Conclusions and future scope of work

This chapter summarizes the main findings of this study and draws out their implications for industry and technological areas.
Owing to their industrial interest, dimeric amphiphiles have attracted the attention of many researchers in technological field. Due to the greater amount of hydrocarbon per molecule, the critical micelle concentrations (CMC) of dimeric are typically one order of magnitude lower than the corresponding monomeric surfactant. They are ten to hundred times more efficient at reducing the surface tension of water and the interfacial tension of the oil-water interface than conventional surfactants. However, synthesizing dimeric or gemini type amphiphiles always requires a complex synthesis route, and the resulting dimeric type surfactants, particularly anionic dimeric surfactants, are expensive, which influences their industrial and household applications. In this work, a new category of dimeric fraternity *i.e.*, carboxylate anionic dimeric is described; the EDTA based carboxylate anionic dimers with secondary fatty amine were synthesized by single-step route. The new anionic dimeric surfactants are expected to have improved surface properties, which could lead to additional economical applications. The work in the present thesis is focused on synthesis of EDTA based anionic dimers and evaluation of their micellization and physico-chemical properties.

Combining all the studies carried out in the present work, it has been concluded that:

Carboxylate type anionic dimers (CADs) were synthesized by ethylenediaminetetraacetic acid (EDTA) dianhydride and fatty amine *viz.*, *N*-methyldodecylamine and *N*-methylhexadecylamine. The yield of synthesized CADs observed were better than reported in the literature, in addition, the duration of reaction was also found to be lesser. The shorter duration of reaction can save the energy to the greater extent for commercial production of CADs. The newly synthesized CADs showed Krafft temperature $< 0^\circ C$ and much lower CMC as well as low surface tension at CMC than conventional monomer and corresponding carboxylate gemini too. As CADs are EDTA-based carboxylate anionic dimers, they can be used in detergents and
may have superior performance even in hard water. The compound also exhibits high capacity of
tolerance to calcium ions as compared to conventional and gemini anionic surfactants. Therefore,
such surfactant can find potential applications as corrosion inhibitor, chelating agent, flotation
agent etc.

The addition of organic and inorganic electrolytes to the CADs surfactants markedly improves
the solution properties. The CMC value of CAD_{12} reduced from $2.5 \times 10^{-2}$ mmol/L to $8 \times 10^{-3}$
mmol/L in the presence of $10^{-1}$ M sodium salicylate, whereas, reduction in CMC of CAD_{16} i.e.,
$1.8 \times 10^{-2}$ mmol/L to $6 \times 10^{-3}$ mmol/L observed with same hydrotrope. In the presence of
inorganic and organic salts CMC value of CADs were obtained to be in order, NaSal < NaBenz
< KCl < NaCl. The critical micelle concentration can be considerably reduced as compared to
the surfactants in the pure state. This makes such mixtures beneficial for wetting processes and
for the solubilization of hydrophobic compounds at low surfactant contents. Therewith, CADs
and its combination with electrolytes may help the commercial formulations to perform better
with lesser deterioration to the environment, as their CMC is too low, therefore, they do not
affect the environment adversely. On the basis of much less CMC values of anionic dimerics
with electrolytes, it is suggested that it may be used for commercial formulation to reduce the
consumption of surfactants.

Besides this, the interaction between anionic dimerics and neutral polymer (polyvinyl
pyrrolidone) has been characterized using conductivity and surface tension measurements. The
critical aggregation concentration (CAC) and critical micelle concentration (CMC) were
measured. The CAC and CMC values increased with the increasing concentration of PVP,
moreover, surface tension of the surfactant solutions also increases in the presence of polymers.
Further, different thermodynamic parameters were also determined, the Gibbs energy i.e., $\Delta G_{agg}^0$
and $\Delta G_{mic}^0$ of surfactants in the presence of polymer had negative values, affirming that the micelles are formed spontaneously. On the basis of experiments, it's revealed that, CADs associate strongly as compared with the conventional one. This study may be useful in several technological areas, such as detergency, formulation of paints and cosmetics, colloid stability etc. Industrial applications of surfactants are found throughout a broad range of fields. Most of these applications depend on mixtures of surfactant/surfactant. Because of better performance and cost effectiveness, mixtures of surfactants are preferred over the single surfactant system in industrial and technological formulations. Therefore, mixed surfactant system has also been reported, the mixed micelles of the anionic dimers, CADs with studied conventional surfactants (CS) i.e., SDS, CTAB and PEG-TMBPE in aqueous solutions show attractive interaction or synergistic behavior. The obtained experimental and ideal CMC values indicate favorable interactions in mixed micelle systems. The activities of the components, micellar compositions, and their mutual associations have been examined from Rubingh’s theory. The $\beta_{avg}$ values were found to be negative for the mixed micelles of the CADs with conventional surfactants combination in aqueous solutions. Further, the interaction parameters increases with increasing stoichiometric mole fraction of CADs. This shows that, these combinations exhibit synergistic behavior. For the binary surfactant mixtures (CADs/CS), $\beta_{avg}$ follows the order: CADs/PEG-TMBPE < CADs/CTAB < CADs/SDS. The properties of such mixed systems are of remarkably significance in perspective of their industrial applications, which help to select the most suitable surfactant combination with desired surface activity.

Furthermore, water solubility enhancements of studied polycyclic aromatic hydrocarbons (PAHs) i.e., naphthalene, phenanthrene and pyrene in single anionic dimeric surfactants and their equimolar binary mixed systems (CAD_{12-16}) have been measured. The associations between their
micelle properties and solubilizing efficiency *i.e.*, molar solubilization ratio (MSR), micelle-water partition coefficient ($K_m$) and standard free energy of solubilization ($\Delta G^0_\text{s}$) towards PAHs have been quantified. The MSR values were found to increase in the order pyrene $<$ phenanthrene $<$ naphthalene, also the observed negative value of $\Delta G^0_\text{s}$ exhibited spontaneous behavior of the solubilization process. The solubilities of selected PAHs also increase linearly over the range of mixed surfactant concentrations above the CMC, which indicates the potential efficiency of the equimolar mixed dimeric surfactants to facilitate the solubilization of PAHs in water. This study also gives significant information for the selection of mixed dimeric surfactants for solubilizing water-insoluble compounds.

To conclude, carboxylate anionic dimeric surfactant represents a remarkable category of amphiphilic compounds, which possess an extremely enhanced property profile as compared to standard conventional surfactants.

**Scope for future work**

The carboxylate anionic dimeric surfactant has model character, as the synthetic hypothesis can be easily extended by the modifying hydrophobic tail, such as alkylamines or dialkylamines and also spacer group *i.e.*, dianhydrides of the resulting dimeric surfactants. The synthesized carboxylate anionic dimeric surfactants can also be interacts with other water soluble polymer for their industrial usability.

As anionic dimeric surfactants gaining popularity due to their versatility and excellent surface properties, therefore in future environmental aspects of carboxylate anionic dimeric may also be studied. The use of enzymes in detergent formulations is now common in developed countries. On the other hand, enzymes are proteins; therefore, they are completely biodegradable, they are non-toxic to animals and plants in the environment. The interaction of carboxylate anionic
dimeric with enzymes have not heretofore been described, and it is hoped that they are of sufficient interest to be pursued further. It is expected that breakthrough will arise in the next few years from such an intensive analysis.