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Metallosurfactants, a “*Novel Portmanteau*”: A Holistic Insight into the Structural–Physiognomies Relationships, Synthesis Stratagems, and Characterization

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1.1 Introduction

Recently, “*surface chemistry*” has gained enormous amount of attention in bringing the vivid paradigm of synthetic chemistry [1]. Owing to the splendid attributes, being offered by it, a vast majority of the leading researchers, scientists, and physical chemists across the globe are putting their exertions to envisage noble advancements in this illustrious domain [2]. The inception of this field can be dated back to the late seventeenth century. It was through the numerous experiments (to study the phenomenon responsible for spontaneous spreading of *oil-on-water*) conducted by the famous physician *Sir Benjamin Franklin* that the early breakthroughs in this domain were achieved [3]. This innovation later on proved to be a souvenir and became the underlying fundamental basis for the upcoming research and development in this field [4].

In subsequent decades, a colossal growth has been witnessed in the dominion of surface chemistry, and the corresponding systematic findings have actually transformed variegated scientific disciplines [5]. It is because of this particular realm that the eminent fields such as colloid chemistry, interface science and surface engineering came into existence.

Several other eminent and impending disciplines *viz.* nanoscience, energy conversion, and catalysis have also momentarily gained from it [6]. In other words, surface chemistry has essentially laid down the underpinning stone for voluminous superlative fields [7]. Henceforth, it can be rightly said that “*surfactants, a portmanteau of surface-active agents*” as we call them have proven to be highly potent agents (Figure 1.1) [8–11]. Amidst, all the molecules investigated in the realm of chemistry, surfactants are most exclusively studied. Owing to their exceptional solution and interfacial properties, they are currently being utilized on a widespread level in several fields.

Surfactants can be defined as the “*materials which when present at low concentrations, alters the interfacial free energies of the interfaces via adsorbing themselves onto*

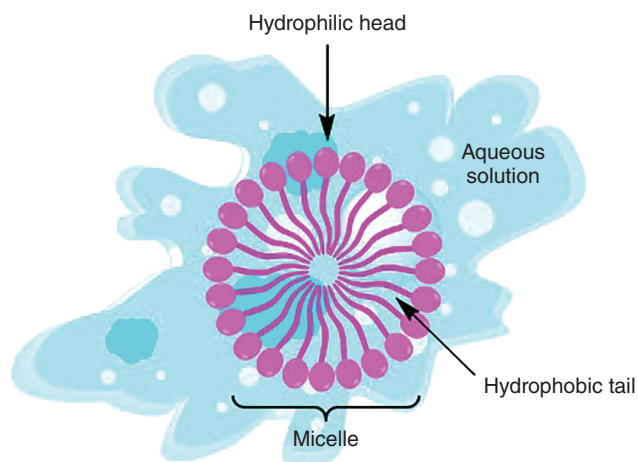


Figure 1.1 Schematic representation of surfactant.

the interface/surface of the system” [8, 12–20]. They generally fall under the category of organic compounds and are truly amphiphilic in nature [21].

When it comes to structural organization, surfactants usually comprises of two vital components the first one being the head (polar) group, which is hydrophilic in nature [22, 23], and the second part often referred to as the tail (non-polar) group is hydrophobic (lipophilic) in nature [24]. It is mostly observed that the polar head group varies greatly in structure and can be multifaceted, while the tail group demonstrates less diversity and as a rule it primarily comprises of a hydrocarbon (alkyl) chain with 8–20 carbon atoms. Broadly speaking, the tail can be branched/linear hydrocarbon, aliphatic, alkyl/aryl, short/long whereas; the head group can be ionic/non-ionic [21–23]. These chemical moieties have an innate ability to affect the air–water interface in an articulate fashion. This might be attributed to the reduction in the surface tension (interfacial tension) of water and formation of assorted assemblies (micelles) at the interface [10, 25]. Upon adsorption at the interface, the two characteristic portions of the surfactants *viz.* head and tail group align themselves according to their polarities/preferential solubilities. The polar head group align itself toward the aqueous (water) part, while the tail group orient itself away from the water (outward direction) thereby resulting in the formation of micelles [26].

When dispersed in aqueous phase, at low concentration these surfactants generally exist in monomeric/dimeric state. An increase in their concentration beyond a designated threshold (*viz.* *critical micellar concentration* [CMC]) leads to the spontaneous accumulation of surfactant monomers. This further results in the formation of assemblies/colloidal-sized clusters also commonly referred to as “*micelles*” [4, 7, 26, 27]. A major share of this potential breakthrough goes to James William McBain, whose discovery inevitably changed the dynamics and lead to significant advancements in the field of surface/surfactant chemistry [12, 27–29]. It was in the year 1916, while conducting his research experiments, he observed

infrequent alteration in the electro-conductive physiognomies as a function of soap concentration and he coined the term “micelles” [30].

Nowadays, a dire need is felt for the upgradation and development of novel technologies, which will play an intricate role in improvising the varied aspects of human lives. This upsurge calls for a quick modification of the surfaces in order to perfectly align with these rapid advancements [31]. Herein, the innate potential to alter the interfaces as per the requisite demand plays a pivotal role in envisaging and devising innovative technological advancements, ranging from energy production to biomedical implants, which will offer promising outcomes [12, 27]. Incessant strides are being made in the field of science and technology on a regular basis to attain the aforementioned goal.

Irrespective of the fact that these chemical moieties possess such dynamic properties yet, they have not been able to secure a place for themselves among the “*catalogue of advanced materials*” [32]. In lieu of this, unique complexes with pre-selected functionalities (*viz.* proteins, carbohydrates, and metal ions) have been developed, which comprehensively aided in triumphing the lacunas associated with conventional surfactant systems. Additionally, incorporation of such modalities resulted in the fabrication of novel surfactants with engineered interfacial attributes [31]. Among all functional groups/modalities, metal ions have played a pivotal role in escalating the physicochemical attributes of the conventional surfactants exponentially. This in particular has lately led to the emergence of remarkable, and idiosyncratic complexes commonly referred to as metallosurfactants (MTS) [33].

1.2 Intrinsic Physiognomies of Metallosurfactants

Self-aggregation/association/assembly above CMC is an intrinsic property, which makes these surfactants and amphiphilic structures an invigorated tool. Length and volume of lipophilic component, size and charge of the polar head group, type of interaction with the solvent system, ionic strength, and molecular framework of the system are some of domineering factors, which tend to govern the hydrodynamic radii (particle size), and surface charge (zeta potential) of these singular entities [34–36]. The whole credit for this fundamental concept of aggregation goes to Zhulina et al. [35]. It was because of their incessant attempts that a comprehensive overview of this distinguishing phenomenon could be deciphered more than 30 years ago [37, 38].

With an advent in time, several triumphant advancements have been accomplished in the field of surfactant chemistry. These progressions have broadened up the horizons of our understanding in lieu of surfactants. Similarly, the underlying concepts providing an inclusive aftermath of the phenomenon have also upgraded in recent years. This upgradation vindicated the fact that it is the metal ion, which plays a pivotal role in regulating the self-aggregation behavior of MTS/MTSC, respectively [34]. Whilst, the positioning of the metal ion component (counter ion/integral component) in the base matrix does not seem to have an obligatory effect on the assembling phenomenon.

When dispersed in aqueous media, these MTS tends to “*diminish the characteristic qualities of metalloenzymes*” [39]. Therefore, the MTSC facilitates a self-aggregation/association of distinct metal-complex-based aggregates reciprocating the aggregation number equivalent to their counterparts *viz.* surfactants [15, 39]. This distinguishing property to self-aggregate, and formulate idiosyncratic complexes bestow these MTS with unique potential applications, which can prove to be handy in real-time scenario [39]. Additionally, the complexes so generated possess multiphasic properties, and can solubilize an array of diverse chemical moieties *i.e.* lipophilic/hydrophilic, and ionic components [13]. Depending upon the CMC value, distinctive structures illustrating assorted geometrical facets *viz.* micelles (spherical, oblate/prolate/ellipsoid, hybrid crystals with layered perovskite structure), and aggregates (vesicles, bilayers, helices, tubules) are customarily formed by this special class of metallic surfactants [40–43].

As compared to their conventional counterparts, CMC of these metal-based surfactant complexes is very less. Henceforth, the presence of MTS at a miniscule concentration is potent enough to bring a substantial saturation at the interfacial point along with a significant micelle formation [44]. Apart from these facts and findings, it has also been deciphered by studies that the self-assembly of MTS is greatly affected by two key factors *i.e.* nature of transition metal ion and differences in coordination at atomic scale. To gain a holistic view of the aforementioned fact, let us briefly discuss the effects of ions, solvents, and structures on micellar morphology with some examples:

- a) **Metal ion** – If a conventional surfactant is dispersed in water, a simple micelle is formed, while incorporation of a metal ion in the base structure results in a significant alteration in the geometrical facet, and surface charge of the MTS. In place of the micelle, formation of a vesicle takes place usually [45–47].
- b) **Solvent system** – A reverse micelle having a metallic amphiphilic bilayer is formed upon the dispersion of an MTS (having multiple alkyl chains attached to a metal ion) in non-polar solvent while, such a phenomenon is absent in conventional surfactant systems [18, 48, 49]. Upon dispersion into less polar organic solvents (*viz.* chloroform, and diethyl ether), these MTS tends to aggregate, and formulation of inverted metallomicelles takes place. This phenomenon can be principally attributed to the non-covalent interactions which encourage the orientation of the reactive head group in a miniscule volume thereby ultimately resulting in the generation of a highly concentrated and catalytically active cavity of colloidal frameworks.
- c) **Structural factor** – Formation of micelle takes place in case of an aqueous dispersion of single-chain MTS while vesicles are formed upon dispersion of double-chain MTS in aqueous media [50–52]. This can be further explained based upon the morphology of the metallic surfactants. Cylindrical morphology of the double-chain MTS, and interaction of metal ion with two surfactant molecules results in the formation of a pseudo-double-chain surfactant (PDCS). During the PDCS generation, the molecules orient themselves in such a manner, that the packing assumes a vesicular structure [53–55].

Apart from this, the cross-sectional area of both the vital components i.e. head and tail region is altered due to the incorporation of metallic ion in the core structure. This alteration creates a demarcating change in the packing volume, thereby inducing a series of phase transition in the metalloaggregates. The phase transitions ultimately result in the fabrication of vesicles with vivid structural forms (*viz.* unilamellar, multi-lamellar/vesicular) [56–58].

With the aid of MTS, an assortment of vivid physicochemical attributes of metal ions can be localized at air–water/oil–water interface. Henceforth, it would be apposite to state, “*the MTS are an exceptional class of surfactant system, which technically amalgamated two diverse area of science i.e. co-ordination and surface chemistry in a coherent manner*” and this leads to the emergence of a noble omnipotent scientific domain. Amidst a wide array of characteristics, redox activity is deemed to be the predominant one. The inculcated metallic ion tends to possess a variable oxidation state, and it is because of this inherent property that these MTS are able to illustrate such a noteworthy ability. The traditional surfactant systems lacks this capability as their core framework is largely composed of elements-like carbon, oxygen and sulfur [45].

On a comparative note, it has been established repeatedly, that MTS essentially bestow enhanced chemical reactivity as compared to their conventional counterparts. Charge, valency, and empty d/f orbitals entangled with metal ions are some of the pivotal factors, which escalates the chemical reactivity of these superior class of metal surfactants to many fold times [18]. In other words, it can be righteously stated that the “*base surfactant itself does not have any chemical reactivity*” [18, 45]. However, it is the embodiment of the metal ion, which brings a radical change in the chemical state of the pristine surfactant, thereby efficaciously circumventing the existing lacuna associated with the traditional surfactant systems [45].

Incorporating metal ions possessing energy levels equivalent to those of the visible transitions (taking place in the UV–visible region) imparts a chromophoric ability to the MTS. It is because of this intricate potential that these metal-based surfactants exhibit illustrious and bright colors (e.g. Cu^{2+} [blue], $\text{Fe}^{2+}/\text{Fe}^{3+}$ [yellowish red], and Ni^{2+} [green]). This might be attributed to the d–d transition of the metal ion, which is positioned in the visible region of the electromagnetic spectrum. Additionally, it is well versed that the alteration in color is exclusively dependent upon the surrounding chemical milieu. This facilitates the user with a tranquil access where he/she can control the reaction conditions in a complacent manner [45].

In an analogous manner, inculcation of a paramagnetic/ferromagnetic metal ion within the framework of the soft matter imparts magnetic properties to the surfactants, which are fundamentally diamagnetic in nature [18]. The stimuli (magnetic field)-responsive surfactants depicts a novel class of surfactants, wherein the surface tension can be simply modulated by switching on/off the applied magnetic field. Distinct from all of this Lewis acidity, pH responsiveness, and structural diversity are some of the other striking attributes, which are exemplified by these MTS [51, 54, 57].

It seems from the aforementioned facts and findings, that the metal ion is the only component, which is responsible for allocating such eminent characteristics however, in real sense it is not so. The soft matter also adds significantly to the metal-ion

chemistry. Active transfer of the above-mentioned attributes to the interface is typically accomplished due to the surface-active property of the surfactant. Henceforth, it is the reunion of the characteristic chattels of both the components, which led to the acquirement of such distinctive physicochemical attributes [48]. Owing to such exceptional attributes, this special class of building blocks have been utilized in many fields vis-à-vis (i) surface activation agents, (ii) monolayers, (iii) emulsions, (iv) contrast agents (medical resonance imaging), (v) catalysts (homogenous photo catalysis), (vi) transporting and sensing agents (fluorescent sensors), (vii) binders and metal extractors, (viii) redox agents (biological system), (ix) vectors for drug delivery (nanoparticles), (x) thin-film optoelectronic devices, (xi) solvatochromic probes, (xii) interfacial photo-physical agents, (xiii) templates for fabrication of diverse frameworks (micelles, vesicles, bilayers, liquid crystals, mesoporous materials, and metallomesogens), and (xiv) antimicrobial agents (*viz.* antibacterial, antiparasitic, anthelmintic) [50, 59, 60].

1.3 Classification of Metallosurfactants

In pertinent literature, a vast majority of systems have been outlined, which tends to intrinsically categorize these tailored/engineered hybrid surface-active moieties based upon certain distinctive characteristics. One such classification system relies upon the type of bonding between the metal ion, and the soft matter (surfactant). According to this system, surfactants comprising of inorganic moieties are generally referred to as inorganic surfactants (*viz.* I-SURFs) [18, 45]. I-SURFs can be categorically sub-divided into two major categories *viz.*

- a) **I-SURFs type I** – These are the simplest type of surfactants, in which the metal ion is incorporated within the conventional surfactant. Herein, the metal ion plays a definitive role, and acts as a counter ion.
- b) **I-SURFs type II** – In such kind of hybrid surfactants, the metal ion acts as an integral part of the polar head group. Type II I-SURFs can be further divided into two prominent types i.e. type II a, and type II b. In type II I-SURFS, the metal ion is localized within the polar head group component of the soft matter. In the latter one, the metal ion itself acts as the head group.

In the pertinent literature, another classification system, which shares analogous fundamental basics to the aforementioned system, has been reported. In this method, the MTS are chiefly classified into three major categories *viz.*

- a) **Group I** – In this kind of metal-based surfactants, the hydrophilic head group acts as a housing cavity for the positioning of the metal ion. Further, attachment of this component with the hydrocarbon tail is accomplished via covalent binding [61].
- b) **Group II** – These MTS represent a newer class of hybrid metallic surfactants. In these hybrid surfactants, the hydrophobic part of the soft matter provides accommodation to the metal ion. Herein, the metal ion acts as an integral part of the long alkyl chain, and it is with the help of co-ordination chemistry that this ionic entity is connected with the hydrophobic segment [62].

- c) **Group III** – In this type of hybrid surfactants, the counter ion of the soft matter provides a housing cavity to the metallic ion. Herein, the metal ion is weakly bonded with the surfactant and is localized within the counter ion segment [63].

Based upon their dissociation in water, a third type of classification system categorizes the MTS into two chief classes *viz.*

- a) **Cationic** – Upon dispersion into an aqueous phase, these MTS are primarily dissociated into two key components i.e. an amphiphilic cation, and an anion. A major share of such MTS chiefly comprises of nitrogenous compounds such as fatty amine salts, and quaternary ammoniums. These nitrogenous functional groups are further attached to elongated single or multiple alkyl tails (e.g. bis(2-phenylpyridine)(4,4-diheptadecyl-2,2-bipyridine)-iridium(III) chloride (Ir-complex)) [64].
- b) **Anionic** – Unlike their predecessors, these MTS also dissociate into two major components upon dispersion into an aqueous phase. However, the demarcation lies in the fact that herein, an amphiphilic anion is generated in place of a cation followed by the generation of a cation. Anionic surfactant *viz.* sodium 1,4-bis(neopentylxy)-3-(neopentylxycarbonyl)-1,4-dioxobutane-2-sulfonate (TCI₄) would constitute a perfect example of such a system [65]

The fourth classification system is distinctly apart from the earlier-described systems. Herein, depending upon the localization of metal ion in the soft matter, the MTS can be classified into two broad categories as;

- a) **Metal ion in hydrophilic head group** – In this class of hybrid metal-based surfactant, hydrophobic component of the MTS primarily comprises of the alkyl chain of the soft matter, while the metal ion along with its primary coordinated sphere constitutes the polar head group [15, 60].
- b) **Metal ion in hydrophobic tail group** – This type of MTS depicts divergent attributes as juxtaposed to the former one. Herein, the metal ion is localized in the hydrophobic (alkyl chain) segment (tail) of the soft matter [16, 40].

The fifth classification system can be considered as the core/base structural characterization scheme. According to this classification schema, the MTS can be classified into five major categories as;

- a) **Single chained** – In this class of MTS; the metal ion is incorporated with the polar head group of the soft matter. Herein, the metal ion tends to play a definitive role, and acts as a counter ion [66].
- b) **Double chained** – This type of hybrid metallic surfactants possess an analogous structure to that of the single-chain MTS. However, the major demarcation lies in tail group. Alike its predecessor, the metal ion along with its primary coordination sphere acquires the functionality of the polar (hydrophilic) head group. Whereas, on the other hand, the ligand along with the alkyl (hydrophobic) tail is coordinated to the metal ion [67, 68].
- c) **Pseudogemini** – With an advent in time, surfactant chemistry exemplified astonishing progressions. These momentous advancements, paved a gallant way

for the fabrication of interesting class of novel surfactants *viz.* pseudogemini surfactants. Pseudogemini MTS are single-chain analogues of gemini surfactants [69]. They possess an explanatory complexed structure, in which the amphiphilic ligands are attached to a centrally coordinated metal ion. MTS complex of an "alkylsulfonatephosphine-functionalized alkyphenol ethoxylate" symbolizes an interesting example of such a system [44].

- d) **Mixed ligand coordination complexes** – These can be piously regarded as the exalted class of MTS. In such MTS, a transition metal complexed with an amphiphilic entity such as Schiff's base is incorporated within the core framework of a conventional surfactant [70].
- e) **Organometallic surfactants** – These hybrid surfactants epitomizes the most advanced series of metallic surfactants. It can be astutely stated, "*it is because of such illustrious moieties that the dynamics of surfactant chemistry has metamorphosed colossally.*" Coming on to the schematic aspect, these MTS are analogous to the traditional surfactants, as they also tend to possess a head and tail group. Nonetheless, a major variance is generated due to the alteration in the chemical nature of the molecular entities, which constitutes both these pivotal segments. Herein, the head group usually constitutes of a transition metal embodied with one of the components of the soft matter. Whilst, in the second region, the alkyl chain is substituted with a functional group tagged π -conjugated chain, which further acquires the functional role of the hydrophobic tail [71].

1.4 Syntheses Stratagems and Characterization of Metallosurfactants

The facts and findings discussed above have provided us with a comprehensive overview of the MTS and their intricate physiognomies. Now, it has become clear that MTS are technically "*amphiphilic entities comprising of coordinated metal ion/ions.*" Coming on to the syntheses part, polar or organic solvents play a vivacious role in the syntheses of these exceptional classes of hybrid surfactants. Till date, three distinctive synthesis routes have been devised for the syntheses of MTS;

1.4.1 Metathesis Reaction

A highly sophisticated and arduous methodology becomes pre-requisite when it comes to the development of MTS possessing cationic metal species, and aliphatic tails. In such circumstances, the following stratagem *i.e.* metathesis reaction (MR), appears to be a unique one and offers several lucrative advantages *viz.* [72]

- (i) One-pot synthesis.
- (ii) Ease of extraction and cost effectiveness.
 - **Efficient recovery of catalyst** – Employment of water-soluble catalyst circumvents the need for re-extraction.

- **Minimized solvent consumption/wastage** – Tranquil extraction of catalyst can be accomplished with an aqueous phase. The aqueous phase can be reused as such for subsequent reactions (continuous batch production).
- **Ordinary reaction conditions** – Does not require any specific reaction conditions such as inert atmosphere, and degassing. The entire reaction can be carried out at room temperature.

In general terms, an MR can be defined as a “*reaction in which two distinct chemical entities react in an aqueous phase to form a novel product.*” Herein, the formation of the new product usually takes place due to the double decomposition/displacement reaction (interchanging of the radicals or ions of the reactant species). MR, in other words, can be technically referred to as “*the phenomenon of cation, and anion exchange in a polar/aqueous phase*” [73].

To understand the dynamics of the aforementioned synthesis schema, let us consider certain examples. Lipshutz et al. carried out the synthesis of a “*designer surfactant*” viz. PQS (nanomicelle-forming amphiphile) using a metathesis reaction [74]. Herein, a well-versed ring-closing ruthenium catalyst i.e. Grubbs Hoveyda 1 Ru(II) was employed as an intermediate substrate for the catalyzing the entire reaction. The present experiment exhibited promising outcomes and the results came out to be extremely significant. Proposed methodology, i.e. micellar catalysis/ring catalysis metathesis (RCM) allowed a successful covalent linking of the Ru carbene with the designated chemical moiety, thereby, leading to a successful synthesis of the novel MTS [74]. The synthesized PQS MTS offered three vivid key elements viz. lipophilic segment (site for solubilization of insoluble organic substrates), hydrophilic segment (solubilizes PQS in polar/aqueous solvent such as water), and free –OH residue within the hydrophobic core (site bearing the metallic part). The proposed methodology also offered a potent solution to overcome the pre-existing lacunas of the conventional methodology. Pure water acted as the solvent system, and during the entire reaction, room-temperature conditions were maintained. The catalyst used was water soluble, and no re-isolation steps were further carried out. Additionally, the proposed methodology facilitated the RCM of water-insoluble dienic substrates [74].

1.4.2 Ligand Substitution Reaction

Ligand substitution reaction (LSR) is the second most preferred type of reaction, when it comes to the synthesis of hybrid metal-based surfactants. As the name itself suggests, the method generally involves the substitution of lesser labile ligands with more labile ligands. In other words, it can be righteously said, that in these types of reactions, interchange of highly susceptible ligands takes place via the lesser ones. In lieu of this, Veeralakshmi et al. synthesized varied types of single- and double-chained MTS possessing idiosyncratic biological functionalities [75]. Facile employment of LSR led to the efficacious synthesis of hybrid ligand-anchored metallic surfactant complexes. Herein, $\text{Co}(\text{dien})\text{Cl}_3$ acted as the

precursor excipient whilst, diethylenetriamine (dien), dodecylamine (DA), and hexadecylamine (HA) were chosen as the model ligands. In the present experiment, one or two amine groups of the alkylamine ligand base played an active role and led to the substitution of one or two labile chloride ligands. This ligand-mediated substitution ultimately resulted in the synthesis of four different types of MTS viz. $[\text{Co}(\text{dien})(\text{HA})\text{Cl}_2]\text{ClO}_4$ (III), $[\text{Co}(\text{dien})(\text{DA})\text{Cl}_2]\text{ClO}_4$ (IV) $[\text{Co}(\text{dien})(\text{HA})_2\text{Cl}](\text{ClO}_4)_2$ (V), and $[\text{Co}(\text{dien})(\text{DA})_2\text{Cl}](\text{ClO}_4)_2$ (VI) [75].

1.4.3 Ligand Insertion Reaction

Last but not the least, ligand insertion reaction (LIR) is the third type of reaction, which is predominantly employed for the synthesis of MTS. A distinctive feature of this method is the maintenance of the integral nature of all the excipients being employed during the reaction. Unlike, its predecessor i.e. LSR, this method does not involve any substitution/elimination. The method preferred is the fabrication of hybrid metal-surfactant complexes via interjecting a chemical moiety (usually a ligand) into another molecule or a bond [19]. Following this approach, Wagay et al. synthesized a hybrid MTS named *cis*-chlorobis(ethylenediamine)dodecylamine cobalt(III) nitrate(I) (viz. CDCN) [67, 68, 76]. Herein, a dropwise addition of the ligand i.e. dodecylamine (ethanolic solution) to *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (aqueous solution) resulted in the attainment of the desired metal surfactant complex.

In another experiment, a double-chained MTS viz. *cis*-bis(1,3-diaminopropane) bis(dodecylamine)cobalt(III) nitrate(II) (DDCN) was synthesized by the same group using LIR methodology [76]. Analogous to the aforementioned methodology, the preset method also involved a dropwise addition of ethanolic dodecylamine solution (ligand) to an aqueous solution of *trans*- $[\text{Co}(\text{tmd})_2\text{Cl}_2]\text{ClO}$ (aqueous solution). This in turn led to a successful synthesis of the desired hybrid metal-surfactant complex i.e. DDCN.

Characterization plays an imperative role in deciphering the electro-physicochemical, structural, and morphological attributes of the synthesized MTS. Determination of such imperious traits can further aid in exploring the practical utility of these versatile systems in real-time scenario. Not only this, the characterization of synthesized MTS using high-tech analytical techniques gives an edge to the researchers/chemists, and allows them to develop versatile MTS with tailored properties. A wide array of analytical techniques ranging from simplistic spectrophotometer to advanced techniques such as electron/ atomic microscopy has been widely employed for the facile elucidation of intricate physiognomies. Table 1.1 illustrates the varied analytical techniques being employed for the characterization of novel MTS.

1.5 Conclusion

MTS represents a class of supra-molecular assemblies which can facilitate an effective bridging between both the explicit domains of chemistry viz. synthetic and inorganic. It is because of this unique bridging that these exhilarating moieties with

Table 1.1 Characterization of MTS via state-of-art analytical techniques.

Techniques	MTS explored	Characteristic attributes probed	Inference	References
Dynamic light scattering (DLS)	Tetradecylpyridinium (TP) TP ₂ [MCl ₄] (M = Mn, Co, Ni, Cu, Zn)	Hydrodynamic radii (size) and surface charge	The micelles depicted ultrafine particle size of 4–7 nm, whilst the zeta potential was found to be +45 mV, respectively.	[68]
Scanning electron microscopy (SEM)	Supramolecular MTS (SMMSS)	Surface morphology	The fabricated SMMSSs illustrated a spherical (polymeric) morphology. Highly dispersed polymeric SMMSSs obtained with increase in the chain length	[77]
	Biscetylpyridiniumtetrachloroplatinate (Pt-CPC) MTS	Surface morphology	Surface pattern found to be profoundly dispersed, highly homogenous, and spherical in nature	[78]
Transmission electron microscopy (TEM)	Double-tailed metallosomes (viz. bishexa decylpyridinium metal tetrachloride (MCPC II) [M: Fe, Co, Ni, Cu]) C _n -Cu-C _n (n = 8, 12, 16) MTS	Morphological attributes Morphometric attributes	Fabricated MTS (50–150 nm) possessed diverse morphologies viz. multivesicular and spherical Primarily vesicular aggregates within a size range of 60–200 nm. Additionally microscopic studies revealed the presence of polydispersions and polyaggregates	[73] [79]
Atomic force microscopy (AFM)	CTA–AgB MTS Copper(II)-surfactant complexes	Molecular geometry Molecular geometry	The aggregates were predominantly spherical Metallovesicles (MTVs) in the size range of 20–50 nm were formed	[80] [81]

(Continued)

Table 1.1 (Continued)

Techniques	MTS explored	Characteristic attributes probed	Inference	References
Ultraviolet-Visible (UV-Vis) spectroscopy	Bis(hexadecyl pyridinium metal(II) tetrachloride (M CPC II) [M: Fe, Co, Ni])	Probabilistic mechanism responsible for binding of BSA to the corresponding MTS	Inclination in the intensity of the absorption maxima (static quenching) of BSA upon addition of MTS. Blue shift (protein stabilization/unfolding).	[82]
	Chromium (III) MTS containing various chelating ligands (ethylenediamine (en), tri-ethylenetetramine (trien), 2,2-bipyridine (bpy), and 1,10-phenanthroline (phen)), and axial amine (dodecylamine/cetylamine)	Geometrical configuration of the corresponding cations within the MTS	Escalated distortion of basal planes in case of "phen" complexes as compared to "bpy" complexes. Both the complexes (viz. $cis-[Cr(phen)_2(C_{12}H_{25}NH_2)_2]^{3+}$ and $[Cr(bpy)_2(C_{16}H_{33}NH_2)_2]^{3+}$) possess an identical structure	[59]
Fourier transform infra-red (FTIR) spectroscopy	Hexadecyltrimethyl ammonium chromium trichloride (CrC I), hexadecyltrimethyl ammonium chromium tetrachloride (CrC II)	Elucidation of functional group bonds generated among the parent excipients.	Interaction of metal chloride with the ammonium group of the MTS resulted in an alteration in the chemical milieu (shifting of -C-N, and NH-Cl stretching band to a lower wavenumber)	[83]
Nuclear magnetic resonance (NMR) spectroscopy	Bistable copper(II) complex	Explication of linkage developed between the varied precursor materials	Free carbonyl groups (ν O-H) played a pivotal role in establishing linkage with the silanol (Si-OH) groups present in the silica walls	[84]
	N-heterocyclic carbene (NHC)-MTS	Vindicating the successful fabrication (linkage of two polymer blocks) of MTS.	Covalent linkage between PS and PMMA established.	[33]
	FeCPC I, CoCPC I, NiCPC I MTS	—	Fabricated MTS comprises of core-shell-shaped particles, resulting in the synthesis of block copolymer Electronic interaction between the cationic (CP ⁺) and anionic (MCl ₃) moieties resulted in the synthesis of corresponding MTS.	[2]

Small-angle X-ray scattering (SAXS)	Lipid mimetic MTS viz. [Ru(bpy)2(dn-bpy)] ²⁺ and [Ir(ppy)2(dn-bpy)] ⁺	Determination of the structural aspects of the corresponding MTS	Sharp Bragg's peaks obtained indicating the formation of crystalline, hollow, and multilamellar (composed primarily of bilayer stacks) MTS-based structures	[85]
X-ray diffraction (XRD)	MTS ionogels Cetylpyridinium chloride metallosomes (METs)	Elucidation of the morphological attributes of the corresponding MTS. Establishment of the morphological arrangement of the as-fabricated METs	All the three MTS ionogels possessed lamellar morphology. METs possessed highly crystalline geometry along with a lamellar metallosomal bilayer	[86] [73]
Differential scanning calorimetry (DSC)	[M(CH ₃ COO) ₄] ²⁻ [C ₁₂ H ₂₅ NH ₃] ₂ ⁺	Physicochemical characteristics of the MTS.	Decomposition occurs with melting in metal complexes, and metal oxides remained as final products. Activation energy order obtained was dependent on the size of transition metal ion and metal ligand bond strength	[87]
Thermogravimetry/differential thermal analysis (TG-DTA)	Pt-CPC MTS	Thermal behavior and stability of the MTS	The fabricated MTS depicted an enhanced thermal stability. The Pt-CPC MTS illustrated an exothermic behavior prior to the transition temperature (TT) whereas; a <i>vice-a-versa</i> phenomenon was obtained on/after the TT.	[78]

tailored physiognomies can be fabricated with ease. Apart from this, the inimitable metal-phase behavior of the MTS bestows them with a unique ability to formulate an extensive array of supramolecular structures. Additionally, the existence of an interrelation between the two vivid domains *viz.* coordination chemistry and surfactant self-assembly offers tremendous opportunities for these MTS to be applied on a full-scale level in varied domains of science, and technology.

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