5. SUMMARY

Amphiphiles substituted with highly functional molecules have shown widespread applications in diverse field areas. The incorporation of peptides, oligopeptides, metals, carbohydrates, etc. into the hydrophilic domains of amphiphiles leads to the formation of new classes of surfactants which can self-aggregate into various supramolecular assemblies. The synthesis of these new surfactants with potential physicochemical properties has thus emerged as one of the most promising fields in the area of colloid and surface science. The present work deals with one such new class of surfactants known as metallosurfactants. The objective of the study undertaken is to synthesize novel metallosurfactants exhibiting both conventional and non-conventional amphiphilic properties and develop a basic understanding of the metallosurfactant chemistry. Further, an attempt has been made to utilize these metallosurfactants synthesized for nanoparticle fabrication and catalysis.

A range of metallosurfactants of the type: \([\text{M(CH}_3\text{COO)}_4]_2[\text{C}_{12}\text{H}_{25}\text{NH}_3]^+\) where M: transition metal ion have been prepared using the first row transition metal elements, namely iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) by a two step procedure. The hydrophobic dodecylamine chain has been kept the same in each case, in order to observe only the effect of metal. The results show interesting spectroscopic, thermal, redox, and self-aggregation properties, which are associated to the metal ion change. The collective spectroscopic results give a fair idea about the framework of the metallosurfactants synthesized. The FTIR spectra reveal that the metal ion binds to the acetate moiety present in the metallosurfactant. The interaction between ammonium group and metal ion is confirmed by the shift in \(^1\text{H}\) signals using \(^1\text{H}\)-NMR spectroscopy. Further, an idea about the geometry surrounding the metal ion is given by UV-vis spectroscopy which infers that the metal ions are present in an octahedral or distorted octahedral environment.

The thermal decomposition studies (TG, DTG, and DSC) of surfactant metal complexes reveal that the complexes decompose by different mechanisms, depending upon the presence of transition metals. Fe (II) complex decomposes by a three step mechanism to give metal whereas Cu (II), Ni (II), and Co (II) decompose by a two-step process to yield metal oxide as the residue. These complexes decompose beginning with the scission of M-N bond and afterwards the M-O bond is ruptured, indicating that the dodecylammonium chain is loosely attached compared to the...
acetate moiety. Various kinetic parameters of the thermal decomposition have also been determined by means of five different non-isothermal methods, namely, Horowitz-Metzger, Coats-Redfern, Madhusudanan-Krishnan-Ninan, Wanjun-Yuwen-Hen-Cunxin, and van Krevelen. Thermodynamic parameters and the activation energy vary as: $E_{Fe} > E_{Co} < E_{Ni} < E_{Cu} > E_{Zn}$. Accordingly, it can be inferred that activation energy depends on (i) the radius as well as electronegativity of the metal ion and hence, the coordination of the metal ion to ligand is responsible for thermal stability; (ii) the mechanism of thermal decomposition. The above inferences also find support from the molecular modeling calculations using Gaussian, which reveal that the minimum energy possessed by the optimized structure follows the trends obtained by TG.

An attempt has been made for the first time to correlate the theoretically optimized structures with experimental data which can prove to be very useful to understand the structure and properties of metal complexes (Figure 90). Another important finding is that the metal counterpart of organic surfactant (dodecyl ammonium acetate) possesses lower activation energy, which may be due to the weakening of bond strength upon changing from ionic bond to coordinate bond due to complexation. Consequently, it is concluded that the relationship between radius of the metal ion and the coordination of the metal ion to ligand is responsible for thermal stabilities of the metal complexes. This study provides key insights into the chemical decomposition pathways that are important during decomposition of transition metal complexes.

Figure 90 Graphical representation of metallosurfactant.
The metallosurfactants are redox active species and show electrochemical behavior without using any probe which is characteristic to purely metallic nature owing to the metal ion. The cyclic voltammograms obtained follow the Nicholson Shain equation for an irreversible system indicating that the overall electrochemical process proceeds by diffusion instead of adsorption. To the best of our knowledge, cyclic voltammetry has been used for the first time to determine the cmc values of the metallosurfactants.

These metallosurfactants show a remarkably high efficiency to self associate, which is evident from the cmc values. Treiner and Makayssi [253] have observed cmc for the conventional surfactants, C_{12}BzBr and C_{14}Br to be 5.5 and 4.0 mM, respectively. But metal ion complexation, decreases the cmc to a great extent, i.e. 0.9 mM. The cmc values followed the order: Zn (0.34 mM) < Fe (0.63 mM) < Co (0.89 mM) ≈ Ni (0.89 mM) ≈ Cu (0.84 mM). The cmc values obtained have been found to be much lower compared to the precursor DDA (2.3 mM). Another reason for this decrease could be the presence of two hydrocarbon chains which increases the hydrophobicity and hence increases the tendency for micellisation. The difference in cmc values of different metal ions is believed to be due to interplay of ionic character or electronegativity and the size of the specific metal ion present in the metallosurfactants. The electronegativity values and the ionic radii of metal ions vary in order: Zn < Fe < Co ≈ Ni ≈ Cu and Fe < Co < Ni < Cu < Zn, respectively. The cmc values also follow the same order because larger metal ion size leads to lower hydration and greater penetration of the metal ion to reduce the electrostatic repulsion, consequently giving lower cmc values. Therefore, the metal ion dramatically influences all the properties – thermal, redox as well as physicochemical. It is established that the metal surfactants synthesized, show different characteristics pertaining to the change in metal ion. The general trends of the various properties of metallosurfactants have been outlined in Figure 91.

Metallosurfactants have further been efficiently utilized as nanoreactors to synthesize metal nanoparticles. Results infer that; (i) the nanoparticles obtained are pure and free from contamination as they are synthesized from a single reactant moiety i.e. the metallosurfactant. The metallosurfactant plays the dual role of the metal ion provider and metal nanoparticle protector, thus eliminating the need for a stabilizer or a capping agent; (ii) these surfactants also offer the possibility to select
and modify the surface of nanoparticles as desired. Depending upon the ligands attached to the metallosurfactant the capping of the nanoparticles can be predetermined. The presence of both hydrophobic and hydrophilic ligands attached to the metallosurfactant provides a handle to disperse the resulting metal nanoparticles either aqueous or non-aqueous solvent; (iii) highly stable, water dispersible nanoparticles have been produced using the polymer PAA, which are highly resistant to oxidation; (iv) size of the nanoparticles can be controlling by changing or altering the metallosurfactant ratio.

**Self assembly for metallosurfactants**

![Self assembly diagram]

![Diagram of micelle formation]

**General trends for the transition metal ions**

![Diagram showing ionic radii, size of metal ions, micelle size, thermal stability]

**Figure 91** Schematic representation of synthesis and general trends showing the effect of metal ions on metallosurfactants.
The nanoparticle synthesis is carried out in metallosurfactant/water/heptane system in the presence of only a reducing agent i.e. NaBH₄. Co, Ni and Cu nanoparticles migrate to heptane phase while Fe and Zn nanoparticles prefer water phase after equilibration. This behavior could be reasoned on the basis of capping agents. The Co, Ni and Cu nanoparticles are stabilized by the hydrophobic dodecylamine chains while Fe and Zn show preferential binding to carboxylate groups as compared to amines. This provides them with increased electrostatic stabilization and they get dispersed in the water phase (Figure 92). Therefore, metallosurfactants provide a facile approach to nanoparticle fabrication with no pH stabilization, or extreme conditions of temperature and pressure.

The nanoparticles of transition metals are expected to undergo oxidation and get surface passivated to form an oxide layer. To counter this effect, highly stable Cu nanoparticles have been synthesized by reducing Cu surfactant complex in the presence of deprotonated polyacrylic acid (PAA) (pH=10). It is interesting to note that other protecting agents like surfactants and even the relatively related polymethacrylic acid (PMAA) have been much less efficient and could not prevent rather quick oxidation to Cu₂O, whereas for PAA the samples are stable against oxidation for several days. The diameter of the relatively monodisperse CuNPs could be controlled in the range of approximately 30–85 nm by varying the ratio of PAA/Cu precursor. This means that this method allows for the formation of nanoparticles of variable size that are stable under air, something that is typically not achieved by simple chemical approaches.

The nanoparticles synthesized have been further used for the catalytic reduction of p-nitrophenol to p-aminophenol, which proceeds to completion with high rates (speeding up the reaction by several orders of magnitude compared to the absence of nanoparticles). Of all the nanoparticles synthesized, the catalytic activity of the PAA-capped Cu nanoparticles is remarkably high, given the fact that PAA is so efficient in preventing the oxidation of the Cu nanoparticles. This is attributed to the fact that PAA might itself help in the reduction process.

Thus, the science of metallosurfactants presents interesting opportunities and challenges to researchers worldwide. The design of these types of surfactants holds a great promise for a wide variety of applications in chemistry and engineering.
Figure 92 Schematic representation of metal nanoparticle fabrication using various metallosurfactants.