calcd: 972, observed: 996, $[C_{36}H_{55}N_4O_8S_2Na]$: calcd: 782, observed: 780.5, $[C_{37}H_{38}N_2O_4SNa]^+$: calcd: 449, observed 450.7, $[C_9H_8N_2O_4SNa]^+$: calcd: 251, observed: 249, $[C_7H_4NO_4SNa]$: calcd: 221, observed: 220.9, $[C_{13}H_{27}]$: calcd: 211.1, observed: 211.1.

3.2. Mixed micellization

The mixed micellization of [BSC14-C6-14CSB] and [BSC16-C6-16CSB] with SDS was observed by conductivity method. The specific conductivity values of gemini surfactant [BSC14-C6-14CSB] and [BSC16-C6-16CSB] with SDS enhanced linearly with the increasing concentration of gemini surfactant in the bulk till a split point is reached at the cmc and then further increases with a reduced slope at higher concentration. The lesser slope beyond cmc is due to the reduced mobility of the micelles as that of the free surfactant monomers. The g values of [BSC14-C6-14CSB] are smaller than that of [BSC16-C6-16CSB], which is due to the more hydration of former ion than the latter, which gets weakly adsorbed on the micellar surface. The cmc value of both the gemini surfactants and pure SDS increase slightly with increase in temperature (Figure: 1), that may be ascribed due to the increased thermal molecular motion, which results from the long-lasting spatial distance and weak interactions between the hydrophobic chains of the surfactants. Thus, enough surfactant concentration is required to form the micelles at higher temperature. Moreover, the value of cmc at a particular temperature lowers with enhance in the gemini surfactant chain length revealing that the hydrophobic alkyl chain has high effect on the gemini surfactant micellization and is in good harmony with the results reported previously [50, 51]. The increase in temperature can speed up the motion of molecules and ions in the solution and gives favourable environment to the counter ions to separate from the electrostatic repulsion of the micelles, As a consequence of this, the degree of dissociation (g) increases with the increase in temperature as given in Table S1. It is also observed that g value of the [BSC14-C6-14CSB] is slightly smaller than those of [BSC16-C6-16CSB] with the identical spacer length. Further, the value lowers with the reduction of the chain length, which is mainly due

to the change in the charged surface density of the micelles. The two anionic head groups of the gemini surfactant [BSC14-C6-14CSB] and [BSC16-C6-16CSB] are bonded collectively by the linker by a covalent bond and gets more closely packed when the length of spacer gets shorter and helps to increase the charge density of hydrophilic head group. Thus, the electrostatic interaction among the surfactant ions and counter ions gets stronger and the degree of dissociation (*g*) is reduced significantly. The micelles are not considered as good charge carriers due to their low mobility, because they have more weight and hydrodynamic radius which reflects the degree of counter-ion binding with negatively charged micelle surface [52, 53]. The values of cmc for each surfactant mixture were evaluated from breakpoint in the plot of specific conductivity vs. surfactant concentration as reported in literature [54] (Figure: S4, Figure: S5). The cmc values of all the mole fractions of SDS with gemini surfactant increases up to certain temperature (308.15 K) and then decreases. The degree of dissociation (*g*) has been obtained from the ratio of the slopes in the post and premicellar regions of the specific conductivity vs. concentration of surfactant. The degree of counter ion binding was evaluated by the following equation [55].

$$\alpha = (1 - g) \tag{1}$$

where g is degree of dissociation, the exactness of cmc determination of the specific conductivity vs. concentration of surfactant profile depends upon an unexpected change of conductivity of the pre and post cmc values[56], that is observed in all binary systems and also for pure SDS and gemini surfactant [BSC14-C6-14CSB]/ [BSC16-C6-16CSB]. The cmc generally defines very supportive nature of the aggregation process of both gemini and conventional amphiphiles determined from conductivity measurements (Table 2) and be in good agreement with each other. The cmc obtained by conductivity measurements were used for further calculations like, X^{ideal} , β , X_I etc. Different mole fractions of SDS (α =0.1, 0.3, 0.5, 0.7, 0.9) were taken and gemini surfactant concentrations was kept as 30 µM for all the mole

fractions. The pseudo phase models were used to examine the properties of ideal or non-ideal behaviour of mixed micelles of SDS+[BSC14-C6-14CSB] and SDS+[BSC16-C6-16CSB] accordingly. The micelles are thought to be a macroscopic phase and are in equilibrium through their subsequent monomers in a solutions[57]. The values of cmc for the binary systems are found to vary as its ideal mixing behaviour evaluated by the Clint equation[58].

$$\frac{1}{cmc^*} = \frac{\alpha_s}{cmc_s} + \frac{(1 - \alpha_s)}{cmc_g}$$
(2)

where α_s represents mole fraction of the SDS in the bulk, cmc_G and cmc_s are the micellar concentrations of [BSC14-C6-14CSB]/ [BSC16-C6-16CSB] and SDS correspondingly and cmc* is the critical micelle concentration of the mixture under ideal mixing states. The Clint model is reliable through a pseudo phase thermodynamic approach[58], that grants the calculation of the micellar mole fraction of the gemini surfactants [BSC14-C6-14CSB]/[BSC16-C6-16CSB] in the ideal state

$$X^{ideal} = \frac{\alpha_s cmc_G}{\alpha_s cmc_G + (1 + \alpha_s) cmc_s}$$
(3)

The cmc ideal (X^{ideal}) values obtained from Clint Model, experimental cmc value and mole fraction of the SDS in the mixed micelle evaluated by ideal mixing behaviour are given Table 1. The X^{ideal} values of SDS with [BSC14-C6-14CSB]/[BSC16-C6-16CSB] predicted by the Clint model reveals non-ideal mixing behaviour due to synergism among the dissimilar amphiphiles in the mixed micelles[59]. These values increase with increasing temperature for all mole fractions. The Rubingh regular solution theory (RST) [59, 60] was applied to binary mixtures in non-ideal state in surfactants with great success, because of its simple approach. The type of interactions in mixed micelle between two surfactant species is confirmed by a dimensionless parameter β . The β can be calculated from equation: 4.

$$\beta = \frac{\ln(\alpha_s cmc_{mix} / X_1 cmc_s)}{(1 - X_1)^2} \tag{4}$$

Here the cmc_{mix} is the experimental cmc of SDS+[BSC14-C6-14CSB] and SDS+[BSC16-C6-16CSB] mixture and X_1 is the mole fraction of the SDS in the mixed micelle and can be evaluated from equation: 5.

$$\frac{X_1^2 \ln(\alpha_s cmc_{mix} / X_1 cmc_s)}{(1 - X_1)^2 \ln[(1 - X_s) cmc_{mix} / (1 - X_1) cmc_G]} = 1$$
(5)

The Gibbs excess free energy (G^E) was evaluated from

$$G^{E} = \beta x_{S} x_{G} R T \tag{6}$$

where β represents interaction, parameter obtained by equation: 4, x_S and x_G stands for the mole fractions of conventional surfactant (SDS) and gemini surfactants [BSC14-C6-14CSB]/[BSC16-C6-16CSB] correspondingly, R represents gas constant and T absolute temperature. The $X_{I, \beta}$, G^{E} were calculated by means of regular solution theory for binary solutions of [BSC14-C6-14CSB]/[BSC16-C6-16CSB] surfactants and are given in Table 1. The value of X_1 increase with rising of mole fraction and shows a uniform trend with increasing temperature, which suggests formation of mixed micelle between gemini surfactants and SDS is favoured and additional molecules of SDS put in to the mixed micelle formation. Also, X^{ideal} enhances with rising of mole fraction at all temperature. The values of X^{ideal} are greater than X_l revealing that the mixed micelle contains enough SDS monomers as compared to the mixed ideal state. The type of interaction in mixed micelles among the components can be studied by using interaction parameter β . The negative value of β reveals synergism and positive value indicates antagonism, which arises due to the attractive or repulsive interactions among the amphiphiles in the supra molecular mixed aggregates[60]. Generally β with negative value reveals a synergistic interaction, which means that in mixing there is a strong attraction among the components than before mixing [54]. Whereas β with positive value means antagonism is the case of weak interaction and zero value demonstrate no interaction[61, 62]. The experimental values of β for the mixed systems of SDS with

[BSC14-C6-14CSB]/[BSC16-C6-16CSB] are negative for entire range of mole fractions at all temperatures. The synergism in the formation of mixed micelles of [BSC14-C6-14CSB]/[BSC16-C6-16CSB] gemini surfactant rich composition arises due to a combined effects of existing hydrophobic interactions between the gemini surfactant chains and the hydrophobic conventional surfactants chains with some hydrogen bonding in the mixed micelles[63, 64].

The β have to be constant above a certain composition range as per regular solution theory for most of the non-ionic surfactants mixtures. Though, for various ionic surfactant binary combinations, variation of β with composition is repeatedly observed. The huge differences in surfactant head group size and hydrophobic tail has been reported as compositiondependent interaction parameter, but RST does not acquire the consideration of size or shape of the supra molecular aggregates [65-67]. The interaction of the SDS with [BSC14-C6-14CSB] gemini surfactant mixtures is synergistic type and increases with increasing mole fraction. This type of result is also reported in the mixtures of CTAB and CPC [66] and also in NaC-sodium dodecanoate in Tris hydrochloric acid buffer, with negative values of β (for $\alpha_{\text{CTAB}} < 0.5$ or $\alpha_{\text{SDS}} < 0.5$ respectively) [68] and positive β value at elevated mole fractions. Hence these surfactants have similar head groups but different hydrophobic tails. The antagonistic interactions in the binary mixtures of different amphiphiles differ either in size of head group or hydrophobic moieties, that can be due to the geometric packing in supra molecular aggregates of amphiphilic molecules [69, 70] and is reported in a few binary mixers of cationic gemini surfactant and the zwitter ionic lipid 1,2-dioleoyl-syn-glycero-3phosphoethanolamine (DOPE).[71] In SDS and gemini surfactant mixed systems the values of X₁ (Table 1/ Table 2) indicates that [BSC14-C6-14CSB]/[BSC16-C6-16CSB] participates in the mixed aggregate formation of gemini surfactants because of same hydrophobicity thus enhances the incorporation to large extent in the mixed micelles. Hence the mixed micelles of

SDS and [BSC14-C6-14CSB]/[BSC16-C6-16CSB] at higher mole fractions are more affluent of SDS surfactant when related to their ideal values obtained from Clint model of ideal mixing behaviour with $X_I < X^{ideal}$ for the entire mole fractions. This type of results has been reported in mixtures of cationic bis-dodecyldimethylammonium gemini cationic surfactants of type 12-s-12 with changeable length of spacer and the NaTDC (bile salt sodium taurodeoxycholate) [72]. The G^E values are negative suggesting that the mixed micelle formation was stable as relevant to those pure components. The value of G^E decreases with increase in micellar mole fraction revealing that mixed micelles formed are not stable due to packing geometry constraints of hydrophilic head group induced by incompatibility of hydrophobic core[73].

3.3 Thermodynamics of micellization

The micelle formation can be viewed as an association, dissociation process by which surfactant molecules and micelles coexist as according to mass action model and show separation and aggregation constantly to reach dynamic equilibrium finally[74]. The process of micellization in gemini surfactant can be represented as given below

$$nG^{2-} + 2\alpha nNa^{+} \rightleftharpoons M^{2n(1-\alpha)-}$$
(7)

where G^{2-} , Na^+ , and $M^{2n(1-\alpha)-}$ corresponds to the anionic gemini surfactant, counter ion, and the aggregation of monomer, respectively, n is the micellar aggregation number and α represents the degree of counter ion binding. The Gibbs free energy of micellization per mole of the gemini surfactant (ΔG_{mic}) is given by

$$\Delta G_{mic} = RT \left[-\frac{1}{n} \ln \alpha_{M^{2n(1-\alpha)-}} + \ln \alpha_{G^{2-}} + 2\alpha n \ln_{Na} + \right]$$
(8)

where R is ideal gas constant, T is the temperature in Kelvin, and a is an activity of an ion. As micelles are formed by means of huge number of monomeric units the n value is very

large and the first term in the parentheses will be minute and could be neglected. Further, the activities of the ions have the following correlation[75].

$$\alpha_{G^{2-}} = \frac{1}{2}\alpha_{Na^+} = cmc \tag{9}$$

Ion activities can be replaced by x_{CMC} i.e. cmc expressed in mole fraction of the surfactant in the aqueous solution at very low concentration. The Gibbs free energy of micellization (ΔG_{mic}) to each gemini surfactant at a given temperature can be expressed as [74, 76, 77] $\Delta G_{mic} = (3 - 2\beta)RT \ln X_{cmc}$ (10)

According to the following Gibbs-Helmholtz equation (11)

$$\left[\partial \left(\frac{\Delta G_{mic}/T}{\partial T}\right)\right]_{P}P = -\frac{\Delta H_{mic}}{T^{2}}$$
(11)

the enthalpy changes of micellization, ΔH_{mic} is evaluated from the subsequent equation:

$$\Delta H_{mic} = -(3 - 2\beta)RT^2 \begin{bmatrix} \partial \ln X_{cmc} \\ \partial T \end{bmatrix}_p$$
(12)

The variation of lnx_{CMC} with temperature has been empirically estimated by a second degree polynomial and has been reported as[78].

$$\ln X_{cmc}(T) = gT^2 + hT + j \tag{13}$$

and

$$d = j' + hT + gT^2$$

$$\tag{14}$$

where *g*, *h*, *j* are polynomial constants and can be obtained from least squares regression analysis by fitting lnx_{CMC} as function of the respective temperature (*T*), after that the value of ΔH_{mic} is calculated. The entropy change (ΔS_{mic}) can be obtained from following expression:

$$\Delta S_{mic} = \frac{\Delta H_{mic} - \Delta G_{mic}}{T} \tag{15}$$

The value of cmc, α , ΔG_{mic} ΔH_{mic} and ΔS_{mic} for SDS, pure gemini surfactant [BSC14-C6-14CSB]/[BSC16-C6-16CSB] are given in Table: S1. The process of micellization is temperature dependent, thus different thermodynamic parameter has been evaluated from the values of cmc. The plots of Gibbs free energy (ΔG_{mic}), enthalpy change (ΔH_{mic}), and entropy change (ΔS_{mic}) of micellization against temperature are given in Figure: 2 respectively. The values of ΔG_{mic} are negative at various temperatures for both the gemini surfactants suggesting that the process of micellization is a spontaneous. However, the values of ΔG_{mic} become more negative with decrease in length of the linker group at a particular temperature. It has been observed that the ΔH_{mic} values are negative at various temperatures, which highlights that the micellization is an exothermic process. The ΔH_{mic} value enhances with the rise of temperature. In ionic surfactant, the increase in temperature affects the ΔH_{mic} generally by two reasons. (i) Increase in temperature can break the structure of water molecular aggregation around the alkyl chain, which increases the value of ΔH_{mic} greatly. (ii) The micelle is negatively associated by condensation of alkyl chains with increase in temperature and induces ΔH_{mic} to decrease negatively[79]. Therefore, for each gemini surfactants [BSC₁₄-6-14CSB], [BSC16-6-16CSB], the values of ΔH_{mic} becomes less negative with the rise of temperature. The values of ΔS_{mic} are observed positive (except 0.7 α in [BSC16-C6-16CSB] and enhance with the rise in temperature, reveals that the icebergs formed by ordering of water molecules surrounding the hydrophobic tails were destroyed by the micellization, and the system gets further disordered. Further, the destruction of structure of iceberg is strong as compared to haphazardly oriented gemini anions by a solvated form to the micelles. Thus with increase of temperature reduces the number of the ordered water molecules and the demolition of the iceberg structure relieves less water molecules free when the micellization process was carried out at higher temperatures[80]. Thus, it is obvious that $T\Delta S_{mic} > \Delta H_{mic}$

indicating that the micellization of each gemini surfactant and its binary mixtures with SDS in aqueous solution is an entropy-driven process.

- 3.4 Fluorescence Measurements.
- 3.4.1 CMC from fluorescence probe

Fluorescent probes are widely used to determine different micellar parameters like cmc (Figure: 3a,3c), micro fluidity, aggregation number (N_{agg}), experimental dielectric constant (D_c)[64]. In micellar medium it depends upon the chemical structure of fluorophore and micellar solution properties. The pyrene solvent polarity is distinct by the I_1/I_3 intensity emission ratio, where I_1 represents S_1 to S_o transition and I_3 corresponds to S_1 (v= 0) to S_0 (v = 1) intensity transition in pyrene. The I_1/I_3 increases with increasing dipolarity of solvent and acts as function of solvent dielectric and refractive index by a dielectric cross term [$f(\varepsilon,n^2)$][81]. The Figure: 3b, 3d shows I_1/I_3 vs. log concentration of gemini surfactant [BSC14-C6-14CSB], [BSC16-C6-16CSB] respectively. A moderately drastic change in I_1/I_3 represents the onset of micelle formation known as cmc. This suggests that hydrophobic pyrene gets incorporated in to the micellar pseudo phase upon micellar formation. The cmc evaluated from pyrene fluorescence in presence of [BSC14-C6-14CSB], [BSC16-C6-16CSB] respectively were 0.45 and 0.31× 10⁻⁶M and are in good conformity with the results obtained from conductance measurements.

3.4.2 Aggregation number and Ksv

The aggregation number of gemini surfactants with different mole fractions of SDS was obtained from quenching of pyrene probe by benzoquinone (BZQ). The fluorescence of the different mole fractions using pyrene probe has been done. It is acknowledged that the quantitative relation of initial and third vibronic peaks (I_1/I_3) of pyrene spectrum (Figure: S6, Figure: S7) shows the polarity of the medium in which it is dissolved. The I_1/I_3 results for all the binary mixtures of the two gemini [BSC14-C6-14CSB]/[BSC16-C6-

16CSB] with SDS over the complete mole fraction range were drained to calculate the micro polarity. Every spectrum shows one to five vibronic peaks at totally different wavelengths. The micellar aggregation numbers (N_{agg}) were measured by steady state fluorescence measurements at totally different mole fractions. The surfactant solution (30×10^{-6} M) was added and pyrene concentration was kept constant (1×10^{-6} M). The quencher concentration was varied from zero to a 120 10⁻⁶M. It has been observed that the presence of a quencher within the micelle is more as compared to life time of fluorescence probe. The pyrene fluorescence quenching by BZQ was accustomed to verifying the N_{agg} . The model planned by Turro and Yekta were utilized to determine the fluorescence quenching and size of micelles. According to this model, the probability P_n of an existing micelle that contain n quencher molecules[79].

$$P_n = \frac{X^n}{n!} \exp(-m) \tag{16}$$

where *m* is the average number of quencher (*Q*) per molecule of micelle (*M*), m = [Q]/[M]. The fluorescence of the probe (pyrene) molecule occurs in absence of quencher in the micelle (i.e. n = 0) and the probability gets equal to $P_0 = \exp(-m)$. The intensity I of pyrene emission is thus directly proportional to P_0 . If the gemini solution do not have any quencher, the fluorescence probe intensity becomes equal to I_0 , and thus probability of fluorescence is equal to 1. Therefore, following expression can be used for calculating aggregation number (N_{agg}).

$$\ln \frac{I_0}{I} = \frac{([GS] - cmc)}{(N_{agg}[BZQ])}$$
(17)

where Gs is concentration of the mixture and BZQ is the quencher concentration of BZQ as a quencher. The ratio of $ln I_0/I$ verses concentration of the quencher [BZQ] (Figure: S8, Figure: S9) give a straight-line having slope equal to reciprocal of micellar concentration. Thus, knowing the total concentration of mixture Gs and the concentration of surfactant non-associated in micelles, this is nearly equal to the cmc, to calculate the aggregation number.

The aggregation numbers were obtained from steady state measurements in pure and mixed systems which are given in Table 2. The observed values of N_{agg} of the various mole fractions of SDS-[BSC14-C6-14CSB] mixture i.e., 0.1, 0.3 and 0.7 is lower than that for pure gemini surfactant, in such cases the presence of SDS as co-solvent in aqueous [BSC14-C6-14CSB] is able to minimize the N_{agg} to higher extent and may be due to the more repulsive interactions[82]. However, the overall trend is increasing suggesting that repulsive interactions among the hydrophilic groups of anionic SDS molecules are dominant. While in SDS-[BSC16-C6-16CSB] mixture N_{agg} values of pure gemini surfactant are lower than that of entire mole fractions used. The increase of N_{agg} with increasing mole fraction is associated with the increase in repulsive interactions between the hydrophilic groups of anionic SDS molecules, which are gradually substituted by gemini surfactants. As a result, the usual surface optimal area per head group of the surfactant increases. Smaller aggregation number means higher charge of density. The size of mixed micelles in solution is determined by the electrostatic repulsions among the hydrophilic groups because of steric hindrance caused by hydrophobic tails. Thus, the above observed findings can be explained based on quenching mechanism. The hydrophobic environment strength can be determined by evaluating the first order quenching constant (K_{SV}), using the relation:

$$\frac{I_0}{I} = 1 + K_{SV}[BZQ] \tag{18}$$

where K_{SV} is a product of lifetime of the probe and rate constant of quenching process in absence of bimolecular quenching and shows a bimolecular quenching and unimolecular decay[83]. Thus, higher the solubility of the quencher and the probe, greater would be the K_{SV} accordingly. The results observed can also be elaborated in terms of micro polarity environment of mixed micelles of gemini surfactant. Usually a value less than 1 reveals that the pyrene is present in non-polar environment where as value more than 1 indicates polar microenvironment for pyrene[81]. The mean values of I_1/I_3 ratio at various mole fractions are

given in Table 2. The values are very near to methanol (1.33) that shows resemblance between the environment of the solubilized pyrene in the system and in methanol[81]. The experimental dielectric constant (D_e) of the solution can be evaluated by using the following relation:

$$\frac{I_0}{I} = 1.00461 + 0.01253D_e \tag{19}$$

and the theoretical dielectric constant (D_{id}) in the mixed micelles has been calculated from the subsequent equation:

$$D_{id} = \sum D_i X_i \tag{20}$$

where D_i is the dielectric constant, X_i is the theoretical micellar value of ith mole fraction. The data suggested that experimental values differ from the calculated ones suggesting that the occurrence of attractive interactions among the surfactant in the mixed micelles.

Conclusion

Two novels anionic gemini surfactants i.e., [BSC14-C6-14CSB] and [BSC16-C6-16CSB] were synthesised and characterised. The physicochemical properties of the SDS with [BSC14-C6-14CSB] and [BSC16-C6-16CSB] were investigated by various methods. The Clint model describing ideal mixing behaviour in all the studied binary mixtures and regular solution theory were used to describe binary systems. The parameters like cmc^{*}, mole fraction in ideal mixtures (X^{ideal}), in real mixed micelles (X_1) and interaction parameter (β) were also determined. The synergistic interaction was observed in all the studied mole fractions of SDS due to the attractive as well as repulsive interactions among the amphiphiles in the mixed aggregates. The negative value of ΔG_{mic} in both pure components and for mixtures indicates micelle formation is thermodynamically favourable as ΔH_{mic} is also negative at lower temperature and then becomes positive at higher temperature. Higher values of ΔS_{mic} than ΔH_{mic} indicates that process of micellization is entropy driven. The value

of N_{agg} (determined by using pyrene probe fluorescence quenching method) increases with increasing mole fraction. Further, with increasing mole fraction of SDS, K_{SV} also increases. This indicates the existence of attractive interactions among the surfactant in the mixed micellar solutions.

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Figure captions:

Figure 1. Plots of specific conductance vs. concentration of (a) BSC14-C6-14CSB, (b)

BSC16-C6-16CSB, and (c) SDS.

Figure 2. Plots of Gibbs free energy, ΔG_{mic} , (a), enthalpy, ΔH_{mic} , (b), and entropy, ΔS_{mic} , (c)

of micellization vs. T (K).

Figure 3. Fluorescence emission spectra and their cmc plots of I₁/I₃ vs. conc. of [BSC14-C6-

14CSB] and [BSC16-C6-16CSB].



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Figure 3. Fluorescence emission spectra and their cmc plots of I_1/I_3 vs. conc. of [BSC14-C6-14CSB] and [BSC16-C6-16CSB].

Mole fraction $(\alpha_{SDS})^a$	cmc ^a (10 ⁻⁴ mM)	cmc* (10 ⁻⁴ mM	<i>X</i> ₁ ()	X ^{ideal} (10 ⁻⁴)	β	f_1	f_2	G^{E}
SDS+[BS	C14-C6-14C	SB]						
298.15 K								
0.1	4.40	6.10	0.126	0.118	-12.56	0.06	0.81	-2.80
0.3	5.70	7.80	0.131	0.457	-10.96	0.25	0.82	-5.70
0.5	7.80	10.9	0.140	1.067	-10.17	0.54	0.81	-6.30
0.7	14.7	18.3	0.115	2.491	-08.11	1.73	0.89	-4.22
0.9	36.9	54.9	0.165	9.602	-07.95	3.90	0.80	-1.77
303.15 K								
0.1	5.60	6.77	0.094	0.128	-11.07	0.11	0.90	-2.46
0.3	7.30	8.71	0.096	0.496	-09.49	0.42	0.91	-4.94
0.5	7.90	12.1	0.158	0.157	-10.79	0.47	0.76	-6.68
0.7	13.7	20.3	0.125	02.70	-08.53	1.45	0.87	-4.44
0.9	41.0	60.9	0.169	10.40	-07.94	4.14	0.79	-1.77
308.15 K								
0.1	8.0	8.11	0.012	0.148	-06.93	1.16	0.99	-1.54
0.3	8.90	10.4	0.089	0.496	-09.04	0.55	0.93	-4.70
0.5	9.90	14.5	0.150	1.339	-10.25	0.60	0.79	-6.35
0.7	17.0	24.3	0.151	3.124	-09.07	1.44	0.81	-4.72
0.9	61.0	79.9	0.169	12.04	-05.90	9.24	0.93	-1.31
313.15 K								
0.1	5.90	6.77	0.076	0.119	-10.41	0.13	0.94	-2.32
0.3	6.70	8.71	0.118	0.461	-10.42	0.30	0.86	-5.42
0.5	7.80	12.1	0.161	01.07	-11.02	0.42	0.75	-6.83
0.7	14.9	20.3	0.147	02.50	-09.25	1.19	0.81	-4.81
0.9	45.1	60.9	0.139	09.67	-07.08	5.23	0.87	-1.58

Table: 1 Micellar parameter like values of (cmc), ideal (cmc*), micellar composition (X_I , X^{ideal}), interaction parameter (β), activity coefficients (f_I , f_2) and excess free energy of mixing (G^E) for SDS + [BS14-C6-14CSB] and SDS + [BS16-C6-16CSB].

318.15 K								
0.1	4.80	4.88	0.016	0.079	-07.98	0.47	0.99	-1.76
0.3	5.50	6.28	0.078	0.305	-09.38	0.34	0.94	-4.88
0.5	7.50	8.79	0.089	0.711	-08.78	0.68	0.93	-5.44
0.7	11.6	14.6	0.115	01.66	-08.64	1.14	0.89	-4.50
0.9	43.4	43.9	0.013	06.40	-03.11	4.81	0.99	-0.69

^aUncertainties in $\alpha_{SDS} = \pm 0.01$ and cmc = $\pm 0.1 (10^{-3} \text{mM})$.

Table: 2 Micellar parameters like values of (cmc), ideal (cmc*), micellar composition (X_1 , X^{ideal}), interaction parameter (β), activity coefficients (f_1 , f_2) and excess free energy of mixing (G^E) for SDS + [BS16-C6-16CSB].

Mole	cmc ^a	cmc*	Y .	Y ideal	R	f,	fa	G^E
fraction	(10^{-4}mM)	$(10^{-4} \mathrm{mN})$		(10^{-4})	μ	JI	J 2	U
$(\alpha_{\text{SDS}})^{a}$	(10 11111)	(20	-, [
SDS+ [BSC	C16-C6-16C	CSB]						
298.15 K			6					
0.1	3.80	3.88	0.019	0.075	-8.22	3.71	0.996	-1.83
0.3	4.80	4.99	0.032	0.291	-7.54	8.60	0.992	-3.92
0.5	6.70	6.99	0.035	0.679	-6.75	18.5	0.991	-4.18
0.7	11.0	11.6	0.045	01.58	-6.25	33.2	0.987	-3.25
0.9	33.9	34.9	0.028	06.11	-4.09	208	0.996	-0.91
303.15 K	\sim							
0.1	4.70	4.77	0.014	0.090	-7.63	6.07	0.998	-1.70
0.3	6.0	6.14	0.020	0.349	-6.67	16.5	0.997	-3.47
0.5	8.30	8.59	0.029	0.815	-6.3	26.4	0.994	-3.9
0.7	13.8	14.3	0.031	01.90	-5.5	57.6	0.994	-2.86
0.9	41.9	42.9	0.028	07.33	-3.66	303	0.997	-0.81
308.15 K								
0.1	5.0	5.11	0.019	0.093	-7.93	4.83	0.997	-1.77

0.3	6.40	6.57	0.022	0.361	-6.77	15.4	0.996	-3.52
0.5	8.80	9.19	0.036	0.843	-5.56	22.4	0.991	-4.06
0.7	14.6	15.3	0.039	01.96	-5.79	47.7	0.991	-3.01
0.9	44.7	45.9	0.026	07.59	-3.75	283	0.997	-0.83
313.15 K								
0.1	4.5	4.66	0.029	0.082	-8.7	2.73	0.992	-1.94
0.3	5.7	5.99	0.039	0.317	-7.75	7.73	0.988	-4.03
0.5	7.90	8.39	0.046	0.740	-7.13	15.1	0.985	-4.42
0.7	13.1	13.9	0.049	01.72	-6.33	32.6	0.984	-3.29
0.9	40.2	41.9	0.037	06.66	-4.38	171	0.993	-0.97
318.15 K				C	5			
0.1	3.60	4.33	0.089	0.070	-11.6	0.65	0.911	-2.59
0.3	4.70	5.57	0.090	0.270	-10	2.53	0.922	-5.2
0.5	6.50	7.79	0.095	0.631	-9.15	5.54	0.920	-5.67
0.7	12.6	12.9	0.027	01.47	-5.53	52.8	0.995	-2.88
0.9	38.4	38.9	0.014	05.67	-3.36	384	0.999	-0.75

^aUncertainties in $\alpha_{SDS} = \pm 0.01$ and cmc = $\pm 0.1 (10^{-3} \text{mM})$.

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Mol-fract.	$\mathbf{N}_{\mathrm{agg}}$	$I_1/1_3$	Ksv (10 ⁻⁹ M)	Dexp	D _{id}
$(\alpha)^{a}$					
SDS+[BSC1	4-C6-14C	SB]			
0	71.2	3.8	1.44	26.4	29.9
0.1	12.0	1.02	4	8.18	8.01
0.3	62.0	3.7	1.4	26	25.4
0.5	86.5	1.36	1.6	9.42	9.23
0.7	41.3	1.24	2.2	8.54	8.3
0.9	141	1.36	4.8	8.02	7.8
SDS+[BSC1	6-C6-16C	SB]	5		
0	5.80	1.5	2.2	11.84	11.6
0.1	8.37	0.8	4.4	6.09	5.96
0.3	13.0	0.81	4.5	5.98	5.86
0.5	14.3	1.21	2.2	7.18	7.03
0.7	18.8	1.22	2.7	7.24	7.09
0.9	27.9	1.08	1.4	6.33	6.2

Table: 3 Aggregation number (N_{agg}), micro polarity (I_1/I_3), Stern–Volmer constant (K_{SV}), calculated dielectric constant (D_{exp}) and ideal dielectric constant (D_{id}) for SDS + [BSC14-C6-14CSB] and [BSC16-C6-16CSB] mixed surfactant systems.

^aUncertainties in $\alpha_{SDS} = \pm 0.01$

Graphical Abstract:



Highlights:

- 1. Mixed micellization behaviour of SDS-[BSC14-6-14CSB]/[BSC16-6-16CSB].
- 2. The synergistic interaction was observed.
- 3. The process of micellization is entropy driven.