CHAPTER-5

SURFACE, FLUORESCENCE AND PHYSICO-CHEMICAL STUDIES OF BIS-SULFOSUCCINATE ANIONIC GEMINI SURFACTANTS
CHAPTER 5
SURFACE, FLUORESCENCE AND PHYSICO-CHEMICAL STUDIES OF ANIONIC BIS-SULFOSUCCINATE GEMINI SURFACTANTS

This chapter is organized into three different sections. Section 5.1 covers the details of surface properties of anionic bis-sulfosuccinate gemini surfactants (BSGSLA’s, BSGSMA’s and BSGSCA’s). The fluorescence or micellization properties of anionic bis-sulfosuccinate gemini surfactants (BSGSLA’s, BSGSMA’s and BSGSCA’s) are discussed in Section 5.2. Section 5.3 deals with the investigation of physico-chemical properties of anionic bis-sulfosuccinate gemini surfactants (BSGSLA’s, BSGSMA’s and BSGSCA’s).

5.1 SURFACE PROPERTIES OF ANIONIC BIS-SULFOSUCCINATE GEMINI SURFACTANTS (BSGSLA’s, BSGSMA’s AND BSGSCA’s)

5.1.1 SURFACE TENSION AT THE CMC (CMC)

Surface properties of anionic bis-sulfosuccinate gemini surfactants were evaluated by using the Du-Nouy ring tensiometer [Du Noüy, P.L. (1925)]. Figures 5.1, 5.2 and 5.3 provide the pictographic illustration of the surface tension values which were measured for the aqueous solutions of all synthesized gemini surfactants (I) Lauryl alcohol based BSGSLA’s viz. BSGSLA\textsubscript{1,4} ; BSGSLA\textsubscript{1,6} and BSGSLA\textsubscript{1,8} (II) Myristyl alcohol based BSGSMA’s viz. BSGSMA\textsubscript{1,4} ; BSGSMA\textsubscript{1,6} and BSGSMA\textsubscript{1,8} and (III) Cetyl alcohol based BSGSCA’s viz. BSGSCA\textsubscript{1,4} ; BSGSCA\textsubscript{1,6} and BSGSCA\textsubscript{1,8} at different concentrations, respectively. From these Figures, it was observed that the value of surface tension gradually reduced with the increased concentration of prepared gemini surfactants and then reached the plateau region, above which the values of surface tension remained constant. Tables 5.1, 5.2 and 5.3 represent the surface active properties of BSGSLA’s; BSGSMA’s and BSGSCA’s, respectively.
Effect of spacer length

The results shown in Tables 5.1, 5.2 and 5.3 illustrate that the surface tension at the CMC (\( \gamma_{CMC} \)) decreases with the elongation of the spacer groups of all prepared anionic bis-sulfosuccinate gemini surfactants. This can be explained on the basis of enhanced flexibility with the enlargement of spacer methylene chain. As the methylene chain length of the spacer groups increases, the flexibility of the spacer group increases and hence reduces the surface tension at the CMC (\( \gamma_{CMC} \)) [Tyagi and Tyagi (2011)].

Effect of alkyl chain length

The results shown in Tables 5.1, 5.2 and 5.3 also revealed that the prepared gemini surfactants viz. BSGSLA’s; BSGSMA’s and BSGSCA’s significantly reduces the surface tension at lower concentration of aqueous surfactant solutions. This indicates that the molecules are adsorbed strongly at air/water interface and were found as efficient aqueous surfactant. From Tables 5.1, 5.2 and 5.3, it was observed that with the increase in alkyl chains length from C\(_{12}\) to C\(_{16}\) in bis-sulfosuccinate anionic gemini surfactant, the value of surface tension at the CMC (\( \gamma_{CMC} \)) decreased.

With increase in alkyl chain length, the values of surface tension at the CMC (\( \gamma_{CMC} \)) of lauryl, myristyl and cetyl alcohol based prepared gemini surfactants were reduced from 38.4 to 36.1 mN/m for BSGSLA\(_{1,4}\) to BSGSCA\(_{1,4}\) with shorter (CH\(_2\))\(_4\) spacer group; decreased from 37.1 to 35.3 mN/m for BSGSLA\(_{1,6}\) to BSGSCA\(_{1,6}\) with (CH\(_2\))\(_6\) spacer group and reduced from 36.2 to 34.2 mN/m for BSGSLA\(_{1,8}\) to BSGSCA\(_{1,8}\) with longer (CH\(_2\))\(_8\) spacer group, respectively. The values of \( \gamma_{CMC} \) obtained for prepared BSGSLA’s, BSGSMA’s and BSGSCA’s gemini surfactants were compared with that of the conventional surfactants viz. sulphonate anionic conventional surfactant (C\(_{12}\)H\(_{25}\)SO\(_3\)Na), commercial sodium dioctyl sulfosuccinate (SDOSS) surfactant, sodium dodecyl sulphonate (AS), sodium dodecylbenzene sulphonate (SDBS), sodium dodecyl sulfate (SDS), sodium laureate (SL) as shown in Tables 5.1, 5.2, 5.3 and 5.4. Due to the presence of two hydrophobic chains in the synthesized gemini surfactants, bis-sulfosuccinate anionic gemini surfactants had greater surface activity and were found to reduce more surface tension in contrast of conventional surfactants.
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Figure 5.1: Plots of surface tension versus surfactant concentrations of BSGSLA’s at 25±1°C

Figure 5.2: Plots of surface tension versus surfactant concentrations of BSGSMA’s at 25±1°C
Critical micelle concentration (CMC) is related to the concentration at which the surfactant monomers abruptly aggregate to form micelles. CMC values for all prepared bis-sulfosuccinate gemini surfactants were determined with the sharp breaking points observed in the plots of surface tension versus concentration profile and are exhibited in Figures 5.1, 5.2, 5.3.

**Effect of spacer length**

The CMC values shown in Tables 5.1, 5.2 and 5.3 indicate that the CMC decreases with increasing the spacer length in case of all synthesized bis-sulfosuccinate gemini surfactants.
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The reduction in the CMC value with increased spacer length may be the result of reduced electrostatic repulsion between the two polar head groups [Tyagi and Tyagi (2011)]. Similar results have been reported by Azira [Azira and Tazerouti (2007)]. In present study, the flexible spacers can easily bend and participate in the formation of micelle hydrophobic core. Due to enhanced flexibility with increased spacer length, more number of methylene groups contribute to micelle formation and as a result, free energy and CMC decreased for the prepared bis-sulfosuccinate gemini surfactants with longer spacer group [Zhu et al. (2011)]. The results in Tables 5.1, 5.2, 5.3 shows that gemini surfactants BGSLA\textsubscript{1,8} ; BGSMA\textsubscript{1,8} and BGSCA\textsubscript{1,8} resulted in the greater reduction in CMC value out of nine synthesized surfactants due to the presence of more flexible and elongated spacer group. The explored CMC values of prepared gemini surfactants were found in good agreement with the cited literature [Abd EI-Salam F.H. (2009)].

Effect of alkyl chain length

The results revealed that cetyl alcohol based bis-sulfosuccinate gemini surfactants (BSGSCA’s) with elongated alkyl chain lengths were observed as the best competitor in reducing the CMC value as compared to other smaller alkyl chain based lauryl and myristyl bis-sulfosuccinate gemini surfactants (BSGSLA’s and BSGSMA’s). The lower CMC values of BSGCA’s as compared to BSGSLA’s and BSGSMA’s anionic bis-sulfosuccinate gemini surfactants can be explained by the fact that hydrophobic part of the surfactant molecule i.e. alkyl chain length is recognized for micellization and hydrophobic interactions in surfactant molecule. With the increase in the alkyl chain length, the hydrophobic part of the surfactant molecules increases, as a result, more water molecules are released which causes more entropy increase. Consequently, the micellization process occurred at lower concentration for the gemini surfactants having longer alkyl chain length. Therefore, the data available on CMC values revealed that with elongated alkyl chain length, more number of water molecules absorbs at air-water interface at low surfactant concentration. Hence, CMC value reduced for cetyl alcohol based gemini surfactant (BSGSCA’s) having longer alkyl chains as compared to BSGSLA’s and BSGSMA’s.
Table 5.1: Surface active properties of BSGSLA’s for different spacer chain lengths

<table>
<thead>
<tr>
<th>Surface active property</th>
<th>BSGSLA_{1,4}</th>
<th>BSGSLA_{1,6}</th>
<th>BSGSLA_{1,8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{\text{CMC}}$ (mN/m)</td>
<td>38.4</td>
<td>37.1</td>
<td>36.2</td>
</tr>
<tr>
<td>CMC (mol/L)</td>
<td>0.0040</td>
<td>0.0035</td>
<td>0.0030</td>
</tr>
<tr>
<td>$pC_{20}$ (mol/L)</td>
<td>4.3</td>
<td>4.7</td>
<td>5.1</td>
</tr>
<tr>
<td>$\pi_{\text{CMC}}$ (mN/m)</td>
<td>33.4</td>
<td>34.7</td>
<td>35.6</td>
</tr>
</tbody>
</table>

Table 5.2: Surface active properties of BSGSMA’s for different spacer chain lengths

<table>
<thead>
<tr>
<th>Surface active property</th>
<th>BSGSMA_{1,4}</th>
<th>BSGSMA_{1,6}</th>
<th>BSGSMA_{1,8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{\text{CMC}}$ (mN/m)</td>
<td>37.3</td>
<td>36.8</td>
<td>35.6</td>
</tr>
<tr>
<td>CMC (mol/L)</td>
<td>0.0025</td>
<td>0.0020</td>
<td>0.0015</td>
</tr>
<tr>
<td>$pC_{20}$ (mol/L)</td>
<td>6.2</td>
<td>6.4</td>
<td>6.7</td>
</tr>
<tr>
<td>$\pi_{\text{CMC}}$ (mN/m)</td>
<td>34.5</td>
<td>35</td>
<td>36.2</td>
</tr>
</tbody>
</table>

Table 5.3: Surface active properties of BSGSCA’s for different spacer chain lengths

<table>
<thead>
<tr>
<th>Surface active property</th>
<th>BSGSCA_{1,4}</th>
<th>BSGSCA_{1,6}</th>
<th>BSGSCA_{1,8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{\text{CMC}}$ (mN/m)</td>
<td>36.1</td>
<td>35.3</td>
<td>34.2</td>
</tr>
<tr>
<td>CMC (mol/L)</td>
<td>0.0010</td>
<td>0.00093</td>
<td>0.00087</td>
</tr>
<tr>
<td>$pC_{20}$ (mol/dm$^3$)</td>
<td>6.7</td>
<td>7</td>
<td>7.2</td>
</tr>
<tr>
<td>$\pi_{\text{CMC}}$ (mN/m)</td>
<td>35.5</td>
<td>36.3</td>
<td>37.4</td>
</tr>
</tbody>
</table>
Table 5.4: Surface active properties of corresponding conventional and gemini surfactants

<table>
<thead>
<tr>
<th>Surface property</th>
<th>Conventional Surfactants</th>
<th>Gemini Surfactants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C\textsubscript{12}H\textsubscript{25}SO\textsubscript{3}Na\textsuperscript{a}</td>
<td>SDOSS\textsuperscript{b}</td>
</tr>
<tr>
<td>C\textsubscript{MC} (mN/m)</td>
<td>39.0</td>
<td>-</td>
</tr>
<tr>
<td>CMC (mol/L)</td>
<td>0.0098</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Anionic bis-sulfosuccinate Gemini Surfactants

<table>
<thead>
<tr>
<th></th>
<th>GA12\textsuperscript{e}</th>
<th>GA16\textsuperscript{e}</th>
<th>GA18\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC (mol/L)</td>
<td>0.00447</td>
<td>0.00126</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

References: \textsuperscript{a}[Shukla and Tyagi (2006)], \textsuperscript{b}[Al-Sabagh et al. (2007)], \textsuperscript{c}[Cao et al. (2009)], \textsuperscript{d}[Zhu et al. (1992)] and \textsuperscript{e}[Abd El-Salam F.H.]

Comparison of CMC values of prepared BSGSLA’s and BSGSCA’s with single and double chain anionic surfactants

The C\textsubscript{MC} and CMC values obtained for prepared BSGSLA’s, BSGSMA’s and BSGSCA’s gemini surfactants were compared with that of the conventional surfactants viz. sulphonate anionic conventional surfactant (C\textsubscript{12}H\textsubscript{25}SO\textsubscript{3}Na), commercial sodium dioctyl sulfosuccinate (SDOSS) surfactant, sodium dodecyl sulphonate (AS), sodium dodecylbenzene sulphonate (SDBS), sodium dodecyl sulfate(SDS), sodium laurate (SL) as depicted in Tables 5.1, 5.2, 5.3 and 5.4. The data showed that the CMC values of all prepared bis-sulfosuccinate anionic gemini surfactants were low as compared to corresponding sulphonate surfactant, C\textsubscript{12}H\textsubscript{25}SO\textsubscript{3}Na [Shukla and Tyagi (2006)], SDOSS [Al-Sabagh et al. (2007)], AS [Cao et al. (2009)], SDBS [Cao et al. (2009)], SDS [Cao et al. (2009)] and SL [Zhu et al. (1992)]. The prepared bis-sulfosuccinate gemini surfactants were better to reduce the surface tension in contrast of conventional surfactants. The prepared BSGSLA’s, BSGSMA’s and BSGSCA’s gemini surfactants had greater surface activity as compared to the corresponding analogues due to the
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The presence of two hydrophobic chains which causes more distortion of water structure. The CMC values of prepared gemini surfactants were compared with that of the anionic sulfosuccinate gemini surfactants (GA12, GA16 and GA18)[Abd El-Salam F.H.]. On comparing the data shown in Table 5.1-5.3 with Table 5.4, it was observed that CMC values of lauryl and cetyl alcohol based prepared gemini surfactants viz. BSGSLA’s and BSGSCA’s were found to be lower in contrast of CMC values of lauryl and cetyl alcohol based gemini surfactants viz. GA12 and GA16. This may be due to elongated spacer group. It was also noticed that the CMC value of BSGSCA1,4 was found to be equal to that of the GA18.

The CMC values of prepared gemini surfactants was also compared with the gemini surfactants m-s-m with a hydrophobic polymethylene spacer [Zana (2002)]. A similar kind of results of CMC value was observed for gemini surfactants derived from hydrophobic polymethylene spacer. The increase of CMC with s observed for s ≤ 6 for m-s-m surfactants is probably due to a conformational change in the surfactant molecule. The two alkyl chains would be in a gauche or trans position at low s values and in a cis position at higher s.

5.1.3 EFFICIENCY OF ADSORPTION OF SURFACTANT (pC20)

The efficiency or effectiveness of adsorption of the surfactant is given by the pC20 value, the negative logarithm of surfactant concentration required to reduce the surface tension of water by 20mN/m. Consequently, pC20 measures the efficiency of adsorption of the surfactant at the water- air interface. The efficiency of anionic bis-sulfosuccinate gemini surfactants to reduce the surface tension of water results in larger pC20 values because of the higher surface activity of the surfactants [Zhu et al. (2011)].

Effect of spacer length

From Table 5.1, 5.2 and 5.3, it was observed that, out of all nine synthesized bis-sulfosuccinate gemini surfactants, BSGSLA1,8 ; BSGSMA1,8 ; and BSGSCA1,8 gemini surfactants exhibited the higher pC20 values i.e. 5.1 mol/dm³, 6.7 mol/dm³ and 7.2 mol/dm³,
respectively due to elongated spacer groups. The results revealed that the higher pC_{20} values were obtained for the identical alkyl chain based gemini surfactants having longer spacer groups i.e. 1,8-dibromo octane [-((CH_2)_8-)] compared to that of shorter spacer groups 1,4-dibromo butane [-((CH_2)_4-)] and 1,6-dibromo hexane [-((CH_2)_6-)]. Consequently, greater efficiency was observed in reducing the surface tension of water and revealed the excellent surface activity for those anionic bis-sulfosuccinate gemini surfactants having longer 1,8-dibromo octane spacer group out of all prepared bis-sulfosuccinate gemini surfactants.

**Effect of alkyl chain length**

The effect of alkyl chain length was also investigated. Table 5.1, 5.2 and 5.3 illustrated the higher pC_{20} values for the prepared gemini surfactants having longer alkyl chain length. This may be due to increasing hydrophobic part of prepared gemini surfactants. The larger value of pC_{20} pointed out the characteristic features of excellent efficiency of the surfactant to reduce the surface tension of water and exhibited higher surface activity with increasing alkyl chain length.

**5.1.4 SURFACE PRESSURE AT THE CMC (π_{CMC})**

The value of surface pressure at the CMC (π_{CMC}) was obtained, when the value of surface tension at CMC (γ_{CMC}) was subtracted from the value of surface tension of pure water (γ_o) [El-Sadek (2011)]. In present study, surface tension of the pure water during the investigation of BSGSLA’s; BSGSMA’s and BSGSCA’s was found as 71.8 mN/m, 71.8 mN/m and 71.6 mN/m, respectively at 25^0C.
Effect of spacer chain length

Tables 5.1, 5.2 and 5.3 exhibited that the enhanced value of $\pi_{\text{CMC}}$ is related with the bis-sulfosuccinate gemini surfactants viz. BSGSLA$_{1,8}$, BSGSMA$_{1,8}$ and BSGSCA$_{1,8}$ having longer spacer groups i.e. larger methylene chain as a flexible spacer. The increased value of $\pi_{\text{cmc}}$ with the enlarged spacer length can be explained on the basis of reduced $\gamma_{\text{cmc}}$ values for the surfactants having larger flexible spacer length.

Effect of alkyl chain length

The data available in Tables 5.1, 5.2 and 5.3 revealed that the value of $\pi_{\text{cmc}}$ increased as the alkyl chain length increased for the prepared bis-sulfosuccinate gemini surfactants. Therefore, the greater effectiveness to lower the surface tension of water was observed for the cetyl alcohol based gemini surfactants BSGCA’s as compared to BSGSLA’s and BSGSM’A’s.

5.2 FLUORESCENCE OR MICELLIZATION PROPERTIES OF BIS-SULFOSUCCINATE ANIONIC GEMINI SURFACTANTS (BSGSLA’s, BSGSMA’s AND BSGSCA’s)

Fluorescent techniques are widely used in biochemical, biomedical, pharmaceutical, agriculture, forensic and environmental pollution control analysis due to their high sensitivity and great selectivity [Lakowicz (2006)]. Initially, Turro and Yekta [Turro and Yekta (1978)] recommended this approach based on the studies performed by Tachiya [Tachiya (1975)] on the kinetics of the fluorescence quenching in micellar solutions, which has been successively applied to determine the mean aggregation numbers [Hierrezuelo et. al. (2004)].
5.2.1 AGGREGATION NUMBER (N)

Aggregation number of the prepared surfactants was investigated with the well known fluorescence technique named as steady-state fluorescence quenching method. This technique is so appropriately designed to investigate the aggregation number that it provides all the information to develop and enhance the knowledge towards the aggregation or micellar properties of the surfactant molecules. Aggregation number is that number of surfactant monomers which is obligatory for micelle formation. In present study, the pair of pyrene-benzophenone was used as a probe-quencher pair, respectively and found to be appropriate to investigate the micelle aggregation number of anionic gemini surfactants [Zhu et al. (2011) and Cao et al. (2009)]. The experimental curves shown in Figures A-5.1 to A-5.10 gave the relationship between [Q] and ln (I₀/Iₚ) for the prepared gemini surfactants. These plots gave straight lines for all prepared bis-sulfosuccinate gemini surfactants and were used to investigate the aggregation number of the three prepared gemini surfactants. From the studies, it was observed that fluorescence intensity reduced with increased concentration of quencher benzophenone.

Effect of surfactant concentration

Aggregation number was also explored at different surfactant concentration such as 3*CMC, 5*CMC and 9*CMC (all above their CMC values) to investigate the trend of variation of aggregation number with the increased concentration of prepared surfactants. The experimental curves of [Q] and ln (I₀/Iₚ) at surfactant concentration (3*CMC) are shown in Figures A-5.1 to A-5.10 at different quencher concentration (2*10⁻⁴ to 8*10⁻⁴) and found to be supportive to investigate the aggregation number. The same method was used to determine aggregation number (N) at surfactant concentration (5*CMC and 9*CMC) for the gemini surfactants. Figures 5.4, 5.5 and 5.6 represents the graphical view of the variation of aggregation number with different surfactant concentrations (3*CMC, 5*CMC and 9*CMC) for prepared BSGSLA’s; BSGSMA’s and BSGSCA’s gemini surfactants, respectively. The
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results shown in Figures 5.4, 5.5 and 5.6 revealed the increased aggregation number with increased surfactant concentration, which indicated the micelles growth and tighter or packed structure of the prepared surfactants with enhanced surfactant concentration. Increased aggregation number with increased surfactant concentration provided the evidence for the micelles growth for all synthesized bis-sulfosuccinate anionic gemini surfactants viz. BSGSLA’s, BSGSMA’s and BSGSCAs. Such behavior of micelles growth with increased surfactant concentration was usually noticed for ionic surfactants [Fang et al. (2001)].

**Figure 5.4:** Aggregation number of BSGSLA’s at different concentrations at 25±1°C.
Figure 5.5: Aggregation numbers of BSGMA’s at different concentration at $25\pm 1^\circ C$

Figure 5.6: Aggregation number of BSGCA’s at different concentrations $22\pm 3^\circ C$
Effect of spacer chain length

Figures 5.7 reveals the increase in aggregation number for synthesized anionic bis-sulfosuccinate gemini surfactants with increase in spacer chain lengths. It was observed from Figure 5.7, aggregation numbers of myristyl alcohol based gemini surfactants viz. BSGSMA\(_{1,4}\); BSGSMA\(_{1,6}\) and BSGSMA\(_{1,8}\) were found to be 25, 28 and 31, respectively at constant concentration 0.01 mol/L. The data shown in Tables A-5.1, A-5.2 and A-5.3 also revealed the aggregation numbers of all bis-sulfosuccinate anionic gemini surfactants.

![Graph showing aggregation numbers of BSGSMA's](image)

**Figure 5.7:** Aggregation number of BSGSMA’s at concentration 0.01 mol/L

From the results, the highest aggregation number was noticed for BSGSLA\(_{1,8}\); BSGSMA\(_{1,8}\) and BSGSCA\(_{1,8}\) having longer flexible spacer group \[-(CH_2)_8-\]. These results suggested that gemini surfactants with elongated flexible spacer aggregates more readily as compared to the gemini surfactants with smaller flexible spacer length. It was all because of more methylene chains as spacers which can easily bend towards micelle core due to which tendency to form micelles in surfactant solutions becomes more as compared to shorter one. As well as the decrease in free energy was found more again for long methylene chains. The reduced CMC value can be explained with the framework of free energy model, according to which low CMC can be directly traced to the larger magnitude of transfer free energy and if spacer of gemini surfactant is long then the buried part of spacer can also contribute to this transfer free
energy. Hence, lower free energy per molecule indicates lower CMC and higher aggregation number for the gemini surfactants BSGSLA$_{1,8}$; BSGSMA$_{1,8}$ and BSGSCA$_{1,8}$ having longer spacer [Zhu et al. (2011) and Camesano and Nagarajan (2000)].

**Effect of alkyl chain length**

It was found that with the longer alkyl chain length in bis-sulfosuccinate gemini surfactants, the micellization occurs at lower concentration. This can be explained on the basis of increase in surface enhancement with elongated alkyl chain length by creating more distortion to the water with hydrophobic tail. Consequently more water molecules are released which results in elevation of entropy [Wang et al. (2004)] and therefore micellization process occur at lower concentration in case of bis-sulfosuccinate gemini surfactant with longer alkyl chain.

**Effect of temperature**

The temperature effect on the aggregation number was also investigated for lauryl alcohol based bis-sulfosuccinate gemini surfactants (BSGSLA’s). Figure 5.4 and Figure 5.8 shows the data of aggregation number of BSGSLA$_{1,4}$; BSGSLA$_{1,6}$ and BSGSLA$_{1,8}$ at room temperature (25°C) and above room temperature (35°C), respectively. From the data, it was found that aggregation number of BSGSLA$_{1,4}$; BSGSLA$_{1,6}$ and BSGSLA$_{1,8}$ decreased with increase in temperature. This may be due to the disruption of water structure around the hydrophobic group which disfavors the micellization process.
5.2.2 MICRO-POLARITY OR MICRO-ENVIRONMENT

Micelle micro-polarity can be determined with pyrene intensity ratio I₁/I₃ by solubilizing the pyrene molecules in micelles. In present study, pyrene was used as a fluorescence probe to investigate the micro-environment or micro-polarity of the micelles. Fluorescence emission spectrum shows the five vibronic peaks in the surfactant solution. The present study was carried out by using the pyrene concentration i.e. 5*10⁻⁶ mol/L to explore the micro-polarity of prepared anionic bis-sulfosuccinate gemini surfactants [Pisarcik et al. (2006) and Fang et al. (2001)]. The fluorescence peak intensities of first (I₁) and third (I₃) vibronic bands were located at the wavelength 376.0 nm and 387.0 nm, respectively in the fluorescence spectrums. Figures 5.9, 5.10 and 5.11 showed the variation of pyrene intensity ratio (I₁/I₃) with the concentration of all prepared bis-sulfosuccinate gemini surfactants viz. BSGSLA’s; BSGSMA’s and BSGSCA’s.
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Effect of surfactant concentration

Micelle micro-polarity can be determined from the intensity ratio \(I_1/I_3\) of pyrene molecules solubilized in the micelle. In general, reduced pyrene intensity ratio \(I_1/I_3\) reflects a less polar micro-environment. The pyrene intensity ratio \(I_1/I_3\) as a function of surfactant concentration is shown in Figures 5.9, 5.10 and 5.11.

![Figure 5.9: Pyrene intensity ratio versus BSGSLA’s concentrations](image)

Increasing the surfactant concentration from 3*CMC to 9*CMC for all prepared bis-sulfosuccinate gemini surfactants viz. BSGSLA’s; BSGSMA’s and BSGSCA’s decreased the pyrene intensity ratio indicating a decrease in micro-polarity. From the fluorescence quenching experiments, we know that micelle aggregation number increases with increasing surfactant concentration. Micellar growth increases packing density causing pyrene to be solubilized towards the micelle core, consequently, micro-polarity decreases with increasing surfactant concentration in all prepared bis-sulfosuccinate gemini surfactants.
Generally, the changes of micro-polarity probably arise from the existence of two compensating effects relating to surfactant packing. The aggregation number increases with the concentration, as if the micelle palisade layer had become less polar upon micelle growth associated with increasing concentration. However, this tighter packing may bring pyrene slightly closer to the micelle surface. Such a change of the pyrene solubilization site towards the micelle surface would also bring about an increase in micro-polarity, which compensates the first effect. Therefore, the micro-polarity sensed by pyrene was relatively low [Cao et al. (2009)].
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Effect of spacer chain length

Figures 5.9 - 5.12 represent the data of pyrene intensity ratio and also show the increased micro-polarity with elongated spacer length. The increase in polarity upon increasing the spacer length was likely due to progressive penetration of the spacer in the micelle hydrophobic core which allows water to enter the palisade layer of the micelle. The increased polarity was most noticed for BSGSLA\(_{1,8}\); BSGSMA\(_{1,8}\) and BSGSCA\(_{1,8}\) having the longest spacer [Zana R (2004)].

![Figure 5.12: Pyrene intensity ratio versus BSGSMA’s concentrations (0.01 mol/L)](image)

**Figure 5.12:** Pyrene intensity ratio versus BSGSMA’s concentrations (0.01 mol/L)

Effect of alkyl chain length

The data of micro-polarity shows the existence of two compensating effects related to surfactant packing [Cao et al. (2009)]. Reduced pyrene intensity ratio was noticed for BSGSLA’s as compared to BSGSMA’s and BSGSCA’s for all prepared bis-sulfosuccinate gemini surfactants. Increased aggregation number was associated with increase or higher concentration for BSGSLA’s at 3*CMC, 5*CMC and 9*CMC (due to higher CMC value for BSGSLA’s compared to BSGSMA’s and BSGSCA’s). The micelle palisade layer had become a less polar upon a micelle growth associated with the increased concentration. Therefore, micro-polarity reduced with increased aggregation number in case of BSGSLA’s at studied concentrations i.e. 3*CMC, 5*CMC and 9*CMC.
Effect of pyrene concentration

The effect of pyrene concentration was studied on the pyrene intensity ratio of BSGSLA’s gemini surfactants. Pyrene intensity ratio was investigated at two different pyrene concentration (1*10^{-6} and 5*10^{-6} M). The result given in Table 5.5 revealed slightly lower value of pyrene intensity ratio at pyrene concentration (1*10^{-6} M) as compared to the concentration of pyrene (5*10^{-6} M). The value of pyrene intensity ratio (I_1/I_3) was found to be reduced. This may be due to low pyrene concentration.

Table 5.5: Pyrene intensity ratio (I_1/I_3) of BSGSLA’s (3*CMC) at different pyrene concentration

<table>
<thead>
<tr>
<th>Pyrene concentration</th>
<th>BSGSLA_{1,4} (3*CMC)</th>
<th>BSGSLA_{1,6} (3*CMC)</th>
<th>BSGSLA_{1,8} (3*CMC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*10^{-6} M</td>
<td>0.9</td>
<td>0.97</td>
<td>1</td>
</tr>
<tr>
<td>5*10^{-6} M</td>
<td>0.92</td>
<td>1.01</td>
<td>1.06</td>
</tr>
</tbody>
</table>

5.3 PHYSICO-CHEMICAL PROPERTIES OF BIS-SULFOSUCCINATE ANIONIC GEMINI SURFACTANTS (BSGSLA’s; BSGSMA’s AND BSGSCA’s)

5.3.1 FOAMING POWER

Effect of spacer length
Tables 5.6, 5.7 and 5.8 revealed the increase in foam volume with increased spacer chain length of all prepared bis-sulfsosuccinate anionic gemini surfactants. The foam volume increases due to the conformational change observed in the structure of anionic bis-sulfsosuccinate gemini surfactant with increased spacer chain length. 

The results shown in Tables 5.6, 5.7 and 5.8 revealed the maximum foam stability of gemini surfactants with shorter \((\text{CH}_2)_4\) spacer length in all synthesized lauryl, myristyl and cetyl alcohol based gemini surfactants viz. BSGSLA\(_{1,4}\); BSGSMA\(_{1,4}\) and BSGSCA\(_{1,4}\) in contrast of other prepared gemini surfactants having longer spacer groups. The results revealed the reduced foam stability with elongated spacer group for BSGSLA\(_{1,8}\); BSGSMA\(_{1,8}\) and BSGSCA\(_{1,8}\). The shorter spacer group may be attributed with the increased area per molecule, which is responsible for the reduced surface cohesive forces in prepared bis-sulfsusuccinate anionic gemini surfactant [Tyagi and Tyagi (2011)]. Hence, high foam stability of bis-sulfsosuccinate gemini surfactants with shorter spacer group increased the effectiveness of the prepared gemini surfactants towards foaming.

**Table 5.6:** Foaming property of BSGSLA’s 

<table>
<thead>
<tr>
<th>Surfactant code</th>
<th>Initial foam volume (V_1) (ml)</th>
<th>Final foam volume (V_2) (ml)</th>
<th>Foam stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSGSLA(_{1,4})</td>
<td>49.8</td>
<td>41.9</td>
<td>84</td>
</tr>
<tr>
<td>BSGSLA(_{1,6})</td>
<td>54.7</td>
<td>43.8</td>
<td>80</td>
</tr>
<tr>
<td>BSGSLA(_{1,8})</td>
<td>66.2</td>
<td>52.0</td>
<td>78</td>
</tr>
</tbody>
</table>

**Table 5.7:** Foaming property of BSGSMA’s 

<table>
<thead>
<tr>
<th>Surfactant code</th>
<th>Initial foam volume (V_1) (ml)</th>
<th>Final foam volume (V_2) (ml)</th>
<th>Foam stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSGSMA(_{1,4})</td>
<td>62.4</td>
<td>53.8</td>
<td>86</td>
</tr>
<tr>
<td>BSGSMA(_{1,6})</td>
<td>67.1</td>
<td>55.7</td>
<td>83</td>
</tr>
<tr>
<td>BSGSMA(_{1,8})</td>
<td>73.9</td>
<td>60.1</td>
<td>81</td>
</tr>
</tbody>
</table>
**Effect of alkyl chain length**

The foam volume increased as the alkyl chain length increased. Tables 5.6, 5.7 and 5.8 show the results of foam property for all prepared bis-sulfosuccinate gemini surfactants viz. BSGSLA’s; BSGSMA’s and BSGSCA’s, respectively. The foam volume was found to be more for the cetyl alcohol based BSGSCA’s gemini surfactants as compared to the lauryl and myristyl alcohol based BSGSLA’s and BSGSMA’s gemini surfactants. This is due to the presence of longer alkyl chain length (C\textsubscript{16}) of BSGSCA’s in contrast of shorter alkyl chain length (C\textsubscript{12}) and (C\textsubscript{14}) of BSGSLA’s and BSGSMA’s gemini surfactants, respectively. The dispersion of water was stabilized with the longer alkyl chains due to increased hydrophobic portion of prepared bis-sulfosuccinate gemini surfactants [Tyagi and Tyagi (2011)]. The CMC of the surfactant is a good measure of its efficiency as a foaming agent. In present study, the low CMC values were found for cetyl alcohol based bis-sulfosuccinate anionic gemini surfactants which has greater efficiency in lowering the surface tension as well as strong adsorption at the air/water interface as compared to lauryl and myristyl alcohol based gemini surfactants. Hence, BSGSCA’s showed better foam stability.

**Table 5.8: Foaming property of BSGSCA’s**

<table>
<thead>
<tr>
<th>Surfactant Code</th>
<th>Initial foam volume V\textsubscript{1} (ml)</th>
<th>Final foam volume V\textsubscript{2} (ml)</th>
<th>Foam stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSGSCA\textsubscript{1,4}</td>
<td>78.3</td>
<td>71.2</td>
<td>90</td>
</tr>
<tr>
<td>BSGSCA\textsubscript{1,6}</td>
<td>85.4</td>
<td>73.7</td>
<td>86</td>
</tr>
<tr>
<td>BSGSCA\textsubscript{1,8}</td>
<td>91.2</td>
<td>76.3</td>
<td>83</td>
</tr>
</tbody>
</table>

The higher foam stability was found for the cetyl alcohol based BSGSCA’s gemini surfactants as compared to the lauryl and myristyl alcohol based BSGSLA’s and BSGSMA’s gemini surfactants. In current findings, it was observed that the foaming stability enhanced for
prepared gemini surfactants having longer alkyl chains. The gemini surfactants with longer alkyl chains BSGSCA’s have increased hydrophobic part. Therefore, bis-sulfosuccinate gemini surfactants viz. BSGSCA’s with longer hydrophobic group were more effective due to higher foaming stability as compared to BSGSLA’s and BSGSMA’s.

The foam stability of bis-sulfosuccinate anionic gemini surfactants viz. BSGSLA’s; BSGSMA’s and BSGSCA’s has been compared with anionic sulfosuccinate surfactant viz. Disodium lauryl ethoxy (6EO) sulfosuccinate (AEO₆-SS) [Gao et al. (2014)] and anionic gemini surfactant viz. D,S-1,4-BPHD [Tyagi and Tyagi (2010)]. The results shown in Figure 5.13 demonstrated the higher foam stability of BSGSLA’s; BSGSMA’s and BSGSCA’s as compared to the reference compounds.

**Figure 5.13:** Foam stability of prepared bis-sulfosuccinate gemini surfactants with reference compounds
5.3.2 EMULSIFICATION POWER

Emulsification power is investigated by the time period required for the separation of 9ml of the aqueous phase from emulsion formed between the two immiscible gemini surfactant solution and benzene. The increased time period for the separation of water phase from the emulsified system point towards the stable emulsion. The more time period of separation means more emulsification power. In the present studies, the influence of spacer and alkyl chain lengths was investigated.

Effect of spacer length

The results represented in Figure 5.14 shows that with increase in spacer chain length, minor increase in emulsion stability was observed for all prepared BSGSLA’s ; BSGSMA’s and BSGSCA’s gemini surfactants. Minor variation was found in the emulsion stability for anionic bis-sulfosuccinate gemini surfactants having same alkyl chain length with longer spacer group. This was due to the presence of identical C_{12}, C_{14} and C_{16} alkyl chains in the respective prepared BSGSLA’s ; BSGSMA’s and BSGSCA’s gemini surfactants. Therefore, it has been observed that length of spacer groups were not able to show any major influence on the emulsion stability.

Effect of alkyl chain length

The experimental data given in Figure 5.14 also shows that higher emulsification power was noticed for the cetyl alcohol based gemini surfactants i.e. BSGSCA’s having longer alkyl chain length as compared to the lauryl and myristyl alcohol based gemini surfactants viz. BSGSLA’s and BSGSMA’s, respectively. Therefore, the results indicated that longer the alkyl chain length, higher the emulsification power. The stability of the formed emulsion increases with the increase in a hydrophobic part i.e. alkyl chain length of the prepared gemini
surfactants. Due to increased alkyl chain length, the solubility of the prepared surfactant in oil phase enhances as a result highly stable emulsions were formed [Kumar and Tyagi (2015)].

![Figure 5.14: Emulsion stability of prepared bis-sulfosuccinate gemini surfactants with reference compounds](image)

The emulsion stability of prepared bis-sulfosuccinate gemini surfactants were compared with the anionic sulfosuccinate surfactant viz. Disodium lauryl ethoxy (6EO) sulfosuccinate (AEO₆-SS) [Gao et al. (2014)], anionic gemini surfactants viz. D,S-1,4-PGTD [Tyagi and Tyagi (2011)]. The data of Figure 5.14 observed the higher emulsion stability of all prepared bis-sulfosuccinate gemini surfactants viz. BSGSLA’s; BSGSMA’s and BSGSCA’s as compared to AEO₆-SS and D,S-1,4-PGTD.

### 5.4 CONCLUSION OF THE CHAPTER

This particular chapter discussed the research work conducted to investigate the influence of flexible spacer lengths on various surface properties including surface tension at CMC (\(\gamma_{CMC}\))
critical micelle concentration (CMC), efficiency of adsorption of surfactant (pC\textsubscript{20}), surface pressure at the CMC ($\pi_{\text{CMC}}$) as well as micellization properties viz. aggregation number and micro-polarity of all prepared anionic bis-sulfosuccinate gemini surfactants. The results of physico-chemical properties viz. foaming ability as well as emulsification power were also described in this chapter for all synthesized gemini surfactants. The lower CMC value obtained for BSGSCA’s with elongated alkyl chain length in contrast of BSGSLA’s and BSGSMA’s with shorter alkyl chain length shows that micellization process occurred at lower concentration in bis-sulfosuccinate gemini surfactants. The prepared gemini surfactants with longer spacer groups $[(\text{CH}_2)_n]$ were more readily able to reduce CMC, to enhance aggregation number and to form micelles with closely packed structures. The results also indicated that greater aggregation number and reduced micro-polarity can be achieved when concentration of gemini surfactants was increased. The results also confirmed that the synthesized anionic bis-sulfosuccinate gemini surfactants exhibited good performance properties. The foam volume increased and foam stability decreased with increased alkyl chain length from BSGSLA’s (C-12) to BSGSCA’s (C-16). The current findings revealed the enhanced emulsion stability with increased alkyl chain length from BSGSLA’s (C-12) to BSGSCA’s (C-16).

The results revealed the good surface activity for prepared bis-sulfosuccinate gemini surfactant as compared to conventional surfactants viz. sulphonate anionic conventional surfactant ($\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}$), commercial sodium dioctyl sulfosuccinate (SDOSS) surfactant, sodium dodecyl sulphonate (AS), sodium dodecylbenzene sulphonate (SDBS), sodium dodecyl sulfate (SDS) and sodium laurate (SL). On comparing, the reduced CMC values were observed for prepared gemini surfactants than that of other anionic sulfosuccinate gemini surfactants (G12, G14 and G18). The prepared gemini surfactants showed superior foaming stability than that of sulfosuccinate surfactant viz. disodium lauryl ethoxy (6EO) sulfosuccinate (AEO\textsubscript{6}-SS), anionic gemini surfactant viz. D,S-1,4-BPHD and higher emulsion stability in contrast of anionic sulfosuccinate surfactant viz. disodium lauryl ethoxy (6EO) sulfosuccinate (AEO\textsubscript{6}-SS) and anionic gemini surfactants viz. D,S-1,4-PGTD.