Chapter 4
Synthesis, surface and physico-chemical properties of carboxylate anionic dimeric surfactants

This chapter is divided into four sections, first section deals with the synthesis of the carboxylate anionic dimeric surfactants. Second section covers the characterization parts of the obtained compounds and finally various surface and physico-chemical properties of anionic dimers have been reported in third and fourth section, respectively.
Most of the research on dimeric surfactant is focused on cationic ones, specifically on the family of alkanediyl-α,ω-bis(dimethylalkylammonium bromide) [Zana et al. (1997), Zana and Lévy (1997), Grosmaire et al. (2002) and Zana (2002)]. On the other hand, the synthesis of anionic dimeric surfactants is generally more complex. Consequently, systematic studies on anionic dimers have been limited so far. Some anionic dimers, for instance sulfate and phosphate were synthesized usually in more than two steps and their properties, such as surface tension, CMC, foaming and wetting abilities were explored. Okahara et al. (1988) proposed a method for producing sulfonates dimers by the reaction of diepoxide with a long chain alcohol and thereafter converted the bis-diol to a propylsulfonic acid followed by alkali; the structure of the surfactant is shown in Figure 4.1.a. Alargova et al. (2001) reported that fatty acid methyl esters were reacted with sulphur trioxide producing α-sulfo fatty acid methyl esters subsequently transesterified with ethylene glycol to obtain a dimeric compound (Figure 4.1.b). Yoshimura and Esumi (2004) documented anionic dimeric surfactants, 1,2-bis(N-β-carboxypropanoyl-N-alkylamino)ethane with two hydrocarbon chains, two amide groups and two carboxylate groups, that were prepared by three-step reactions (Figure 4.1.c). In another strategy, nonylphenol based sulfonates dimeric surfactants with different alkyl spacer length were synthesized by two-step procedure [Zhu et al. (2006)] (Figure 4.1.d). Recently, anionic dimeric surfactants, bisphosphodiester bearing C_{14} hydrophobic tail and different methylene chains as a spacer derived from α-ω-alkyl dibromide, were synthesized by two-step reactions [Tyagi and Tyagi (2011)]. The structure of prepared compound is shown in Figure 4.1.e.
Figure 4.1 Few examples of anionic dimeric surfactants
Carboxylate anionic dimers are new members of the dimeric surfactants category, and there have been few studies of anionic dimeric surfactants with carboxylate head groups. Therefore, to fill this gap carboxylate anionic dimeric surfactants have been synthesized by one step reaction with readily available reagents. For the preparation of carboxylate dimeric surfactants the reaction would be carried out by using symmetric dianhydride with a secondary fatty amine.

4.1 Synthesis of carboxylate anionic dimeric surfactants (CADs)

In the current study, an attempt has been made to prepare EDTA based carboxylate anionic dimeric surfactants. Anionic dimeric surfactants with carboxylate head group, CADs (s = 12 and 16) were synthesized as described by Wattebled and Laschewsky (2007). However, in the present work a modified scheme for their preparation along with higher yield in a less duration has been reported.

4.1.1 Preparation of CAD_{12}

CAD_{12} was synthesized with EDTA dianhydride (10 mmol, 2.56 g) and N-methyldodecylamine (20 mmol, 3.98 g) using green solvents e.g., methanol and ethanol, with refluxing and constant stirring for 20 h at three different temperatures viz. 40 °C, 50 °C and 60 °C. The solid EDTA anhydride slowly dissipates as the reaction progresses. After the 20 h, only few small particles of EDTA remained visually undissolved. After cooling the mixture to room temperature, mixture was filtered to remove the remaining small particles. Subsequently, the filtrate was evaporated to give yellowish oil and acetone was added slowly to the oil until a white solid precipitate was formed. The precipitate was filtered and then remnant was cleaned with chloroform. Further, white powder was acquired. The reaction route for the synthesis of the dimeric anionic surfactants is shown in Figure 4.2.
Figure 4.2 Synthesis pathway of carboxylate anionic dimeric surfactants (CADs, $s = 12 \& 16$) by fatty amine, 1 and EDTA dianhydride, 2, ($n = 11 \& 15$ for CAD$_{12}$ & CAD$_{16}$, respectively)
Finally, prepared product was neutralized with NaOH (1 M, 2 equivalents). The resulting clear, strongly foaming solution was freeze-dried to provide a colorless powder. Data of the synthesized CAD$_{12}$ at various reaction conditions are shown in Table 4.1. Six different CAD$_{12}$s were prepared to optimize the reaction parameters, while CAD$_{16}$ had been prepared at optimized conditions of the CAD$_{12}$.

**Table 4.1** Effect of solvent and varying temperatures on yield of synthesized dimerics (CAD$_{12}$) $^{[a]}$

<table>
<thead>
<tr>
<th>Surfactant (CAD)</th>
<th>Temperature ($^0$C)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECAD1</td>
<td>40</td>
<td>EtOH</td>
<td>64.0</td>
</tr>
<tr>
<td>MCAD1</td>
<td>40</td>
<td>MeOH</td>
<td>67.6</td>
</tr>
<tr>
<td>ECAD2</td>
<td>50</td>
<td>EtOH</td>
<td>66.1</td>
</tr>
<tr>
<td><strong>MCAD2</strong></td>
<td><strong>50</strong></td>
<td><strong>MeOH</strong></td>
<td><strong>80.0</strong></td>
</tr>
<tr>
<td>ECAD3</td>
<td>60</td>
<td>EtOH</td>
<td>61.7</td>
</tr>
<tr>
<td>MCAD3</td>
<td>60</td>
<td>MeOH</td>
<td>76.6</td>
</tr>
</tbody>
</table>

$^{[a]}$ Reaction conditions: Reactants- N-methyldodecylamine and EDTA dianhydride, Molar ratio- 2:1, Duration of reaction- 20 h, (MCAD2 finally called CAD$_{12}$)
4.1.2 Effect of solvent and temperature on the yield of carboxylate anionic dimeric surfactants

Two solvents methanol and ethanol have been tried to study the effect of solvent on the yield of anionic dimeric surfactants. The synthesis of anionic dimers have been studied with a constant molar ratio of EDTA dianhydride and N-methylundecylamine which was kept constant i.e., 1 : 2. The duration of the reaction was also maintained constant i.e., 20 hours for both solvents. But the parameter like, reaction temperature was varied and studied temperatures were 40 °C, 50 °C and 60 °C to optimize the temperature of reaction. Quantitative observations of data shown in Table 4.1 indicated that methanol proved better solvent for higher yields of carboxylate anionic dimers as compared to ethanol.

The effect of temperature and solvent on the yield of anionic dimers was also studied. The anionic dimers prepared at 50 °C with methanol as the solvent (MCAD2) gave 80.0 % yield. A rise in temperature from 40 °C to 50 °C increased the yield of anionic dimers, irrespective of the solvent; whereas a further rise in temperature lowered the yield, and at 60 °C neither solvent caused an appreciable rise in yield rather a decrease in yield was noticed, perhaps due to initiation of a reversible reaction. Thus, the use of methanol as solvent and 50 °C as the reaction temperature are optimum reaction conditions for commercial production of carboxylate anionic dimeric surfactants. The prepared compound, MCAD2 finally symbolized by CAD12.

4.1.3 Preparation of CAD16

The CAD16 was also synthesized at experimental conditions optimized for CAD12 according to the reaction shown in Figure 4.2. The CAD16 was synthesized using EDTA dianhydride (10 mmol, 2.56 g) and N-methylhexadecylamine (20 mmol, 5.11 g) in methanol, refluxing and constant
stirring for 20 h at 50 °C. Same reaction methodology was followed as mentioned in section 4.1.1 for synthesizing CAD\textsubscript{16}. The yield of the final product was found to be 76.0 % (5.82 g).

4.2 Characterization of the CADs

The characterization of prepared compound \textit{viz.} CAD\textsubscript{12} and CAD\textsubscript{16} have been done by FT-IR, \textsuperscript{1}H and \textsuperscript{13}C-NMR spectroscopy techniques. Elemental analysis and thermo gravimetric analysis (TGA) were also carried out. The interpretation of peaks of FT-IR spectra has been done with the help of books of Spectrometric identification of organic compounds [Silverstein (1981)]. The proton and carbon NMR peaks have been identified by using Vogel’s Textbook of Practical Organic Chemistry [Furniss et al. (1994)].

4.2.1 FT-IR spectra of the CAD\textsubscript{12}

The FT-IR of synthesized, CAD\textsubscript{12} was done in Nujol mulls and selected bands in cm\textsuperscript{-1}, which are described by Table 4.2, and also illustrated by Figure A-4.1 (cf Appendix). The infrared spectral analysis was acquired before to neutralization of the compound and spectra verified the amide formation. The bands observed at 3383.62 cm\textsuperscript{-1} and 3176.22 cm\textsuperscript{-1} indicates the N–H stretching and very broad –OH stretching for acid group, respectively. The bands found at 2924.13 cm\textsuperscript{-1} and 2854.21 cm\textsuperscript{-1} is characteristic for –CH\textsubscript{2} asymmetric stretching and –CH\textsubscript{3} symmetrical stretching, respectively. The peak observed at 1742.02 cm\textsuperscript{-1} confirmed the C=O stretching of carboxylic acid group. The band at 1652.36 cm\textsuperscript{-1} is characteristic C=O stretching for the tertiary amide. Two sharp peaks observed at 1463.54 cm\textsuperscript{-1} and 1377.47 cm\textsuperscript{-1} intimated –N–CH\textsubscript{3} deformation and C–N stretching, respectively. The peaks appeared at 1303.46 cm\textsuperscript{-1}, 961.65 cm\textsuperscript{-1}, and 720.03 cm\textsuperscript{-1} confirmed the –CO stretching, –OH deformation and –(CH\textsubscript{2})\textsubscript{h}, skeletal, respectively in prepared compound. It can be seen that the absence of the bands at ca. 1808 cm\textsuperscript{-1}, which is characteristic
for the six membered cyclic anhydride, indicate that the product is free from the starting anhydride.

4.2.2 NMR spectra of the CAD$_{12}$

The structure and purity of the synthesized CAD$_{12}$ was measured by the $^1$H and $^{13}$C-NMR. The NMR spectrum of the prepared compound was taken by 300 MHz and by using CDCl$_3$, $\delta$ in ppm. The obtained spectral data are tabulated in Table 4.2 and also stated in Figure A-4.3 and A-4.4 (cf Appendix).

$^1$H-NMR spectra of the CAD$_{12}$

The triplet peaks at 0.889 $\delta$ ppm indicated the protons of the terminal methyl groups at the end of the hydrophobic chains. Also, mutliplets at 1.265 $\delta$ ppm and 1.485 $\delta$ ppm are characteristic for the nine methylene groups included in each hydrophobic tail and to the methylene in beta-position of the amide group, respectively. Furthermore, the CH$_2$ protons of the spacer group were observed as a multiplet at 2.772 $\delta$ ppm. Another characteristic peak observed as a singlet at 2.894 $\delta$ ppm corresponds to the CH$_3$ groups of the amides. From 2.922 $\delta$ ppm to 3.716 $\delta$ ppm, peaks overlap, indicating a broad multiplet. This multiplet affirmed the existence of 12 remaining protons, three couples of CH$_2$ in alpha position of the amide, between the amide and the nitrogen of the spacer and in alpha position of the carboxylate. Additional peaks at ca. 7.1 $\delta$ ppm and 7.3 $\delta$ ppm were found for the solvent CDCl$_3$. The spectrum does not show any further peaks, consequently confirming the purity of the compound.
\textit{\textsuperscript{13}C-NMR spectra of the CAD\textsubscript{12}}

The singlet peak at 14.08 $\delta$ ppm is indicative of the presence of terminal CH$_3$ groups. The peak appeared at 22.65 $\delta$ ppm is characteristic for CH$_2$ at alpha position of CH$_3$ group. The two peaks at 27.18 $\delta$ ppm and 28.28 $\delta$ ppm illustrated the presence N-CH$_2$-CH$_2$-CH$_2$, whereas, from 29.32 $\delta$ ppm to 29.63 $\delta$ ppm indicated the (CH$_2$)$_6$ group. The CH$_3$-CH$_2$-CH$_2$ groups were proved by the peak observed at 31.88 $\delta$ ppm while two other peaks at 33.57 $\delta$ ppm and 34.36 $\delta$ ppm showed the presence of CH$_3$-N-CH$_2$ group. The presence of N-CH$_2$-CH$_2$-N group was indicated by the 48.19 $\delta$ ppm and 49.10 $\delta$ ppm. The CH$_3$-N-CH$_2$ group was also confirmed by the peak obtained at 51.88 $\delta$ ppm. The presence of CH$_2$-CO-N + CH$_2$-CO-O was verified by the peaks at 55.30 $\delta$ ppm to 57.41 $\delta$ ppm, whereas, peaks appeared at 169.32 $\delta$ ppm and 173.98 $\delta$ ppm are characteristic for N-C=O, and O-C=O, respectively.

\textbf{4.2.3 FT-IR spectra of the CAD\textsubscript{16}}

The FT-IR of synthesized, CAD$_{16}$ was also done in Nujol mulls and selected bands in cm$^{-1}$, which are described in Table 4.3, and also illustrated by Figure A-4.5 (cf Appendix). The infrared spectral analysis was acquired before to neutralization of the compound and spectra verified the amide formation. The peaks observed at 3443.59 cm$^{-1}$ and 2955.24 cm$^{-1}$ indicates the N–H stretching and –OH stretching for acid group, respectively. The bands appeared at 2922.71 cm$^{-1}$ and 2853.02 cm$^{-1}$ is characteristic for –CH$_2$ asymmetric stretching and –CH$_3$ symmetrical stretching. The peak found at 1742.97 cm$^{-1}$ verified the C=O stretching of carboxylic acid. The band observed at 1626.20 cm$^{-1}$ is characteristic C=O stretching for the tertiary amide. Two sharpest peaks obtained at 1462.63 cm$^{-1}$ and 1377.59 cm$^{-1}$ intimated −N–CH$_3$ deformation and C−N stretching, respectively. The peaks observed at 1168.62 cm$^{-1}$, 909.26 cm$^{-1}$, and 720.59 cm$^{-1}$ confirmed the –CO stretching, –OH deformation and –(CH$_2$)$_n$, skeletal, respectively in
synthesized compound. It can be found that the absence of the bands at ca. 1808 cm\(^{-1}\), which is characteristic for the six membered cyclic anhydride, demonstrate that, the product is free from the starting anhydride.

4.2.4 NMR spectra of the CAD\(_{16}\)

The structure and purity of the prepared CAD\(_{16}\) was also checked by the \(^1\)H and \(^{13}\)C-NMR. The NMR spectrum of the synthesized compound was taken at 300 MHz by using CDCl\(_3\), \(\delta\) in ppm. The obtained spectral data are tabulated in Table 4.3 and also stated in Figure A-4.7 and A-4.8 (cf. Appendix).

\(^1\)H-NMR spectra of the CAD\(_{16}\)

The triplet peaks at 0.821 \(\delta\) ppm affirmed the protons of the terminal methyl groups at the end of the hydrophobic chains. The multilplets at 1.186 \(\delta\) ppm and 1.455 \(\delta\) ppm are characteristic for the thirteen methylene groups associated in each hydrophobic tail and to the methylene in beta-position of the amide group, respectively. Besides, the CH\(_2\) protons of the spacer group were observed as a multiplet at 2.393 \(\delta\) ppm. Another characteristic peak appeared as a singlet at 2.744 \(\delta\) ppm corresponds to the CH\(_3\) groups of the amides. From 3.257 \(\delta\) ppm to 3.607 \(\delta\) ppm, peaks overlap, indicating a broad multiplet. This multiplet indicated the presence of twelve remaining protons, three couples of CH\(_2\) in alpha position of the amide, between the amide and the nitrogen of the spacer and in alpha position of the carboxylate.

\(^{13}\)C-NMR spectra of the CAD\(_{16}\)

The singlet peak at 13.95 \(\delta\) ppm indicated the presence of terminal CH\(_3\) groups. The peak appeared at 22.55 \(\delta\) ppm is characteristic for CH\(_2\) at alpha position of CH\(_3\) group. The two peaks appeared at 26.27 \(\delta\) ppm and 29.24 \(\delta\) ppm illustrated the presence N-CH\(_2\)-CH\(_2\)-CH\(_2\), whereas,
from 29.35 δ ppm to 29.57 δ ppm indicated the \((\text{CH}_2)_6\) group. The \(\text{CH}_3\)-\(\text{CH}_2\)-\(\text{CH}_2\) groups were identified by the peak observed at 31.80 δ ppm while another peak appeared at 44.11 δ ppm revealed the presence of \(\text{CH}_3\)-N-\(\text{CH}_2\) group. The presence of N-\(\text{CH}_2\)-\(\text{CH}_2\)-N group was identified by the 51.29 δ ppm. The \(\text{CH}_3\)-N-\(\text{CH}_2\) group was also verified by the peak obtained at 52.14 δ ppm. The presence of \(\text{CH}_2\)-CO-N + \(\text{CH}_2\)-CO-O was verified by the peaks at 55.31 δ ppm to 58.82 δ ppm, while, observed peaks at 172.24 δ ppm and 176.46 δ ppm are characteristic for N-C=O, and O-C=O, respectively.

4.2.5 Elemental analysis of the CADs

Furthermore, the purity of dimeric surfactants was also checked by elemental analysis expressed as mass fraction in percent given in Table 4.4.
### Table 4.2 Interpretation of instrumental data (FT-IR, $^1$H and $^{13}$C-NMR) of CAD$_{12}$

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>FT-IR (cm$^{-1}$)</th>
<th>$^1$H-NMR (δ ppm)</th>
<th>$^{13}$C-NMR (δ ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAD$_{12}$</td>
<td>3383.62 [N-H stretching], 3176.72 [-OH stretching for acid group], 2924.13 [-CH$_2$ asymmetric stretching], 2854.21 [-CH$_3$ symmetrical stretching], 1742.02 [C=O stretching of carboxylic acid], 1652.36 [C=O stretching of tertiary amide], 1463.54 [N=CH$_3$], 1377.47 [C=N stretching], 1303.46 [-CO stretching], 961.65 [-OH deformation], 722.03 [-(CH$_2$)$_n$, skeletal].</td>
<td>0.889 [t, 6H, -CH$_3$], 1.265 [m, 36H, - (CH$_2$)$_9$], 1.485 [m, 4H, -CH$_2$-C-N=C=O], 2.772 [m, 4H, N-CH$_2$-CH$_2$-N], 2.894 [s, 6H (C-O-N-CH$_3$), 2.92-3.716 [m, 4H+4H+4H, CH$_2$-N=C=O, N-C-CH$_2$-N, N-CH$_2$ – COO].</td>
<td>14.08 [CH$_3$-], 22.65 [CH$_3$-CH$_2$-], 27.18 [N-CH$_2$-CH$_2$-CH$_2$-CH$_2$-], 28.28 [N-CH$_2$-CH$_2$-CH$_2$-], 29.32-29.63 [-CH$_2$-], 31.88 [CH$_3$-CH$_2$-CH$_2$-], 33.57, 34.36 [CH$_3$-N-CH$_2$], 48.19, 49.10 [N=CH$_3$-CH$_2$-CH$_2$-N], 51.88 [CH$_3$-N=CH$_2$], 55.30, 57.41 [CH$_2$-CO-N + CH$_2$-CO-O], 169.32 [N=C=O], 173.98, [O-C=O].</td>
</tr>
</tbody>
</table>
Table 4.3 Interpretation of instrumental data (FT-IR, $^1$H and $^{13}$C-NMR) of CAD$_{16}$

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>FT-IR (cm$^{-1}$)</th>
<th>$^1$H-NMR (δ ppm)</th>
<th>$^{13}$C-NMR (δ ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAD$_{16}$</td>
<td>3443.59 [N-H stretching], 2955.24 [-OH stretching for acid group], 2922.71 [-CH$_2$ asymmetric stretching], 2853.02 [-CH$_3$ symmetrical stretching], 1742.97 [C=O stretching of carboxylic acid], 1626.20 [C=O stretching of tertiary amide], 1462.63 [N-CH$_3$], 1377.59 [C-N stretching], 1168.62 [-CO stretching], 909.26 [-OH deformation], 720.59 [- (CH$_2$)$_n$, skeletal].</td>
<td>0.821 [t, 6H, -CH$_3$], 1.186 [m, 3H, - (CH$_2$)$_3$], 1.455 [m, 4H, -CH$_2$-C-N-C=O], 2.393 [m, 4H, N-CH$_2$-CH$_2$-N], 2.744 [s, 6H (C-O-N-CH$_3$), 3.257-3.607 [m, 4H+4H+4H, CH$_2$-N-C=O, N-C-CH$_2$-N, N-CH$_2$ – COO].</td>
<td>13.95 [CH$_3$-], 22.55 [CH$_3$-CH$_2$-], 26.27 [N-CH$_2$-CH$_2$-CH$_2$-], 29.24 [N-CH$_2$-CH$_2$-CH$_2$], 29.35-29.57 [-(CH$<em>2$)$</em>{10}$-], 31.80 [CH$_3$-CH$_2$-CH$_2$-], 44.11 [CH$_3$-N-CH$_2$], 51.29 [N-CH$_2$-CH$_2$-N], 52.14 [CH$_3$-N-CH$_2$], 55.31, 58.82 [CH$_2$-CO-N + CH$_2$-CO-O], 172.24 [N-C=O], 176.46, [O-C=O].</td>
</tr>
</tbody>
</table>
Table 4.4 Elemental analysis results of the synthesized dimeric surfactants (CADs)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAD&lt;sub&gt;12&lt;/sub&gt;</td>
<td>66.02</td>
<td>65.29</td>
<td>10.77</td>
</tr>
<tr>
<td>(C&lt;sub&gt;36&lt;/sub&gt;H&lt;sub&gt;70&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAD&lt;sub&gt;16&lt;/sub&gt;</td>
<td>68.88</td>
<td>68.09</td>
<td>11.29</td>
</tr>
<tr>
<td>(C&lt;sub&gt;44&lt;/sub&gt;H&lt;sub&gt;86&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Obt. (Obtained), Cal. (Calculated)
4.3 Surface and micellization properties of CADs

4.3.1 Surface tension and critical micelle concentration (CMC)

The surface tension of CADs examined by the du Noüy tensiometer and obtained data in the Table 4.5, demonstrates that the CADs surfactants significantly reduce the surface tension of the aqueous solution at low concentration, indicating that these molecules adsorb strongly at the air/water surface, and they are highly effective aqueous surfactants. The value of surface tension at CMC ($\gamma_{\text{cmc}}$) decreases as the length of their carbon chains increases. Figure 4.3 and 4.4 displays that the plots have significant changes in the slope of the surface tension versus surfactant concentrations curves as a minimum surface tension was reached. This substantial change is generally interpreted as the commencement of surfactant aggregation into micelles in bulk aqueous solution.

The critical micelle concentration (CMC) was evaluated for CAD$_{12}$ and CAD$_{16}$ and was compared with conventional monomeric sodium dodecyl sulphate (SDS) by tensiometry measurements. The surface tension ($\gamma$) of CADs and SDS in aqueous solutions depended on the concentrations of surfactants. The surface tension gradually decreases with increase in concentration of surfactants and then attains a plateau region, above which almost constant values of surface tension were obtained. The CMC values for newly synthesized surfactants were determined from the breakpoint of the plot of surface tension versus concentration.
Figure 4.3 Plots of the surface tension vs. surfactants concentration of anionic dimeric surfactant, CAD\textsubscript{12} (●) and conventional monomeric surfactant, SDS (■) in the aqueous solution at 25 °C.

Figure 4.4 Plots of the surface tension vs. surfactants concentration of anionic dimeric surfactant, CAD\textsubscript{16} (▲) and conventional monomeric surfactant, SDS (■) in the aqueous solution at 25 °C.
As expected, the carboxylate anionic dimerics have much greater efficiency in reducing surface tension than the conventional monomeric surfactant, *e.g.*, SDS. The values of surface tension at CMC (\(\gamma_{\text{cmc}}\)) for CAD\(_{12}\), CAD\(_{16}\) and SDS were observed as 31.0, 30.1 and 36.1 dyne/cm, respectively. The surface tension plots of CAD\(_{12}\) and CAD\(_{16}\) in comparisons to SDS are shown in above mentioned Figure 4.3 and 4.4, respectively. The experimental data shows that the value of surface tension and CMC decrease with increased side chain length. The slight differences in \(\gamma_{\text{cmc}}\) for dimerics CADs, *i.e.*, CAD\(_{12}\) and CAD\(_{16}\) may be attributed to the nature of chain length. As listed in Table 4.5, the CMC value of CAD\(_{16}\), *i.e.*, 0.018 mM was also found to be lower than CAD\(_{12}\), *i.e.*, 0.025. The reduction observed in the CMC was due to the increase of hydrocarbon chain length. The surfactant’s chain length is main driving factor for the micellization as well as hydrophobic interactions. As the hydrophobic chain length of dimeric surfactant increases, much water molecules are released bringing about more entropy increase, therefore micellization of anionic dimeric with longer hydrophobic tail becomes at lower concentration.

The CMC values of synthesized CADs have further been determined by electrical conductivity method. The plots of specific conductance (\(\kappa\)) against CADs concentration are display in Figure 4.5 and 4.6. The break in the plot of specific conductivity versus surfactant concentration was taken as the CMC. The obtained CMC value through conductivity measurement was found to be in good agreement with value determined by tensiometric method and exhibits the similar trend of decrease in CMC values of CADs with distension of alkyl chain length.

The surface activity parameters of the synthesized CADs along with corresponding carboxylate surfactants, *viz.* carboxylate anionic gemini (2C\(_{12}\)H\(_{25}\)C\(_{2}\)Am), sodium laurate (SL) and conventional surfactant, *viz.* sodium dodecylsulfate (SDS) are shown in Table 4.5. It was found that the CMC of synthesized amphiphiles, CADs was much lower than conventional monomeric
surfactant SDS, and corresponding carboxylate surfactants, $2\text{C}_{12}\text{H}_{25}\text{C}_2\text{Am}$ [Chen et al. (2013)] and SL [Zhu et al. (1992)]. The dimeric surfactant has two hydrophobic chains and causes increased distortion of the water structure, resulting in greater surface activity of CADs compared with conventional surfactants. This result demonstrates that synthesized CADs surfactants have superior micelle forming ability at low concentration, and also more potent in reducing the surface tension as compared to corresponding analogs.

**Table 4.5** Micellization properties of anionic dimeric surfactants (CADs) in aqueous solution

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>*CMC mmol/L</th>
<th>$\gamma_{\text{cmc}}$ (dyn/cm)</th>
<th>$\Pi_{\text{cmc}}$ (dyn/cm)</th>
<th>pC_{20}</th>
<th>$K_T$ ($^\circ$C)</th>
<th>$\Gamma_{\text{cmc}} \times 10^{10}$ (mol/cm$^2$)</th>
<th>$A_{\text{cmc}}$ (nm$^2 \times 10^7$/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAD$_{12}$</td>
<td>0.025$^{[1]}$, 0.029$^{[2]}$</td>
<td>31.0</td>
<td>41.0</td>
<td>2.22</td>
<td>&lt; 0</td>
<td>4.09</td>
<td>40.6</td>
</tr>
<tr>
<td>CAD$_{16}$</td>
<td>0.018$^{[1]}$, 0.021$^{[2]}$</td>
<td>30.1</td>
<td>41.9</td>
<td>2.31</td>
<td>&lt; 0</td>
<td>4.67</td>
<td>35.6</td>
</tr>
<tr>
<td>SDS</td>
<td>8.1</td>
<td>36.1</td>
<td>35.9</td>
<td>0.30</td>
<td>16</td>
<td>3.41</td>
<td>48.7</td>
</tr>
</tbody>
</table>
| SL              | 20          | 37.5                          | -                          | -      | -                 | 21.5                                          | 2.34                                         | 69 [Zhu et al. (1992)]

$2\text{C}_{12}\text{H}_{25}\text{C}_2\text{Am}$ 0.0259 33.1 - - - 3.67 45 [Chen et al. (2013)]

*The reported values are average of three values
$^{[1]}$ Obtained by tensiometric method
$^{[2]}$ Obtained by conductivity method
Figure 4.5 Electrical conductivity (κ) vs. concentration plot for CAD\textsubscript{12} at 25 °C

Figure 4.6 Electrical conductivity (κ) vs. concentration plot for CAD\textsubscript{16} at 25 °C
4.3.2 Efficiency (pC$_{20}$) and effectiveness (Π$_{cmc}$)

The pC$_{20}$ value was also analyzed to measure the efficiency of dimeric surfactant. The pC$_{20}$ is another parameter to display the surface action of any surfactants indicating logarithm of the surfactant concentration required to decrease the surface tension of the solvent by 20 mN/m [Zana (2004)]. The pC$_{20}$ is determined using the following equation;

\[
pC_{20} = -\log C_{20} \quad (4.1)
\]

In this equation C is the molar concentration of surfactant and C$_{20}$ stands for the concentration required to suppress the surface tension of the pure solvent by 20 mN/m [Rosen (2004)]. Thus C$_{20}$ becomes a measure of adsorption efficiency of surfactant molecules at the air–water interface. The pC$_{20}$ values of CADs were found to be larger in comparison with SDS (Table 4.5), indicating that the synthesized amphiphiles CAD$_{12}$ and CAD$_{16}$ have higher adsorption efficiency than their corresponding analogs.

The values of surface pressure (effectiveness) at the CMC (Π$_{cmc}$) were calculated for CADs and SDS by following expression [Rosen (2004)];

\[
\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \quad (4.2)
\]

where,

$\gamma_0$ is the surface tension examined for the pure water at the appropriate temperature, and

$\gamma_{cmc}$ is the surface tension at the CMC
The $\Pi_{\text{cmc}}$ values for CADs were found to be higher than conventional anionic surfactants; therefore CADs have greater capacity to decrease the surface tension of aqueous system. The maximum reduction in surface tension caused by the dissolution of amphiphilic molecules has been indicated by $\Pi_{\text{cmc}}$ and as a result $\Pi_{\text{cmc}}$ becomes a measure for the effectiveness of the amphiphile to lower the surface tension of the water. The obtained values are given in Table 4.5. The effectiveness of surfactants is also an important factor to determine the other properties of surfactant, such as foaming, wetting and emulsification.

4.3.3 Maximum surface excess concentration ($\Gamma_{\text{cmc}}$)

The maximum surface excess concentration is defined as the surfactant concentration at surface saturation; the maximum surface excess concentration $\Gamma_{\text{cmc}}$ is a useful measure of the effectiveness of adsorption of the surfactant at the air–water interface. The maximum surface excess or adsorption values ($\Gamma_{\text{cmc}}$) of CADs and SDS were computed from the Gibbs adsorption equation [Zana (2002), Rosen (2004) and Chen et al. (2013)].

$$
\Gamma_{\text{cmc}} = \left( - \frac{1}{2.303 \, nRT} \right) \left( \frac{dy}{d \log C} \right) T \quad (4.3)
$$

where,

- $R$ is the gas constant (8.314 J/mol K)
- $T$ is the absolute temperature,
- $(dy/d \log C)$ is the slope of the $\gamma$ versus $\log C$ plot at 25 $^\circ$C.
- $n$ is the number of adsorption species,
For dimeric surfactants, various researchers have used 2 or 3 for \( n \). The values of \( n \) is taken as 3, Table 2, are based upon \( n = 3 \) [Tsubone et al. (2003)]. As can be seen in Table 4.5 the \( \Gamma_{\text{cmc}} \) values of the CADs surfactants increase with an increase in the hydrocarbon chain length, this occurred because of the increased tendency of \( \text{CAD}_{16} \) toward micellization. In addition, the \( \Gamma_{\text{cmc}} \) values of newly synthesized anionic dimers were also found to be higher than those of their corresponding and monomeric surfactants. This result also supports that the CADs have better surface activity due to the presence of the two hydrocarbon chains.

Surface excess is a measure of potency of the amphiphiles adsorption, the increase of which has significant effect in applications such as, detergency, improved oil recovery, floatation, soil remediation, surfactant based separation process, since coherently packed interfacial films have different properties from that of non-coherent loosely packed films [Ao et al. (2009)].

The working function of the surfactants has been assessed primarily through the surface tension measurements. Most often sigmoidal curve is obtained from the plot of concentration of surfactants versus surface tension. According to Gibbs, to know surface excess of the surfactant molecules, a polynomial equation is used. This is based on the assumption that the amphiphile saturation is completed at the CMC point [Rosen (2004)]. In contrast, recent research exhibited that a complete saturated Gibbs monolayer may not form at CMC. Thus, there may be formation of multilayer of micelles below the Gibbs monolayer, which cannot be estimated by surface tension method. Therefore, the uncertainty may be raised on the data reported on the basis of Gibbs assumption based calculations [Menger et al. (2009), Menger et al. (2010), Mukherjee et al. (2013) and Li et al. (2013)].
4.3.4 Occupied area per molecule ($A_{\text{cmc}}$)

The $A_{\text{cmc}}$ is the minimum area per molecule of the prepared compounds at the interface and was calculated from the following equation [Rosen (2004)]:

$$A_{\text{cmc}} = \frac{1}{N_A \Gamma_{\text{cmc}}} \quad (4.4)$$

where,

- $N_A$ is the Avogadro’s number and,
- $\Gamma_{\text{cmc}}$ maximum surface excess concentration.

The $A_{\text{cmc}}$ gives the information of the packing degree of surfactant molecule adsorbed at the air/water interface [Li et al. (1999) and Oda et al. (1999)]. It was expected by the $A_{\text{cmc}}$ values in Table 4.5 that the surface area per molecule of CADs surfactants at the interface decrease as the length of their hydrocarbon chain increases. The amphiphilic molecules at the interface can be packed much tighter as the hydrophobic interaction increases between the surfactants, and the $A_{\text{cmc}}$ would be smaller. The $A_{\text{cmc}}$ values of CADs were also found to be lower than corresponding and monomeric amphiphiles. The lowest $A_{\text{cmc}}$ values of CAD$_{12}$ and CAD$_{16}$ surfactants can be attributed to tighter packing of the longer chains at the interface.

4.4 Physico-chemical properties of CADs

4.4.1 Krafft temperature

The Krafft point or Krafft temperature ($K_T$) is defined as the temperature, where the concentration of the surfactants becomes equal to the CMC and surfactants form micelles [Zana (2004) and Kumar and Tyagi (2015)]. The $K_T$ of surfactants can be used to examine their solubilization
power. The lower the $K_T$ values of surfactants, the greater the solubility. The value of the Krafft temperature for CAD$_{12}$ and CAD$_{16}$ are given in Table 4.5. Experimental result reveals that the $K_T$ of prepared anionic dimers, CADs was below to 0 °C (solution remains clear at 0°C). The obtained low Krafft point allows using of prepared CADs in cold water. This displays that excellent solubility of prepared anionic dimeric surfactants.

4.4.2 Emulsification power

Emulsions are generally contained two or more immiscible liquids where one liquid is in the form of droplets that is dispersed in the other. The surface of every droplet is an interface between hydrophilic and hydrophobic molecules and therefore thermodynamically unstable. Emulsifying agents are required to decrease the interfacial tension, which reduces the free energy resulting from the increase in the interfacial area between the two phases. Emulsifier decreases the rate of coalescence of the emulsified drop by forming mechanical electrical and steric barriers around them. Therefore, emulsifying power measures the efficiency of a product to help in the formation of an emulsion.

In the present study, the emulsifying efficiency was measured by the time required for separation of 9 ml of water from the emulsion layer. The synthesized dimers CADs showed good responses toward emulsion stabilization. Experimental results exhibited that the emulsion formulated of similar quantity of benzene and water with 0.1 % CAD$_{12}$ as emulsifier retained its stability for 513 s, whereas in the case of CAD$_{16}$ the time taken was 544 seconds. The period for 9 ml water phase to detached from the mixture was used to measure the emulsification power. Increasing the time required for separation of the desired amount of water from the emulsified system indicates the stability of the formed emulsion. The longer the duration, higher the emulsifying power. In the current findings, the emulsion stability increases with the increase in
length of the hydrophobic tail of the surfactants. Figure 4.7 shows the emulsification tendency of the synthesized CAD$_{12}$ and CAD$_{16}$ as a function of time. It is clear that the emulsifying power depends on the variation of alkyl chain length. In addition, the emulsion power of the reference surfactant anionic gemini (D,S-1,4-PGTD) [Tyagi and Tyagi (2011)] has also been compared with CADs. On observation of Figure 4.7, it was found that CADs had higher emulsion stability than D,S-1,4-PGTD. The stability of the emulsion formed using synthesized CADs predicts their appropriateness as emulsifiers in several applications including, cosmetic, shampoos emulsion paints and the textile industry.
Figure 4.7 Emulsification ability of the prepared anionic dimers, CADs with reference D,S-1,4-PGTD
4.4.3 Performance of CADs in hard water

Hardness is the amount of dissolved calcium and magnesium in the water, which prevents the lathering of soap. In hard water, soap reacts with the calcium to form soap scum or precipitates. These precipitates are formed, because of the formation of insoluble soaps of calcium and magnesium. Therefore, water does not produce lather with soap solution easily, but forms a white scum, is called hard water. Figure 4.8 shows the water hardness throughout the India as determined by Central Pollution Control Board, Ministry of Environment & Forests, India. This Figure shows that more than 75 % of India is affected by the hard water [Status of Water Quality in India (2012)].

Water hardness causes mineral accumulation on appliances like washing machine and decreases the life of these appliances, as well as reduces the efficiency of detergents. These mineral deposits can cause clothes to appear dilapidated and become harsh and scratchy to touch. Continuous washing in hard water can cause considerable damage to fibers and shorten the life of a fabric due to edge abrasion [Cameron (2011) and Munson (1991)]. Ordinary soaps and detergents are not relatively effective in the hard water. Besides this, hard water requires more soap and synthetic detergents for home laundry and washing purpose. On the other hand, large quantity of surfactants in cleaning application also raises the environmental problems.

Ethylene diamine tetraacetic acid (EDTA) is known to be a chelating agent or efficient metal ion trapper, hence, in the present study attempts have been made to measure the efficiency of synthesized EDTA based carboxylate anionic dimeric surfactants in hard water.
*Figure 4.8* Affected regions of India by hard water

*Data taken from Report on "Status of Water Quality in India – 2012"*
Synthesized anionic dimeric surfactants, CADs showed good efficiency to use in hard water, because they are EDTA based dimerics surfactants and EDTA is a dexterous metal ion trapper. Hence, sodium salts of EDTA confine the calcium ion of hard water and improve the efficiency of these surfactants in hard water.

Foaming method was used to determine the potential of CADs in hard water with the sodium stearate (soap). The foam ability was examined by comparing the height of foam remained after five minutes duration. For the assessment of foam stability of CADs in hard water, following solutions were prepared;

A = 1 wt % sodium stearate (soap) in hard water,

B = 1 wt % soap solution in hard water with 0.1 wt % of CAD\textsubscript{12}, and

C = 1 wt % soap solution in hard water with 0.1 wt % of CAD\textsubscript{16}

<table>
<thead>
<tr>
<th>Compound</th>
<th>*Foam height (mm)</th>
<th>Foam stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial ($V_1$)</td>
<td>After 5 min. ($V_2$)</td>
</tr>
<tr>
<td>A</td>
<td>47.3</td>
<td>39.1</td>
</tr>
<tr>
<td>B</td>
<td>84.6</td>
<td>73.1</td>
</tr>
<tr>
<td>C</td>
<td>80.7</td>
<td>71.4</td>
</tr>
</tbody>
</table>

*The stated values are average of three observations
On the observation of Table 4.6, it was found that prepared anionic dimerics had superior foam stability compared with sodium soap. The reason behind this phenomenon is that, EDTA bounds the Ca$^{2+}$, Mg$^{2+}$ and other metal ions. Once bound to EDTA, these metals do not build precipitates to hinder with the action of the soaps, which results in increases in the foam stability. For similar reasons, cleaning solutions often contain EDTA. On the perusal of Figure 4.9, it was observed that the foam ability of sodium soap increased from 83 % to 86 % when very less amount (0.1 %) of CAD$_{12}$ was added. The foam stability further increased up to 88 % with 0.1 % CAD$_{16}$. It was found that the foaming stability of the sodium soap with CADs increased with increase in the hydrophobic parts of surfactants.
Figure 4.9 Foam stability of the synthesized anionic dimerics, CAD$_{12}$ (B) and CAD$_{16}$ (C) with sodium stearate (A)
4.4.4 Calcium tolerance and thermal stability

Calcium tolerance

In addition to foaming stability, calcium tolerances of CADs have also been measured by Hart’s method [Sreenu et al. (2014)]. Usually, the anionic surfactants are used as cleaning agents in household detergents, shampoos, etc. and they are very sensitive to acidic solution and hard water. For this reason, the tolerance of CADs to hard water (calcium salts) was also studied. Interestingly, the synthesized surfactants, CAD\textsubscript{12} and CAD\textsubscript{16} exhibited better calcium tolerance 1353.2 ppm and 14272 ppm, respectively. The obtained results are shown in Figure 4.10, and were also compared with recently reported conventional anionic, SDS [Sreenu et al. (2015)] and anionic gemini, SBMNM [He et al. (2014)]. It can be seen that, the monomeric SDS (11.0 ppm) and gemini SBMNM (750.0 ppm) showed very less calcium tolerance as compared to CADs (Table 4.7).
Figure 4.10 Calcium tolerance of CADs with reference surfactants
As CADs are EDTA based dimers and EDTA confine the calcium ions of hard water which increase the efficiency of these surfactants in hard water, they markedly increase the sensitivities to $\text{Ca}^{2+}$.

**Table 4.7** Calcium tolerance of CADs with the reference surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Calcium Tolerance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAD$_{12}$</td>
<td>1353.2</td>
</tr>
<tr>
<td>CAD$_{16}$</td>
<td>1427.2</td>
</tr>
<tr>
<td>SBMNM</td>
<td>750.0</td>
</tr>
<tr>
<td>[He et al. (2014)]</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td>11.0</td>
</tr>
<tr>
<td>[Sreenu et al. (2015)]</td>
<td></td>
</tr>
</tbody>
</table>
Thermal stability

Thermo gravimetric analysis (TGA) has been carried for the determination of thermal stability of prepared anionic dimers. This finding demonstrates that prepared dimeric surfactants display almost identical behavior and thermally stable up to 150 °C, the thermal dissolution onset above 180 °C. The onset temperature is the intersection of the baseline weight after the loss of the water of hydration and the tangent of the weight versus temperature curve as decomposition occurs. The start temperature is the temperature at which the decomposition of the surfactant begins [Fredlake et al. (2004)]. The thermogram of the dried powder of CAD_{12} and CAD_{16} are depicted in Figures 4.11 and 4.12, respectively. Thermal stability measurements reflected that synthesized CADs have better thermal stability.
Figure 4.11 TGA graph of carboxylate anionic dimeric, CAD\textsubscript{12}

Figure 4.12 TGA graph of carboxylate anionic dimeric, CAD\textsubscript{16}
4.5 Conclusions
This chapter covers the synthesis of carboxylate anionic dimeric surfactants. The experimental results revealed that, 20 h reaction duration at 50 °C, with methanol as the solvent and a 2 : 1 molar ratio of fatty amine and EDTA dianhydride were the most favorable reaction parameters resulting in the highest yield of prepared CADs. An earlier study [Wattebled and Laschewsky (2007)] reported duration of 22 h, but present study found that 20 h duration of reaction was optimal. A shorter reaction might be cost-saving for commercial production of CADs. Fourier transform infrared spectroscopy was used to identify the functional groups of CADs, and $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy were used to determine the type of proton and for carbon atom confirmation in the synthesized moieties, respectively. Further, the total carbon, hydrogen and nitrogen were also examined using a CHNS analyzer. The synthesized surfactants CADs have CMC almost 400 times lower than that of the conventional monomer SDS and almost 900 times lower than that of the carboxylate monomer sodium laurate. In addition, the Krafft temperatures of prepared CADs were found to be $< 0 °C$, revealing higher solubility aspect of the compound. Besides, CADs are EDTA based dimerics; therefore, they exhibited superior performance in hard water and had higher calcium tolerance.

------------------