Chapter 8

Overall Conclusion

This work was started to develop certain materials which are modified by various ionic surfactants. The modified material has been utilized for the removal of both water soluble and water insoluble organic compounds (dyes or polyaromatic hydrocarbons, PAHs) from the background aqueous system. The first part of the study (Chapters 2, 3 and 4) is related to synthesis, modification, characterization and physicochemical behaviour of the adsorbent and surface active ionic liquid. Graphene-based surfactant modified adsorbents were found distinctly more efficient than a typical natural bio-adsorbent (eggshell powder in pure as well as surfactant modified form). Among the surfactant-modified adsorbents, cationic gemini surfactant modified graphene-zirconium oxide material shows better adsorptive removal of anionic azo-dyes (Methyl Orange or Congo Red). Both dye show Langmuir type adsorption process with Pseudo-second order kinetic model.

Both surface active ionic liquids and ionic gemini surfactants are not known for showing clouding phenomenon in aqueous solution at elevated temperature (this is a well-known phenomenon in aqueous non-ionic surfactant solutions where they show turbidity at a fixed temperature known as *cloud point, CP)*. However, when a surface active ionic liquid (tetra *n*-pentylammonium bromide, TPeAB) has been present in the combination of an anionic gemini surfactant (12-4-12A) starts showing clouding phenomenon. In another set of experiment, CP was tuned using bio-additives (glycine and β-Cyclodextrine). On the basis of [TPeAB] – [12-4-12A] relationship, towards CP, different mixtures were finalized for solubilisation of PAHs. The enhanced aqueous solubility of PAH has been found as the system approaches CP. Systems show variation in MSR values of each PAH if it is solubilised in the presence of other PAH. This is probably due to the fact that overall solubilisation depends on nature and site of solubilisation for a typical PAH. Cloud point extraction with a typical PAH (anthracene) shows nearly 90% removal from the background aqueous phase (surfactant lean phase, SLP).

In another approach of material modification, solution behaviour of oppositely charged gemini surfactants has been studied by using various physicochemical methodology (Chapters 5 and 6). Cmc data were acquired and analysed, for various gemini mixtures, on the basis of different regular solution theories. Interaction parameter data show synergistic interactions between two components of the mixture. The overall interaction behaviour has been found to be dependent on chain-length, spacer nature and mixing composition. Surprisingly, equal chain-length components of the mixture show better interaction hinting towards some chain-length compatibility effect. The information acquired has latter been used for the morphological studies in oppositely charged mixed geminis.

Internal morphological modifications were achieved by mixing oppositely charged gemini surfactants at relatively higher total fixed concentration (10mM). It has been found that various morphological transitions take place by simple changing of composition or alkyl chain-length or spacer nature. A composition range of mixing was found (0.4- 0.6 mole fraction of 12-4-12A) under which most of the system show the formation of higher order aggregates (rod-shaped micelles or vesicles). Mixtures with a typical spacer (e.g., polymethylene) forms vesicles at all chain-length. However, dodecyl chain gemini mixtures at above composition range given vesicles with each spacer (whether hydrophobic or hydrophilic). Even multilamellar vesicles were observed with the mixture containing spacer of 4 carbon atom (12-4-12 +12-4-12A). Probably, charge neutralization (based on zeta-potential measurements) effect takes place on mixing oppositely charged geminis and responsible for the increase in surfactant packing parameter (P) with a concomitant effect on the aqueous morphology.

The morphologies were established on the basis of scattering and electron microscopic basis. Higher morphologies so obtained (rod-shaped micelles or vesicles) have shown a different degree of thermal stability depending upon the nature of the spacer present.

The morphologies obtained based on the studies mentioned in Chapter 6 are utilized in enhancing the aqueous solubility of otherwise nearly water insoluble PAHs. The order of solubility was: Fluorine > phenanthrene > pyrene> anthracene. The solubility has been found to be dependent on composition, spacer nature, alkyl tail length and site of solubilisation. Vesicular aggregates showed distinct solubility enhancement (MSR value) over other morphologies. Moreover, gemini mixtures (of equal chain-lengths and different spacers) are found appropriate to facilitate PAH solubilisation process. Some PAHs showed enhance solubility in their mutual presence.