5. SUMMARY

Micellar aggregates have served as an important bridge between microscopic and macroscopic chemical species for a number of technological applications, including detergency, catalysis, pharmaceuticals, cosmetics formulations and tertiary oil recovery etc. The self organizing principle behind micelle formation is relevant for understanding the activities of biomembranes. The present work deals with the ample role of surfactants with specific prominence with their association behavior in water and other organic solvents. The structural capabilities of surfactants have been explored for solubilization of hydrophobic organochalcogenides. The micellar assemblies have also been utilized for synthesizing metallic and semiconducting nanoparticles.

(i) Micellization of Cetylpyridinium chloride (CPyCl)

In aqueous media

A complete physicochemical characterization of the micellization of CPyCl has been carried out on the basis of spectroscopic and thermodynamic results. UV-vis and fluorescence measurements have been performed using MO as an external probe to understand the behavior of surfactant association in water. The results indicate quenching of intensity on increasing the concentration of CPyCl via a complex formation of MO with CPyCl. The excited probe molecules deactivate by the transference of electron to the amino group of the cetylpyridinium ring. The probable structural interaction of the probe molecules closer to the interface in the micellar media of CPyCl has been confirmed via FTIR and $^1$H-NMR techniques. The influence of temperature on the micellization of CPyCl has also been assessed through surface tension and conductivity measurements. Evaluation of the thermodynamics of the involved processes specifies their exothermic nature and spontaneity. Moreover, the negative value of $\Delta C_{p,m}^\circ$ (-41.2 Jmol$^{-1}$K$^{-1}$) confirms the removal of large areas of non-polar surface from contact with water on micellization.

In mixed solvent media

The micellization of CPyCl have further been exploited to investigate the effect N,N-dimethylformamide (DMF) on the self assembly of CPyCl. The structural changes have been well illustrated by observing the behavior of spectroscopic, conductometric, tensiometric and density studies of the given formulations. Two different absorption probes (MO and MB) have been used to measure the solvent
polarity to obtain some insight about the microenvironment created by the polar solvent in micellar interior. The transition energy values ($E_t$) calculated from the wavelength of charge-transfer absorption maxima (61.56-61.97 and 42.87-43.08 for MO and MB) confirm the enhancement of solvent polarity as wt% of DMF increases in CPyCl micellar system. The association characteristics of DMF in micellar media of CPyCl have also been analyzed using conductivity and surface tension measurements over the temperature range of 288.15-323.15 K. The comparison of cmc and other thermodynamic parameters of CPyCl in water and DMF-water show that the presence of solvent brings considerable changes in the nature of micellar media. The addition of moderate concentration of DMF (0-30 wt %) has been found to delay in micellization. The results have been discussed on the basis of preferential solvation of the surfactant monomers due to the participation of the cosolvent (DMF) in the micellar region.

The effect of presence of glycols viz. monoethylene (EG), diethylene (DEG), triethylene (TEG) and tetraethylene glycol (TeEG), on the micellization of CPyCl has also been investigated. The interfacial properties of CPyCl estimated using UV-vis and fluorescence results indicate an increase in the polarity of the interfacial region in the presence of different glycols. This increase has been rationalized taking into account the penetration of the solvent molecules in the palisade layer due to the less packed micelles, resulting in a more polar environment for the probe molecules. To comprehend the behavior of surfactant association in water and water-glycol solution, the systematic FTIR investigations of the samples have been carried out at room temperature. The -CH$_2$ anti symmetric stretching peak shows a significant height increase, peak sharpening and shift slightly towards the lower frequency with the incorporation of glycols in water media. The results have been discussed on the basis of the modification of the structural dynamics of the hydrophobic layer of CPyCl in presence of glycols. The shift in peak position and changes in bandwidths of $^1$H-NMR spectra also confirm the interaction of CPyCl with glycol molecules. The cmc values estimated using conductivity and surface tension follows the order TeEG > TEG > DEG > EG > water. The cmc values further increase with increase in the glycol content. The above results have been explained on the basis of preferential solvation by glycols. The thermodynamics of the involved processes has been shown to be exothermic and spontaneous.
(ii) Solubilization enhancement of Organochalcogen compounds

After the basic understanding of the micellization process in aqueous media, the structural capabilities of surfactants have been applied to solubilize the water-insoluble organic derivative of diselenide including dipyridyl diselenide (Py$_2$Se$_2$), bis(diphenylmethyl) diselenide [(C$_6$H$_5$)$_2$CHSe]$_2$, (3,3'-dibromo-4,4'-dimethyl-2-pyridyl diselenide) [C$_{12}$H$_{10}$N$_2$Se$_2$Br$_2$] and 1,2-bis(bis(4-chlorophenyl)methyl) diselenide [(ClCeH$_2$CHSe)$_2$ using anionic (SDS), cationic (CTAB, CTAC, CPyCl) and nonionic (Brij 58) surfactant micellar media. The micellar behavior of anionic (SDS), cationic (CTAB, CTAC, CPyCl) and nonionic (Brij 58) surfactants in aqueous media has also been investigated on the basis of surface tension and conductivity measurements. UV-vis, fluorescence, FTIR and $^1$H-NMR techniques have been applied to understand the structural interactions of organochalcogenides with the surfactant. The observations reflect the surfactant-additive interactions and rationalized by assuming a densely packed arrangement of the amphiphilic molecules in the aggregates with the additive molecule adhering to the micellar interface. The efficiency of solubilization enhancement of organochalcogen compounds using surfactants have further been quantified by means of two parameters, the molar solubilization ratio ($\gamma$) and the micelle-water partition coefficient (K). The aqueous solubilities of organodiselenides amplify linearly with surfactant concentration, demonstrating their solubility enrichment over that in water. This phenomenon has been presumable associated to the micellar solubilization. Also, compared to cationic or anionic surfactant, the nonionic surfactants showed higher values of $\gamma$ and $K_m$, indicating higher solubilizing power of nonionic surfactants for the given organochalcogen compound. Additionally, their solubilization studies for cationic, anionic and nonionic surfactants pointed out that $K_m$ values are better to be related to nonpolar part of the surfactant than with the micelle size, leading to the conclusion that micellar size may not be a prime factor for observed variations in $K_m$ values for ionic and nonionic surfactants.

However, the equimolar binary surfactant mixtures of cationic-nonionic mixed surfactants demonstrate higher $\gamma$ and $K_m$ values than cationic-cationic mixed system. The values are still elevated than those of single nonionic surfactant representing synergism in organochalcogen solubility improvement over the single surfactant system. Moreover, $\gamma$ and $K_m$ values of cationic-cationic systems are appreciably
enhanced on adding nonionic surfactant as observed in the case of ternary system. This might be interrelated to higher micellar core solubilization characteristic of nonionic surfactant in addition to the micelle-water interface. Attempts have also been made to estimate the binding constant, $K_i$, of organochalcogenides in micellar media. The value of $K_i$ for $\text{Py}_2\text{Se}_2$ has been found to be higher than $[\text{ClC}_6\text{H}_4\text{CHSe}]_2$, $[\text{C}_{12}\text{H}_{16}\text{N}_2\text{Se}_2\text{Br}_2]$ and $[(\text{C}_6\text{H}_3)_2\text{CHSe}]_2$. This may be an indication of the different solubilization capacity of the four compounds. Among the cationic and nonionic surfactants, latter shows a greater magnitude of $K_i$ values compared to former. The standard free energy of solubilization, $\Delta G^\circ_s$ has also been estimated using $K_m$ values. For all the systems, $\Delta G^\circ_s$ is negative, indicating spontaneous solubilization. The largest negative value has been observed for the CTAB-Brij 58 micellar system showing that the solubilization of organochalcogens is energetically more complimentary in cationic-nonionic system, due to additional micelle-water interface adsorption.

(iii) Surfactant mediated synthesis of nanoparticles

The salient features of surfactants have also been utilized for synthesizing metallic (silver, Ag) and semiconducting (selenium, Se and cadmium selenide, CdSe) nanoparticles.

**Synthesis of silver (Ag) nanoparticles in surfactant media**

The controlled synthesis of silver nanoparticles has been carried out via the modified Tollen’s reagent method involving the chemical reduction of the $\text{AgNO}_3$ by sugars. The generation of silver nanoparticles and their stabilizing tendency in different aqueous micellar solution have been preliminarily identified by visual inspection of color change in the dispersion after completion of the reaction. It appears that the particles are stable in SDS, CTAB and TX-100 in contrast to AOT, CPyCl and Brij 58 micellar media. The in-plane quadrupole plasmon resonance mode of silver nanoparticles has been estimated using UV-vis spectroscopic technique. The surface plasmon resonance (SPR) bands have been observed at 410, 425 and 420 nm for glucose, fructose and sucrose reduced silver in SDS, 419, 423 and 425 nm in CTAB and 428, 431 and 433 nm for TX-100. Moreover, the in-plane dipole resonance peaks gradually red shifted (from 390 to 410 nm for glucose) as a function of $\text{Ag}^+$ concentration, due to the sensitivity of in-plane dipole resonance to the size of the particles. The formation mechanisms of colloidal silver particles using surfactant
media in aqueous solution have also been investigated. The result infers the slow reduction rate of sucrose as compared to glucose. The shape of the temporal profile for the plasmon band peak intensity suggests that the autocatalysis is involved in the silver particle formation using different saccharides in micellar media.

The effect of the surfactant concentration on the evolution of the intensity of the plasmon band has also been analyzed for a constant value of $5 \times 10^{-4}$ M silver ion and variable molar concentrations of surfactant ($5 \times 10^{-4}$, $8.3 \times 10^{-3}$, $10. \times 10^{-3}$, $12 \times 10^{-3}$ and $15.0 \times 10^{-3}$ M). Form the broadening of XRD peaks, the sizes of the nanocrystallites have been calculated using Debye Scherer’s formula. The average crystallite are 9.7, 12 and 11.3 nm utilizing the diffraction peak of (220) lattice plane in SDS, CTAB and TX-100 micellar media, respectively. The sizes and morphology of synthesized silver nanoparticles have also been imaged using TEM and AFM techniques. All the nanoparticles appear to be nearly spherical. The variation in the average particle sizes has been observed due to different reducing abilities of sugars in SDS, CTAB and TX-100 micellar media. The size distribution has been observed to be narrow for glucose synthesized silver nanoparticles in contrast to the fructose and sucrose as reducing media. These differences can be ascribed to different reducing tendencies of sugars towards metal salt reduction in the micellar system. The effect of different concentration of surfactants has been investigated with TEM and AFM. The observation depicts that as the concentration of surfactant increases, the size of the particles decreases. This behavior can be explained on the basis of restricted capping molecular movement of nanoparticles due to the formation of reasonably close packed surfactant layer on the silver nanoparticles surface.

The stabilization mechanism underlying the association of SDS, CTAB and TX-100 molecules with the silver particle via their terminal functional groups has been examined by comparing the FTIR spectra of neat SDS, CTAB and TX-100 and the FTIR spectrum of the surfactant-capped silver nanoparticles synthesized using different saccharides.

**Synthesis of semiconducting nanoparticles in micellar media**

Efforts have also been made to synthesize semiconducting Se and CdSe nanoparticles in single step using surfactant media of different polarities. UV-vis spectroscopy has been applied to find out the excitonic peak of Se and CdSe nanoparticles. The UV–vis spectra of reaction solutions containing SeO$_2$ and
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$\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in aqueous AOT, CTAB and TX-100 depict a characteristic absorption shoulder in the 300–500, 500–600, 325–550 nm regions, respectively. On the other hand, the spectra of CdSe give a characteristic absorption shoulder in 500–700 nm regions. The absorption data have also been used to estimate band gap values and the size of the particles. The results clearly indicate that this method allows the preparation of Se nanoparticles in three different surfactant media with tunable band gaps in the range 3.28–4.08 eV. For CdSe, maximal $E_g$ increase relative to $E_g^{\text{bulk}}$ (1.7 eV) is 2.3 eV for SDS, 2.04 eV for CTAB and 2.25 eV for TX-100, respectively. The evolution of the Se and CdSe nanoparticles in AOT, SDS, CTAB and TX-100 micellar media has been confirmed by recording the time dependent absorption spectra. The calculation of $k_a$ shows the reduction rate of reducing agent in different micellar media.

To verify the effect of Se and CdSe concentrations on the emission spectra, fluorescence measurements have been recorded at constant surfactant concentration with different SeO$_2$ concentrations. The fluorescence of the Se, CdSe nanoparticle solution shows red shift in all the systems. The result suggests that both surface structure and the size of the Se and CdSe nanoparticles change with change in concentration. The average particle size estimated using XRD has been found to be 14.3, 16.1 and 16.9 nm in AOT, CTAB and TX-100 micellar media, respectively for Se nanoparticles. On the other hand, for CdSe, the average crystallite size is 12.9, 13.8 and 9.3 nm in SDS, CTAB and TX-100 micellar media. The size variations of the particles have also been confirmed using TEM and AFM results. On the basis of TEM and spectroscopic measurements, it has been proposed that the function of surfactant molecules is to kinetically control the growth rate of particles through adsorption and desorption process.

It may be concluded that the detailed investigation of surfactant assisted synthesis of metallic as well as semiconducting nanoparticles has given a fair success not only to synthesize particles but also provide a new interface for self assembly and formation of ordered nanoparticles arrays with controlled morphology and framework that allows tuning of chemical and physical properties.