

Edited by Surinder K. Mehta and Ravneet Kaur

Metallosurfactants

From Fundamentals to Catalytic
and Biomedical Applications



Table of Contents

[Cover](#)

[Title Page](#)

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[Preface](#)

[1 Metallosurfactants, a “*Novel Portmanteau*”: A Holistic Insight into the Structural-Physiognomies Relationships, Synthesis Stratagems, and Characterization](#)

[1.1 Introduction](#)

[1.2 Intrinsic Physiognomies of Metallosurfactants](#)

[1.3 Classification of Metallosurfactants](#)

[1.4 Syntheses Stratagems and Characterization of Metallosurfactants](#)

[1.5 Conclusion](#)

[References](#)

[2 Metallosurfactants: A Surface and Interface Perspective](#)

[2.1 Introduction](#)

[2.2 Micellization and Surface Parameters](#)

[2.3 Adsorption of Surfactant Monolayers](#)

[2.4 Conclusions](#)

[References](#)

[3 Metallosurfactant Self-Assembly: Structures and Chemistry of Interfacial, Biphasic, and Phase Transfer Catalysis](#)

[3.1 Introduction](#)

[3.2 Self-Aggregation Behavior](#)

[3.3 Chemistry of Catalysis](#)

[3.4 Conclusions](#)

[Acknowledgment](#)

[References](#)

[4 Hydrolytic Metallosurfactants: Nanocatalysts for Esterolytic Reactions](#)

[4.1 Introduction](#)

[4.2 Metallosurfactants as Nanocatalyst for Esterolytic Reactions](#)

[4.3 Catalytic Hydrolysis of Carboxylate Esters](#)

[4.4 Catalytic Hydrolysis of Phosphate Esters](#)

[4.5 Quantitative Treatment of Observed Rates: Application of Kinetic Models](#)

[4.6 Conclusion](#)

[References](#)

[5 Metallosurfactants as Catalysts in Organic Reactions and Energy-Based Applications](#)

[5.1 Introduction](#)

[5.2 Metallosurfactants as Catalysts in Organic Reactions](#)

[5.3 Metallosurfactants as Catalyst in Water Oxidation](#)

[5.4 Light-Driven Hydrogen Generation](#)

[5.5 Conclusions](#)

[References](#)

[6 Metallosurfactants as Drug-Delivery Vehicles](#)

[6.1 Introduction](#)

[6.2 Distinct Assemblies of Metallosurfactants in Drug Delivery](#)

[6.3 Metallosurfactants as MRI Contrast Agents](#)

[6.4 Conclusion](#)

[Acknowledgments](#)

[References](#)

[7 Metallosurfactants as Molecular Machines for the Preparation of Hybrid Silica-Based Porous Material](#)

[7.1 Introduction](#)

[7.2 Porous Silica-Based Materials](#)

[7.3 Different Types of Porous Silica-Based Material](#)

[7.4 Future Perspectives](#)

[7.5 Conclusion](#)

[References](#)

[8 Metallosurfactants as Non-viral Vectors in Transfection](#)

[8.1 Introduction](#)

[8.2 Metallosurfactant Monomers](#)

[8.3 Metallomicelles](#)

[8.4 Metalloliposomes \(Metallosomes\)](#)

[8.5 Future Perspectives](#)

[Acknowledgments](#)

[References](#)

[9 Metallosurfactants as Nanoreactors for Nanoparticle Synthesis](#)

[9.1 Introduction](#)

[9.2 Metallosurfactants as Reactors for Nanoparticle Synthesis](#)

[9.3 Future Perspective](#)

[9.4 Conclusion](#)

[Acknowledgments](#)

[References](#)

Note

10 Metallosurfactants and Their Biological Attributes: Anticancer and Antimicrobial Properties

10.1 Introduction

10.2 Antimicrobial Activity

10.3 Anticancer Activity

10.4 Conclusion and Future Challenges

References

11 Metallosurfactants as Carbon Monoxide-Releasing Molecules

11.1 Why CO?

11.2 How to Deliver CO?

11.3 CO-releasing Metallosurfactants

11.4 Conclusions

Acknowledgments

References

12 Supramolecular Metal-Modified Nanocontainers Based on Amphiphilic and Hybrid Matrix: Self-Assembling Behavior and Practical Applications

12.1 Introduction

12.2 Structure, Properties, and Biomedical Application of Metallosurfactants

12.3 Amphiphilic System Based on Metallosurfactants and Macrocycles

12.4 Nanocomposites Based on Amphiphilic Resorcinarenes and Metal Nanoparticles

12.5 Conclusions

Acknowledgments

References

[13 Metallosurfactants in Nanoscale Molecular Containers as Sensors](#)

[13.1 Introduction](#)

[13.2 Metallosurfactants as Nanosized Containers for Self-assembled Molecular Devices](#)

[13.3 Surfactant Aggregates in Chemical Detection](#)

[13.4 Self-Assembled Moieties as Fluorescent Sensors](#)

[13.5 Metallosurfactants and Detection Protocol](#)

[13.6 Conclusions](#)

[Acknowledgments](#)

[References](#)

[Index](#)

[End User License Agreement](#)

List of Tables

Chapter 1

[Table 1.1 Characterization of MTS via state-of-art analytical techniques.](#)

Chapter 2

[Table 2.1 Critical micelle concentration \(CMC\) and area occupied per molecu...](#)

[Table 2.2 The CMC values of the various Cr\(III\) coordination complexes at 30...](#)

[Table 2.3 Comparison of CMC values and thermodynamic parameters for Pt-CPC a...](#)

[Table 2.4 Calculated parameters from surface tension measurements: critical ...](#)

Chapter 3

[Table 3.1 Several reactions catalyzed by vesicles \(vscl\) and amorphous \(amps...](#)

Chapter 5

[Table 5.1 Reaction of 2-aminobenzophenone 1a with ethyl acetoacetate 2a cata...](#)

Chapter 9

[Table 9.1 Some examples of metallosurfactants as nanoreactors.](#)

Chapter 12

[Table 12.1 Different types of metallosurfactant structures.](#)

[Table 12.2 Catalytic activity of nanocomposites based on resorcinarene nanoc...](#)

[Table 12.3 Suzuki reaction using Pd, Ni nanocomposite with p\(MVCA-St\).](#)

List of Illustrations

Chapter 1

[Figure 1.1 Schematic representation of surfactant.](#)

Chapter 2

[Figure 2.1 Potential self-assembly structures possible for metallosurfactant...](#)

[Figure 2.2 \(a\) Structure of ligand L where \$R = C_{10}H_{21}\$, L1 and L2 \(b\) Surface...](#)

[Scheme 2.1 Structure of the metal-surfactant complex or metallosurfactant co...](#)

[Figure 2.3 Proposed organization of copper surfactant complex \(a\) at the air...](#)

[Scheme 2.2 Schematic representations of complexes in the interface showing t...](#)

[Figure 2.4 \(a\) The structure for redox active, amphiphilic metal complexes \(...\)](#)

Chapter 3

[Figure 3.1 Representative structure of a metallomicelle \(Green sphere: head ...\)](#)

[Figure 3.2 Structures of synthesized \[Cu\(1\)\]Cl₂ and \[Cu\(2\)\]Cl₂ metallosurfac...](#)

[Scheme 3.1 Schematic representation of ruthenium and iridium metallosurfacta...](#)

[Figure 3.3 \(a\) Structure and \(b\), \(c\) TEM images for \[2\]\[NO₃\]₄, M = Pd and \[](#)

[Figure 3.4 Cryo-TEM images for 1 wt% solution of Co\(III\) surfactant showing ...](#)

[Figure 3.5 Ru metallosurfactant \(a\) Representation of inverted aggregates of...](#)

[Figure 3.6 \(a\) Fourier transforms of Fe\(III\) sites in sedimented Cd\(II\)- and...](#)

[Figure 3.7 \(a\) Preparation of molybdenum metallosurfactants \[4-9\] \(L = 1, 2, ...\)](#)

[Scheme 3.2 \(a\) Molecular structure of Ru metallosurfactant and image represe...](#)

[Figure 3.8 Structures of \(a\) PQS, \(b\) PQS-attached Grubbs-Hoveyda-1 metathes...](#)

[Scheme 3.3 \(a\) As-synthesized Hoveyda-type surface active catalysts - 2,3 \(b...](#)

[Figure 3.9 Proposed mechanism of the ATH using chiral surfactant-type cataly...](#)

[Scheme 3.4 \(a\) Vesicle formation via self-assembly of amphiphilic pincer com...](#)

[Figure 3.10 Proposed mechanism of interfacial catalysis in bifacial esterifi...](#)

Chapter 4

[Figure 4.1 \(a\) Structure of common surfactant, \(b\) structure of metallosurfa...](#)

[Figure 4.2 Commonly investigated carboxylate and phosphate esters: \(a\) PNPA;...](#)

[Figure 4.3 Imidazole-based metallosurfactant ligands prepared by Tagaki et a...](#)

[Figure 4.4 Selective activation of primary and secondary -OH groups of ligan...](#)

[Figure 4.5 Pyridine-based ligands prepared by Tonellato and coworkers.](#)

[Figure 4.6 Phenanthroline-based ligands synthesized by Engbersen and coworke...](#)

[Figure 4.7 Proposed mechanisms of hydrolytic cleavage of PNPP catalyzed by Z...](#)

[Figure 4.8 PNPP hydrolysis by \$\text{Cu}^{2+}\$ metallomicelles in the presence of ge...](#)

[Figure 4.9 Active species formed by the tetradentate ligand.](#)

[Figure 4.10 Proposed mechanism of the BNPP hydrolysis by metallomicelles of](#)

[Figure 4.11 Proposed mechanism for metallosurfactant-mediated breakdown of B...](#)

[Scheme 4.1 \(a\) general scheme for partitioning of the reactants between the ...](#)

Chapter 5

[Figure 5.1 Effect of the length of catalyst chain on the ATH of aliphatical ...](#)

[Figure 5.2 Recycling test of the catalyst Mo1.](#)

[Figure 5.3 Kinetics of our authors' model reaction with different alkyl chai...](#)

[Scheme 5.1 Schematic representation of synthesis and self-assembly of surfac...](#)

[Figure 5.4 \(a\) Polarization curves of CPC, PdCPC\(I\), and Pt/C, \(b\) Tafel slo...](#)

[Figure 5.5 \(a\) Cyclic voltammetry of CoCPC\(I\) in 0.5 N H₂SO₄ at 100 mV s⁻¹ ...](#)

[Figure 5.6 Polarization curves, initial and after 100 cycles at pH 11 for 1 ...](#)

[Figure 5.7 CV measurement \(black\) and Randles-Sevcik plot \(blue\); OER = circ...](#)

[Figure 5.8 Solvent study. Variation of organic solvent, with the final solut...](#)

[Figure 5.9 Kinetic traces at 510 nm for the back reactions of \(a\) \[Ru\(bpy\)₂M...](#)

Chapter 6

[Figure 6.1 Representation of a cobalt-based metallosurfactant complex.](#)

[Figure 6.2 \[Ru\(bipy\)\(4,4'-diheptadecyl-2,2'-bipyridine\)₂\]Cl₂ metallosurfacta...](#)

[Figure 6.3 Structure of molybdenum metallosurfactant \(left\) and TEM image of...](#)

[Figure 6.4 Schematic diagram of metallosomes comprising a metal complex \(DAC...](#)

[Figure 6.5 Construction of pH-responsive mesostructured surfactant silica hy...](#)

[Figure 6.6 HIFU-responsive process of Cu\(II\)-terpyridine bonds containing bl...](#)

[Figure 6.7 Fabrication of reversible metallo-supramolecular pH and thermores...](#)

[Figure 6.8 An illustration of synthetic route for carbon dots \(CDs\) and self...](#)

[Figure 6.9 Illustration of fabrication of bimodal nanoparticulate contrast ag...](#)

Chapter 7

[Figure 7.1 Porous materials with different size of pores.](#)

[Figure 7.2 Structural representation of a Catenanes.](#)

[Figure 7.3 Pictorial representation of surfactant-based template synthesis o...](#)

[Figure 7.4 Copper surfactants based on sarcophagine and TEM image of mesopor...](#)

[Figure 7.5 Crystal structure of deprotonated and protonated bistable copper ...](#)

[Figure 7.6 Ruthenium metallosurfactant used as template for porous silicate ...](#)

[Figure 7.7 Representation of templating phenomena of Co soap.](#)

[Figure 7.8 Schematic illustration of synthetic pathway for magnetic mesoporo...](#)

[Figure 7.9 Graphical representation of single iron atom-loaded mesoporous si...](#)

[Figure 7.10 Schematic representation of the strategy used for the encapsulat...](#)

Chapter 8

[Figure 8.1 Structures of different viral vectors.](#)

[Figure 8.2 Structures of different non-viral vectors.](#)

[Figure 8.3 Stages involved in gene transfection process using surfactant mon...](#)

[Figure 8.4 Structures of the Ru metallosurfactants.](#)

[Figure 8.5 Structural representations of RuC11C11/cyclodextrin complexes wit...](#)

[Figure 8.6 Dependence of both the apparent emission intensity values \(EI\) an...](#)

[Figure 8.7 Sigmoidal dependence of the binding constant \$K_b\$ with the \[DNA\] fo...](#)

[Figure 8.8 Structural representations of RuC19C19/cyclodextrin complexes wit...](#)

[Figure 8.9 AFM images of DNA \(a\) and RuC1C19/DNA complexes at \$\[S\]/\[DNA\] = 0....\$](#)

[Figure 8.10 Metallosurfactant \$\[Pt\(L\)_2Cl_4\]\$.](#)

[Figure 8.11 Metallosurfactant \$\[Cu\(L\)Br_3\]\$.](#)

[Figure 8.12 Metallosurfactants \$\[Cu\(L_{dt}\)_2\]^{2+}\$ and \$\[Cu\(L_{ot}\)_2\]^{2+}\$.](#)

[Figure 8.13 Cu-based metallosurfactants.](#)

Chapter 9

[Figure 9.1 Proposed organization of metallo-surfactants, \(a\) at the air-wate...](#)

[Figure 9.2 Schematic representation of the steps involved in the formation o...](#)

[Figure 9.3 High resolution transmission electron microscope \(HRTEM\) images o...](#)

[Figure 9.4 TEM images and corresponding histograms of CeO₂ NPs obtained afte...](#)

[Figure 9.5 TEM of gold particles: \(a\) CPC1 \(20 mmol dm⁻³\), irradiation...](#)

[Figure 9.6 Schematic illustration of NPs structure: \(a\) the normal bilayer b...](#)

[Figure 9.7 \(a\) Schematic illustration of NPs synthesis using water-in-oil in...](#)

[Figure 9.8 Representation of the apparatus employed by the authors for synth...](#)

[Figure 9.9 \(a\) TEM image of TiO₂ particles obtained by injecting dimethyl su...](#)

[Figure 9.10 Synthetic procedure for obtaining monodisperse g-Fe₂O₃ NPs.Sourc...](#)

[Figure 9.11 TEM images of MnS nanocrystals. \(a\) MnS nanorods. Inset is an HR...](#)

[Figure 9.12 Schematic representation of metal NPs fabrication using various ...](#)

[Figure 9.13 \(a\) TEM image \(b\) XRD pattern \(c\) Field emission scanning electr...](#)

[Figure 9.14 Schematic representation of Pd\(0\) NPs via two-phase redox reacti...](#)

[Figure 9.15 Pictorial representation of CuNP synthesis. Source: Kaur et al. ...](#)

[Figure 10.1 Metallosurfactants and their biological attributes: anticancer a...](#)

[Figure 10.2 Heterocyclic cationic surfactant with tin and copper as counteri...](#)

[Scheme 10.1 Micelles containing chelated cisplatin for anticancer therapy by...](#)

[Figure 10.3 \(a\) Activation of photodissociative amphiphilic Ru\(II\) complex a...](#)

[Figure 10.4 Concentration-dependent mechanisms of cell death in amphiphilic ...](#)

[Figure 10.5 Blueprint of an emissive Ru\(II\) amphiphilic complex depicting re...](#)

Chapter 11

[Figure 11.1 Successive steps of the degradation of heme group and release of...](#)

[Figure 11.2 Examples of several CORM structures.](#)

[Figure 11.3 Metallosurfactant with the metal-carbonyl complex into the headg...](#)

[Figure 11.4 \(a\) Synthesis of the ligand \(L\) with 6 carbon atoms \(L6\). \(b\) Sy...](#)

[Figure 11.5 Center: scheme of the obtention of Mo-CORMs/phosphatidylcholine ...](#)

Chapter 12

[Scheme 12.1 One-stage synthesis of metallosurfactant with Cu\(II\) in the head...](#)

[Scheme 12.2 Two-stage synthesis of metallosurfactant with Co\(III\) in the hea...](#)

[Scheme 12.3 Two-stage synthesis of metallosurfactants with Cu\(II\), Ni\(II\) in...](#)

[Scheme 12.4 Chemical formulas of sulfonate calix\[4\]resorcinarene and complex...](#)

[Scheme 12.5 Synthesis of Ag@p\(CRA-B\) and Ag@CRA-C10.](#)

[Figure 12.1 Plots of \$\ln\(A/A_0\)\$ versus time for the catalytic reduction of *p*-n...](#)

[Scheme 12.6 Synthesis of p\(MVCA-St\) nanocomposites with PdNPs on the surface...](#)

Chapter 13

[Figure 13.1 Basic components of a surfactant.](#)

[Figure 13.2 Micellar, bilayer, and vesicular arrangements.](#)

[Figure 13.3 Chemical structure of lipids **1a**, **1b**, and **2**.](#)

[Figure 13.4 Structure of the lipids **1-4**.](#)

[Figure 13.5 Schematic representation of the self-assembled chemosensor. \(a\) ...](#)

[Figure 13.6 Schematic illustration of synthetic process of hybrid QC₁₂Et₃Br-...](#)

[Figure 13.7 Schematic representation of complexes 1 and 2 and their self-agg...](#)

[Figure 13.8 Typical time-resolved intensity decay curves of four-month-old R...](#)

[Figure 13.9 Schematic illustration of the fabrication of the bio-modal nanop...](#)

[Figure 13.10 Schematic diagram of attachment of complexes and surfactants to...](#)

[Figure 13.11 Schematic representation of the formation of the iridium aggreg...](#)

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Preface

This book introduces its readers to a very special class of amphiphiles termed as “metallo surfactants” from here on, incorporating a metal in the usual surfactant system. A book in this area has been long outstanding. When we started working on the metallo surfactants a few years back, we always felt the need for a holy grail or a guiding text to delve deeper into the realm of metal surfactant complexes or metallo surfactants. Something which could explain the fundamentals of the metal surfactant complexes in detail while highlighting the current progress as well as the future prospective. Back then, we would have been thrilled to get our hands on something like this. So, a lot of the topics included in this book stem from the difficulties we faced while doing the literature survey and understanding this complex topic a little better. The book has, therefore, been designed in such a way to provide a gradual evolution starting from the very basics to the more advanced concepts and then finally dealing with the applications of metallo surfactants including but not limited to catalytic, sensing, and biomedical fields. The book has been divided into 13 chapters. The first three chapters are associated with the synthesis and characterization of metallo surfactants followed by an investigation of their surface, interfacial and aggregation behavior. Accordingly, building on their properties, a variety of applications for the metallo surfactants have been discussed, highlighting the current status and development in the areas including catalysts for organic and esterolytic reactions, hydrogen generation, drug-delivery vehicles, molecular machines, transfection, nanoparticle synthesis, anticancer and antimicrobial activities, CORMs, and sensors in the subsequent [Chapters 4-13](#). This book is intended for

introductory graduate-level metallosurfactant chemistry and the researchers working in this field. We believe that fellow scientists from both academia and industry would find this book to be a concise, informative yet interesting read.

14th November 2021	
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1

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 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].

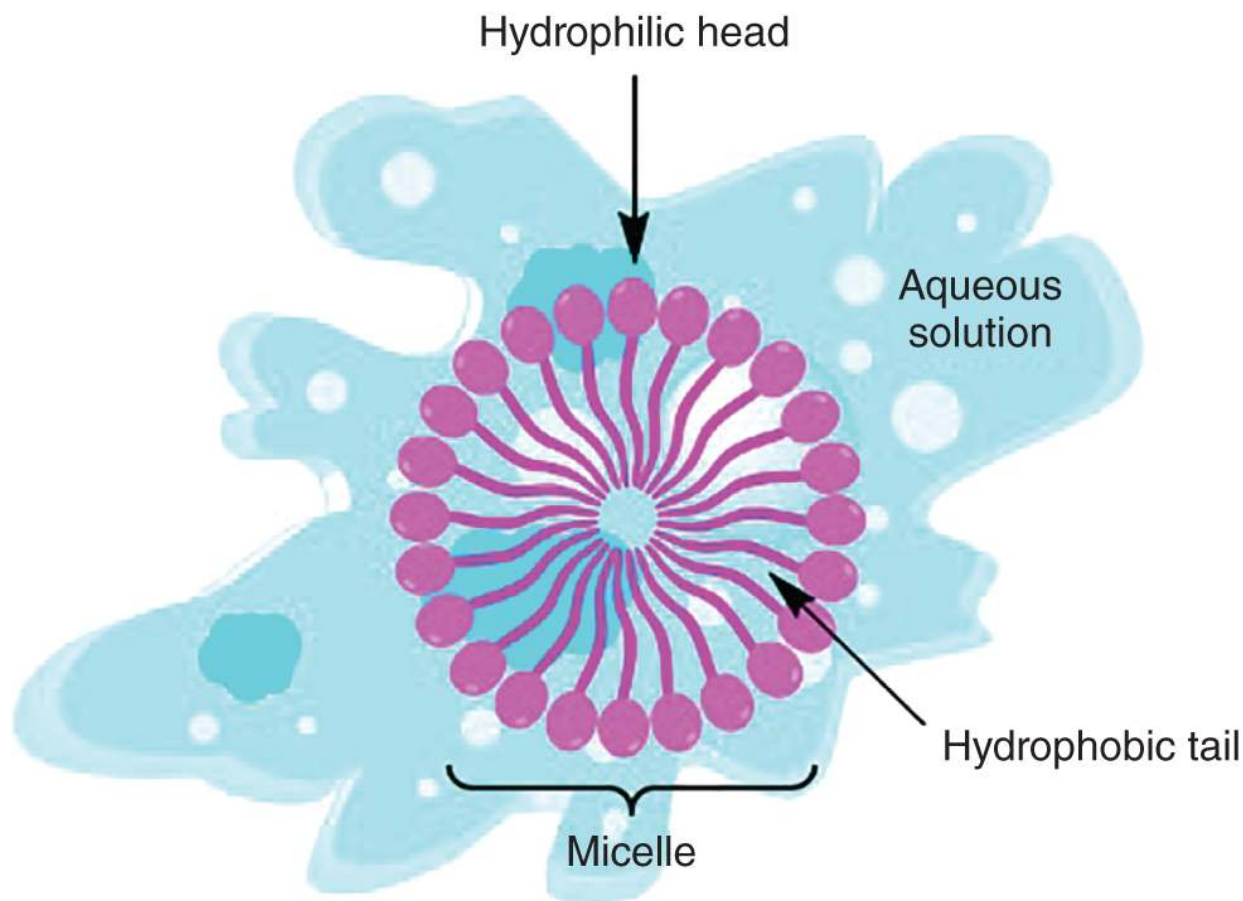


Figure 1.1 Schematic representation of surfactant.

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 felicitates 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(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate (TCl₄) 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;

self aggregation behavior
inverted micelles [44](#)-45
lamellar phases [49](#)-50
micelles [40](#)-44
vesicles [46](#)-49
self-assembly [120](#)
of lipophilic Cu(II) complexes [148](#)
magnetic mesoporous silica synthesis [126](#)
self-assembly of metallo-supramolecule based block copolymers [108](#)
single atom catalyst (SAC) [127](#)
single chained MTS [7](#)
single iron atom loaded mesoporous silica [127](#)
single-photon emission tomography [227](#)
small angle neutron scattering (SANS) [40](#)
small angle X-ray scattering (SAXS) [40](#)
sodium dodecanoate (SD) 229
sodium dodecyl benzenesulphonate [166](#)
sodium dodecyl sulfonate (SDS) 229
sodium molybdate [227](#)
sodium tungstate [227](#)
soft supramolecular nanocontainers [223](#)
solid lipid Nps and copper-cetylpyridinium chloride surfactant [122](#)
solvatochromic effect [235](#)
solvatochromic properties [261](#)

spherical metallosomes [150](#)
standard free energy, of micellization value [227](#)
stem cell regulation [198](#)
stimuli responsive metallosurfactant catalysed reactions [90](#)
superamphiphilic complexes [235](#)
supramolecular aggregation [203](#), [233](#)
supramolecular-based copolymer micelles [108](#)
supramolecular nanocontainers [236](#)
supramolecular systems [205](#)
supramolecular transformation [46](#)
surface chemistry [1](#)
surfactant-Co (III) complexes [189](#)
surfactant molecules [22](#)
surfactants [103](#), [179](#)
 defined [1](#)
 schematic representation [2](#)
surfactants based porous material [124](#)-126
Suzuki cross-coupling reaction [239](#)
Suzuki-Miyaura reactions of aryl bromides [91](#)
Suzuki reaction [239](#)
synthetic amphiphilic receptor [232](#)

t

target-based cancer therapy [189](#)

template based synthesis, of porous silica based material [120](#)

terminal carboxylate moieties [46](#)

ternary complex kinetic model [77](#)

terpyridine-containing double hydrophilic diblock copolymer [109](#)

tertridentate ligand [73](#)

tetraanionic porphyrin [232](#)

tetrabutylammonium [260](#)

tetracarboxylic (TCO) compounds [205](#)

tetradecylpyridinium (TP) based metallosurfactants [30](#), [31](#)

tetradentate ligand [73](#)

tetraethylorthosilicate (TEOS) [255](#)

thermal decomposition [168](#), [169](#)

thiazole/imidazole group [262](#)

thioether-cholesterol ligand [186](#)

transfection processes [151](#)

transfer hydrogenation reaction [86](#)

tributylphosphine (TBP) [166](#)

tributylphosphine oxide (TBPO) [166](#)

trinitrophenylmethylnitramine (tetryl) [252](#)

trinitrotoluene (TNT) [252](#)

trioctylphosphine oxide (TOPO) [166](#)

tris-bipyridyl ruthenium hexaphosphate [261](#)

true liquid crystal templating (TLCT) approach [124](#)

two alkyl chains [6](#) carbon atoms (TCOL6) [205](#)

type II I-SURFs [6](#)

type I I-SURFs [6](#)

u

ultrasound responsive metallo-supramolecular diblock PPG-PEG copolymers [108](#)

v

Van der Waals interactions [31](#)

vesicular catalysis [91](#)

vesicular shaped Co (II) based metallosurfactants [94](#)

vigorous stirring, of emulsion [58](#)

w

water electrolysis [84](#)

water/methyl methacrylate (MMA) emulsion [57](#)

water oxidation, metallosurfactant catalyst in [91](#)

water/proton reducing catalyst (WRC) [57](#)

water-soluble monomers [52](#)