



# Exploring the versatility of chelating surfactants: A review

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## Abstract

Chelating surfactants are amphiphilic molecules capable of forming coordination complexes with metal ions and self-assembling into organized structures. These compounds have gained significant attention in recent years due to their multifaceted applications in environmental remediation, industrial processes, and material sciences. This review provides an overview of the characterization techniques and recent advancements in the applications of chelating surfactants over the past few years. The review begins by elucidating the characterization methods employed to understand the physicochemical properties of chelating surfactants and gain insight into their complex behavior and interactions in various systems. The applications of chelating surfactants in remediation of wastewater and soil, flotation of minerals, oil recovery processes, and corrosion inhibition in metallic structures are explored. Through examination of recent fundamental research activities, innovative approaches, mechanisms of action, and advancements in the different application domains are highlighted. Lastly, some recent progress in the related field of metallosurfactants is explored, even though not all metallosurfactants are chelating.

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## Keywords

Chelating surfactants, Metallosurfactants, Metal-coordination, Sequestering agents, Complexing agents, Flotation, Metal recovery, Remediation, Electron transfer calculations, Amino acid-based surfactants

## Introduction

Chelating surfactants represent a unique class of compounds that combine the properties of chelating agents and surfactants. These compounds possess the ability to form stable complexes with metal ions while simultaneously reducing surface tension and enhancing cleaning efficiency, thus holding significant importance in industries where metal ion control is crucial. Typically, the chelating ability is incorporated in the surfactant headgroup, offering a multifunctional approach to various industrial, pharmaceutical, and personal care applications. The development of chelating surfactants can be traced back to the 1950s and 1960s [1–3], when researchers began to explore the potential of combining surfactant and chelating functionalities into single molecules. This led to the synthesis and characterization of various chelating surfactants with improved performance and versatility compared to traditional surfactants or chelating agents alone. Throughout the latter half of the 20th century and into the 21st century, the development of chelating surfactants has been driven by the demand for more efficient and environmentally friendly solutions in different industries.

Chelation of a metal ion involves the formation of a minimum of two coordinate bonds between a polydentate ligand and the central metal ion, meaning that the hydrophilic part of a chelating surfactant must contain at least two donor atoms. The donor atom, for instance, a carboxylate oxygen or a nitrogen from an amine group, donates the two electrons forming the covalent bond to the metal ion. The larger the number of donor atoms, the stronger the chelating ability due to entropic reasons when water of hydration is released from the coordinated metal ion. Compared to nonchelating (monodentate) ligands, chelating (polydentate) ligands show a stronger affinity for metal ions, evident from the larger stability constants for complexes formed with chelating ligands. This can be explained by considering the thermodynamics of complex formation between two monodentate ligands and a metal ion and between a bidentate ligand and a metal ion. For similar donor atoms, the enthalpy of the complex formation will be similar. The entropy loss for the case of a bidentate

ligand will, however, be significantly lower. Ring formation between the chelating ligand and metal ion further contributes to the high stability of the complex. A thorough literature review reveals that the term chelating surfactant is not always used in conjunction with compounds that fulfill the criteria of chelating surfactants. A number of amino acid-based surfactants described in the literature qualify as chelating surfactants since both amino and carboxylic acid groups can act as ligands, forming coordination complexes with metal ions [4]. Amino acid-based ligands can range from bidentate in the simplest case, where the metal ion is coordinated by one carboxylate oxygen atom and one nitrogen atom (from the amine group), to more complex structures involving several donor atoms in the case of amino polycarboxylic acids. The synthesis, properties, and applications for amino acid-based surfactants have been recently reviewed by Guo et al. [5]. Because the donor atoms are pH-responsive, chelating surfactants can be described under this term, or as amphoteric, in the literature [6]. There is also significant overlap with the term metallosurfactants, where a metal ion is incorporated in the surfactant structure. Lorenzetto et al. have provided a recent review regarding metallosurfactants for sustainable catalysis in water [7], whereas the biological activity of amphiphilic metal complexes has been reviewed by Schattschneider et al. [8]. However, not all metallosurfactants can be described as chelating surfactants due to the requirement of at least two coordinate bonds to the central metal ion.

Chelating surfactants play a crucial role in many industrial processes. Applications can be found across diverse fields beyond the scope of this review, such as low-rank coal flotation [9], separation of carbon nanotubes [10], stabilizing firefighting foams [11], and superfast gelation of silk fibroin for treating noncompressible hemorrhage [12]. This review article aims to provide an overview of the characterization and applications of chelating surfactants where there have been frequent research activities during the past five years, focusing on remediation of wastewater and soil, flotation of minerals, oil recovery, corrosion inhibition, and recent progress in the related field of metallosurfactants. A comprehensive compilation of earlier research on chelating surfactants can be found in the review by Eivazihollagh et al. [13].

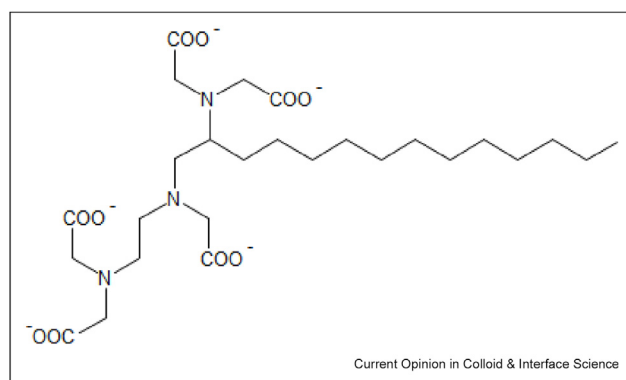
### Characterization

Chelating surfactants exhibit pH-responsive behavior due to titrating donor atoms in their headgroups. The number of donor atoms influences the chelating ability, with more donor atoms enhancing the strength of chelation. However, this results in a complex dissociation behavior as the headgroup charge may vary significantly with pH, and this needs to be considered when characterizing or utilizing chelating surfactants in various

applications. Furthermore, multiple overlapping  $pK_a$  values result in the co-existence of differently charged species in solution, particularly evident in chelating surfactants containing many titrating donor atoms. The headgroup charge directly impacts surfactant properties such as solubility, surface activity, and self-assembly. Consider the polyaminocarboxylate-based chelating surfactant 2-dodecyldiethylenetriaminepentaacetic acid ( $C_{12}$ -DTPA) shown in Figure 1, which we have studied thoroughly. The structure features several carboxylate oxygen atoms and tertiary amine nitrogen atoms that undergo titration, leading to variable headgroup charges. Adjusting the pH changes the headgroup charge from highly positive at low pH to strongly negative at high pH [14]. Additionally, the coordination of metal ions by chelating surfactant donor atoms further influences these properties.

The solution behavior of  $C_{12}$ -DTPA is strongly influenced by pH, with significant variations observed in critical micelle concentration (CMC) and adsorption efficiency across the examined pH range of 3–10 [14]. The solubility is notably compromised around the isoelectric point, beyond which several zwitterionic species with net negative charges emerge. As pH increases,  $C_{12}$ -DTPA becomes more hydrophilic, leading to an increase in CMC and a decrease in surface tension reduction. This trend suggests increased electrostatic repulsion and entropy penalty of counter-ion binding at higher pH levels. A maximum surface tension reduction was found at pH 5, attributed to an optimal balance between hydrophilic and hydrophobic characters facilitating strong adsorption at the air/water interface, potentially due to electrostatic attraction and hydrogen bonding between headgroups. The amphoteric nature of chelating surfactants like  $C_{12}$ -DTPA allows for the detection of CMC through pH versus concentration measurements [14]. Amphoteric surfactants can accept or donate protons to

Figure 1



Molecular structures of the chelating surfactant  $C_{12}$ -DTPA at alkaline pH, showing a headgroup charge of  $-5$ . At acidic pH, the headgroup carries a charge of  $+3$  due to protonation of carboxylate and tertiary amine groups.

adjust their electrical charge, leading to variations in  $pK_a$  values influenced by electrostatic interactions within the molecule. During micellization, the increased charge density at the micellar surface affects the dissociation of aggregated surfactants. A structure with a net negative charge results in a higher degree of protonation for surfactants within micelles than free monomers, which is evident from increasing bulk pH at CMC. For the same reason, pH-concentration plots of C<sub>12</sub>-DTPA, its metal complexes, and mixtures with ionic surfactants, in combination with calculations of interaction parameters, provide valuable insights into micellar interactions [15,16]. A detailed view of the chelating surfactant interactions with an anionic surfactant was extracted from neutron reflectivity measurements, where it was found that the surface composition changed significantly with concentration, from consisting primarily of the chelating surfactant at low total concentration to primarily anionic surfactant at high concentration [6].

The determination of CMC for C<sub>12</sub>-DTPA using tensiometry was ambiguous due to a minimum in the surface tension plot, which was explained by the formation of differently charged species because of the overlapping  $pK_a$  values in the surfactant structure. Nuclear magnetic resonance (NMR) diffusometry, neutron reflectivity, or pH measurements were necessary to confirm the CMC's location [14,17]. From combined neutron and X-ray reflection measurements, the adsorbed layer of C<sub>12</sub>-DTPA at the air/water interface was described by a two-layer model comprising a thin upper layer of dehydrated tails and a thicker lower layer of hydrated headgroups, with some intermixing between layers [17]. The thicknesses of the two layers imply limitations in surfactant packing from the bulky, hydrated headgroups.

The interaction between divalent or trivalent metal ions and chelating surfactants deviates from conventional surfactants due to the formation of coordinate bonds to the metal ion, resulting in heterocyclic rings. This implies that the counterions are tightly bound and not regularly exchanged. Coordination of a metal ion significantly alters the headgroup of the chelating surfactant, affecting its net charge and reducing the titrating ability due to engagement of donor atoms in coordination. This process also decreases steric flexibility in configuration and proton allocation within the headgroup. The coordination of a metal ion affects the surface activity of the chelating surfactant. Whether the surface activity is increased or decreased depends on the pH of the system or rather on the degree of protonation of the donor atoms (when not involved in chelation). If the coordination of a metal ion results in reduced net headgroup charge, the coordination will result in increased surface activity, but if the coordination increases the net headgroup charge, the surface activity decreases. For C<sub>12</sub>-DTPA, it was shown that

coordination of Ni<sup>2+</sup> increased the surface activity at pH 7, while at pH 5, where C<sub>12</sub>-DTPA has a lower net negative charge, coordination of Cu<sup>2+</sup> reduced the surface activity [18]. The coordination of a metal ion significantly reduces the pH-dependency of the surface activity. Despite this, pH-response may persist if the number of donor atoms exceeds the coordination number of the metal ion, as demonstrated in divalent metal complexes with C<sub>12</sub>-DTPA [18]. Chelating surfactants effectively coordinate metal ions by utilizing different donor atoms, typically elements with higher electronegativity, such as sulfur, nitrogen, oxygen, and phosphor. Basic coordinating groups contain atoms with a lone pair of electrons that can interact with the metal cation, while acidic groups can lose a proton to coordinate the metal ion. The stability of the metal–ligand complex depends on the nature and number of donor atoms, the size and number of chelate rings, and the size and polarizability of the metal ion. Selectivity towards specific metal ions was investigated for C<sub>12</sub>-DTPA by determination of conditionally stability constants, showing strong similarities with the conventional chelating agent diethylenetriaminepentaacetic acid (DTPA) [18].

Recent articles have highlighted important techniques for characterizing physicochemical properties of chelating surfactants as well as their complex behavior and interactions in various systems. Characterization of metallosurfactants is also discussed in the last section of this review. Li and Zheng have investigated the performance of a chelating anionic foaming agent, abbreviated SDPN, synthesized from sodium fatty acid methyl sulfonate and N, N'-Dimethyl-1,3-propyldiamine through ester amination reaction [19]. They used Du-Nouy ring surface tensiometry to determine surface activity and CMC of SDPN under different pH levels. The foam performance was characterized by evaluating the effects of mass concentration SDPN, temperature, pH, and salinity on the foam height, using the Roche foam method and liquid carrying capacity. Furthermore, they utilized polarized light microscopy to study the influence of different concentrations and mineralization degrees on the foam microstructure. In a study by Wang *et al.*, two pH-responsive dicarboxylic amino acid surfactants, sodium N-lauroyl glutamate (SLG) and sodium N-lauroyl aspartate (SLA) were characterized using several different techniques [20]. The studied surfactants were dissolved in excess alkali and titrated with acid to determine their respective  $pK_a$  values. Surface tension was measured using the Wilhelmy plate method to determine surface activity and CMC at different pH levels. The size distribution and zeta potential of surfactant aggregates were examined using Dynamic light scattering (DLS), while the morphology of the aggregates was observed by transmission electron microscope (TEM). Foamability and foam stability were analyzed by the FoamScan

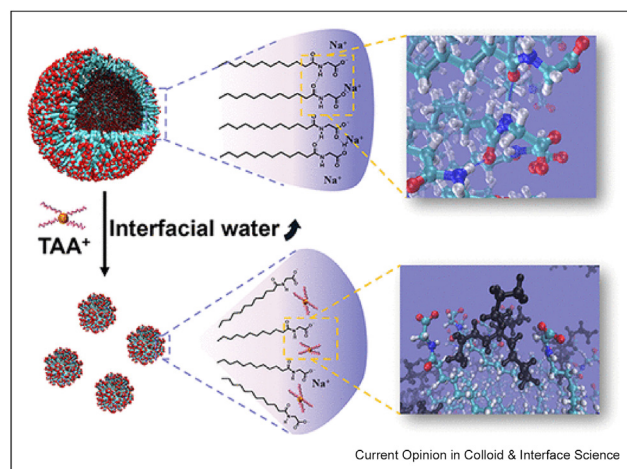
instrument, and the emulsion stability of SLG/SLA to liquid paraffin was determined by the time of water separation from the emulsion.

The complex formation between zinc(II) and alkyl-N-iminodiacetic acids was studied by Häggman et al. [21]. The complex structures in solid state and aqueous solution were determined by extended X-ray absorption fine structure (EXAFS). Acidic and stability constants for zinc(II) alkyl-N-iminodiacetate systems were simultaneously evaluated by potentiometry using pH and zinc amalgam electrodes. However, the researchers reported difficulties in exact determinations of the constants in the studied systems. Adding specific salts has been shown to influence the aggregation behavior of amino acid-based chelating surfactants. The micelle-to-vesicle transition of a gemini lipoamino acid surfactant (SDDC) induced by metallic salts were explored by Gómez et al. [22]. The formed core-shell type micelles of SDDC were studied by small-angle X-ray scattering (SAXS). The morphology of the formed vesicles, induced by adding copper or silver ions, was observed using TEM. Electron paramagnetic resonance (EPR) measurements, using a spectrometer equipped with an X-band microwave source, in combination with UV-visible spectrophotometry, were performed to characterize the oxidation state of copper in a complex with SDDC. In a study by Sun et al., the opposite transition, i.e., vesicle-to-micelle, was observed for the amino acid surfactant sodium lauroyl glycinate (SLG), induced by the addition of tetraalkylammonium cations ( $TAA^+$ ) [23]. They studied the specific effects of different  $TAA^+$  ions by DLS and TEM on the SLG aggregates. They used chemical trapping (CT) to follow the changes in interfacial molarities of water, amide bonds, and carboxylate groups during the partial vesicle-to-micelle transitions. Furthermore, molecular dynamic simulation was performed to confirm the salt-induced cleavage of amide-amide bonds between SLG head-groups, accompanying the observed aggregate transition, shown in Figure 2.

### Remediation of wastewater and soil

Heavy metals, radionuclides, and organic pollutants in wastewater and soil pose significant environmental and public health concerns due to their persistence, toxicity, and potential for bioaccumulation in the food chain. These contaminations often originate from improper industrial disposal practices, and efficient remediation techniques are required to mitigate health risks and economic losses. Removing contaminants from soil typically involves using additives like surfactants and chelating agents, individually or in combination, depending on factors such as contaminant composition, soil texture, and experimental parameters affecting leaching efficiency [24,25]. Chelating agents are particularly effective in enhancing the removal of metals

Figure 2



Vesicle-to-micelle transition for the amino acid surfactant sodium lauroyl glycinate (SLG), induced by addition of tetraalkylammonium cations ( $TAA^+$ ). Reprinted with permission from Ref. [23]. Copyright (2022) American Chemical Society.

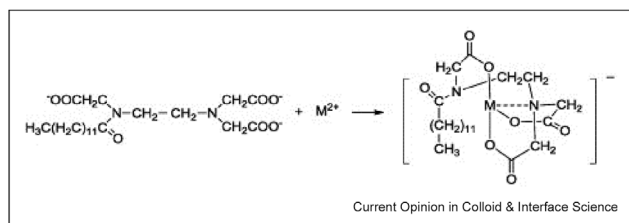
from soil, owing to their selective coordination of metal ions. Their acid-base characteristics extend the solubility of metals through the formation of water-soluble metal-chelate complexes and influence the species present at different pH values. The selectivity for specific metals is determined by the donor atoms contained within the chelating agent, as reflected in conditional stability constants for metal-chelate complexes at various pH values. Remediation of heavy metals and organic contaminants from soil using surfactants can be performed either below the CMC, where surfactants aid in soil roll-up mechanisms, or above this concentration, promoting solubilization in micelles [26]. However, treatment duration and removal yield may be a concern when surfactants are used exclusively for metal removal. Furthermore, remediation using chelating agents and surfactants often implies a high cost and generation of secondary wastes.

Chelating surfactants are promising agents for solubilizing and sequestering heavy metals from wastewater and soil due to their dual functionality as chelating agents and surfactants [27]. Through the formation of coordination complexes, chelating surfactants can mitigate leaching of heavy metals into groundwater or uptake by plants. Besides the capability of the headgroup to chelate metal ions, the hydrophobic tail provides surfactant properties, facilitating interactions with organic co-contaminants and enhancing their accessibility for remediation. Furthermore, the amphiphilic character offers the possibility of separation using flotation [16,28]. This section delves into the recent progress in utilizing chelating surfactants for remediation of heavy metals, organic pollutants, and radionuclides.

Sodium N-lauroyl ethylenediamine triacetate (LED3A) is one of the most studied chelating surfactants for remediation of different contaminants such as copper, lead, zinc, cadmium, petroleum, and phenanthrene (Phe) from contaminated soils [29–31]. LED3A has recently been thoroughly investigated in a series of articles by Diao et al. regarding its adsorption mechanism on soil [32], effectiveness in remediation of heavy metals and organic compounds from co-contaminated soil [33,34], and assisting phytoremediation of heavy metals from water [35]. LED3A was reported to be efficient for simultaneous removal of copper and the polycyclic aromatic hydrocarbon phenanthrene from artificially contaminated soil under pH ranging from 5.0 to 9.0 [33]. At the optimum concentration of 18 g/L LED3A, 60% of Cu and 52% of Phe could be removed from the co-contaminated soil. The researchers reported consistent equilibrium time (12 h) for desorption of both Cu and Phe, and the desorption kinetics correlated well with the Elovich and two-constant rate equations. Competitive adsorption of lead and zinc on loess soil in the presence of LED3A was examined by Qiao et al. [36]. The chelation of a heavy metal (where M equals Pb or Zn) by the LED3A headgroup is illustrated in Figure 3. The researchers found that LED3A decreased the equilibrium time of competitive adsorption and reduced Pb and Zn adsorption capacities on the soil by 2.56 and 4.97 g/kg, respectively.

LED3A, also referred to as N-LED3A, was utilized by Zhang et al. in electrokinetic (EK) remediation of copper and decabromodiphenyl ether (BDE209) co-contaminated low permeability soil [37]. They found that the removal efficiency increased with applied voltage gradient and concentration of N-LED3A, and the optimal synchronous elution efficiencies of 65% for Cu and 50% for BDE209 were reported under the conditions of pH between 6 and 8 and N-LED3A concentration of 4000 mg/L. Without any addition of N-LED3A, only 23% of Cu and negligible amounts of BDE209 could be removed. Under the most cost-effective operating conditions, the removal efficiencies of Cu and BDE209 were 55% and 31%, respectively, in

Figure 3



Formation of a coordination complex between LED3A and a metal ion, where M equals Pb or Zn. Reprinted with permission from the authors [36].

the N-LED3A enhanced EK experiments, with accumulated energy consumption of 377 kWh/m<sup>3</sup> after the 21-day treatment.

Chen et al. applied the bayberry tannin-based surfactant (BTBS) to remove uranyl, UO<sub>2</sub><sup>2+</sup>, from aqueous environments and solid surfaces using ion flotation [38]. They reported maximum removal performance at pH 11 and 90 and 95% uranyl removal from water and cotton cloth, respectively. The mechanism was attributed to chelation of uranyl by phenolic hydroxyls in BTBS.

### Flotation of minerals

Froth flotation of minerals is a fundamental process in the mining industry, enabling the selective separation of valuable minerals from gangue materials based on differences in their surface properties. Traditionally, flotation reagents, such as collectors, frothers, and modifiers, enhance the mineral surface hydrophobicity and thereby promote adsorption to air bubbles during the flotation process. Chernyshova et al. have provided a recent review regarding emerging applications of biosurfactants in metal extraction [39]. Chelating surfactants are efficient alternatives to conventional flotation reagents due to their unique ability to form stable complexes with metal ions on mineral surfaces [40–42]. By selectively adsorbing onto mineral surfaces and coordinating with metal ions, chelating surfactants can modify the surface chemistry of selected minerals, enhancing their hydrophobicity and facilitating their attachment to air bubbles. This selective interaction enables the efficient separation of valuable minerals from gangue materials, improving concentrate grades and potentially reducing processing costs. However, selectivity toward metal ions is characterized by conditional stability constants, which vary with pH, and careful design of collectors and processes is crucial for effective flotation. Researchers utilize various computational methods such as molecular mechanics, quantitative structure–activity relationship analysis, first-principle theory, and density functional theory (DFT) to aid in the design and development of novel flotation collectors with enhanced selectivity and efficiency [43]. This section explores the application of chelating surfactants in mineral flotation, highlighting their potential advantages, mechanisms of action, and recent advancements in this field.

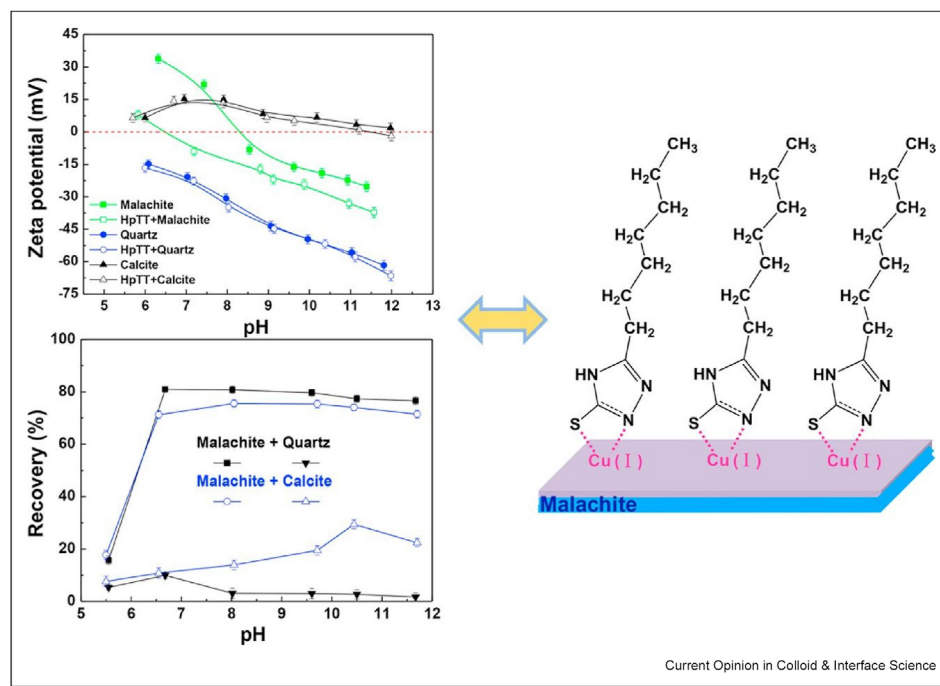
Huang et al. investigated the selective flotation performance of the chelating surfactant 5-heptyl-1,2,4-triazole-3-thione (HpTT) for separating the copper-containing mineral malachite from calcite and quartz [44]. Compared to the commonly used collector octyl hydroxamic acid (OHA), HpTT exhibited better selectivity for the desired malachite against calcite and quartz under pH 6.5–11.5. Through a combination of contact angle, zeta potential, UV spectra, Fourier transform infrared spectroscopy (FTIR), and X-ray

photoelectron spectroscopy (XPS) measurements, they elucidated the mechanism behind the separation of malachite from the mineral mixture. Their results showed that HpTT selectively responded to  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions (malachite) but hardly to  $\text{Ca}^{2+}$  ions (calcite), explaining the significantly increased hydrophilization of malachite particles. Furthermore, they suggested that copper atoms might bond with the S and N atoms of HpTT's triazole-thione group to form a conjugated ring, generating HpTT–Cu complexes on malachite surfaces, shown in Figure 4.

Dicarboxylic amino acid-based surfactants have proved to be efficient selective collectors for flotation of minerals [45], thus acting as chelating surfactants. Sun et al. thoroughly investigated the 2-dodecanoylamino-pentanedioic acid (DPA). They found that it exhibited collecting performance superior to that of the common collector sodium oleate, enabling the separation of the manganese-containing rhodochrosite from quartz and calcite under neutral pH without adding foaming agents or activators [46]. Contact angle measurements showed that the increase in hydrophobicity after DPA treatment was greater for rhodochrosite than for quartz and calcite. Their results from zeta potential, FTIR spectroscopy, and XPS showed that DPA was chemically adsorbed to manganese atoms on the surface of rhodochrosite, indicating the formation of 8-membered or two 4-

membered ring structures. Solution chemistry analyses showed that  $\text{DPA}^{2-}$ , with the two carboxylic groups deprotonated, was the dominant species throughout the examined pH interval between pH 5 and 11. Under neutral pH, the two carboxylic groups of DPA were expected to coordinate manganese ions at the rhodochrosite surfaces. The decreased flotation efficiency of DPA at increasing pH was explained by competitive adsorption of hydroxyl ions to the rhodochrosite surfaces, reducing the adsorption of DPA to the mineral. Sun et al. continued to investigate the performance of DPA for flocculation and flotation of fine mineral particles of rhodochrosite. They found that DPA induced the formation of larger aggregates, thereby enhancing the recovery of fine mineral particles to 82.5%, compared to 35.3% recovery using sodium oleate (under the same molar concentration of the respective collector) [47]. From Zeta potential, contact angle, in-situ Atomic force microscopy (AFM) imaging, and the extended Derjaguin-Landau-Verwey-Overbeek (EDLVO) theory calculations, the researchers found that along with hydrophobic forces, the electrostatic repulsions, van der Waals forces, and weak interactions between collector molecules (e.g., hydrogen bonding) could explain the hydrophobic flocculation of fine particles. FTIR, XPS, and DFT results indicated the formation of hydrogen bonds between amide groups and carboxyl groups in adjacent DPA molecules, forming net-like

Figure 4



Selective recovery of the copper-containing malachite against quartz and calcite utilizing the chelating surfactant 5-heptyl-1,2,4-triazole-3-thione (HpTT) and the proposed mechanism forming HpTT–Cu complexes on malachite surfaces. Reprinted from Ref. [44], with permission from Elsevier.

“macromolecules” bridging fine rhodochrosite particles and enhancing the flocculation and flotation effect.

The significance of inter- and intramolecular interactions in collector molecules on flotation of fine rhodochrosite was further examined by Fei *et al.*, utilizing a hydroxamate-modified N-acyl amino acid surfactant, 2-decanoylamino-4-hydroxycarbonyl-butyrac acid (DHBA) [48]. The superior flocculation and flotation performance of DHBA, compared to the common collector OHA, was explained by chelation of manganese leading to strong adsorption of DHBA on the mineral surfaces and intermolecular hydrogen bonds between collectors promoting enhanced hydrophobic association and agglomeration of fine mineral particles. In a study by Miao *et al.*, the non-toxic and low-cost amino acid-based surfactant N-decanoysarcosine sodium (SDAA) was utilized to separate the two calcium-containing minerals fluorite and scheelite by reverse flotation [49]. Metal ions are chelated by the carboxylate oxygen atom and the tertiary amide nitrogen in the headgroup of SDAA. Based on adsorption capacity detections, zeta potential tests, and FTIR analysis, the researchers found that the negatively charged SDAA adsorbed preferentially onto the positively charged fluorite surface due to the electrostatic interaction, even though the minerals have the same active sites ( $\text{Ca}^{2+}$ ) [49]. Results of crystal chemistry and DFT calculations could further reveal that SDAA had a stronger chemical interaction and more

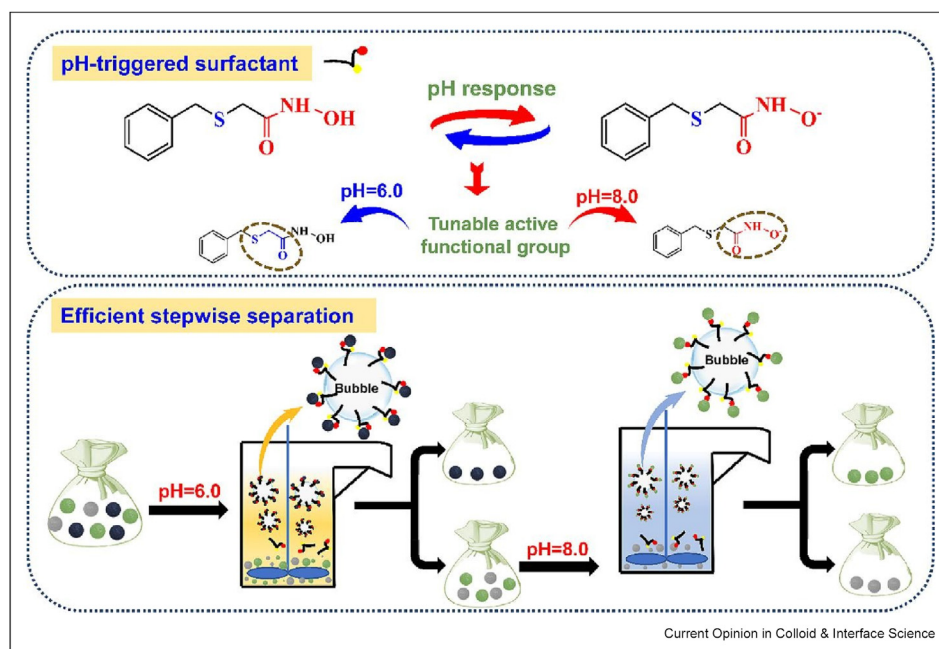
electron transfer numbers to the Ca atoms on the fluorite surface, forming Ca-SDAA complexes.

An interesting approach for separating multi-component mineral systems is to utilize the pH-responsiveness of chelating surfactants by tuning the system stepwise for selective flotation of individual components. The pH-responsive surfactant 2-(benzylthio)-acetohydroxamic acid (BTHA) has been applied for stepwise separation of pyrite, diaspore, and kaolinite in high-sulfur bauxite [50]. By modulating the solution pH, the active functional groups of BTHA (i.e., thioether and hydroxamate) were tuned to promote its preferred adsorption to different mineral surfaces, as illustrated in Figure 5. Under mild acid conditions (pH 6.0), the hydroxamate group of BTHA was deactivated, leaving the thioether groups interacting with Fe sites on pyrite and thus resulting in selective recovery of pyrite (86%). Increasing the pH to 8.0, the active hydroxamate group of BTHA interacted strongly with diaspore through chelation, leading to efficient separation of diaspore from kaolinite.

### Oil recovery

Enhanced oil recovery (EOR) techniques are important for maximizing hydrocarbon extraction from reservoirs in mature oil fields where conventional recovery methods have reached their limits. In surfactant-based EOR technology, the ability of surfactants to reduce the

Figure 5



Application of the pH-responsive surfactant 2-(benzylthio)-acetohydroxamic acid (BTHA) (shown in the upper part) for stepwise separation of pyrite and diaspore from kaolinite in high-sulfur bauxite by pH adjustments (lower part). Reprinted from Ref. [50], with permission from Elsevier.

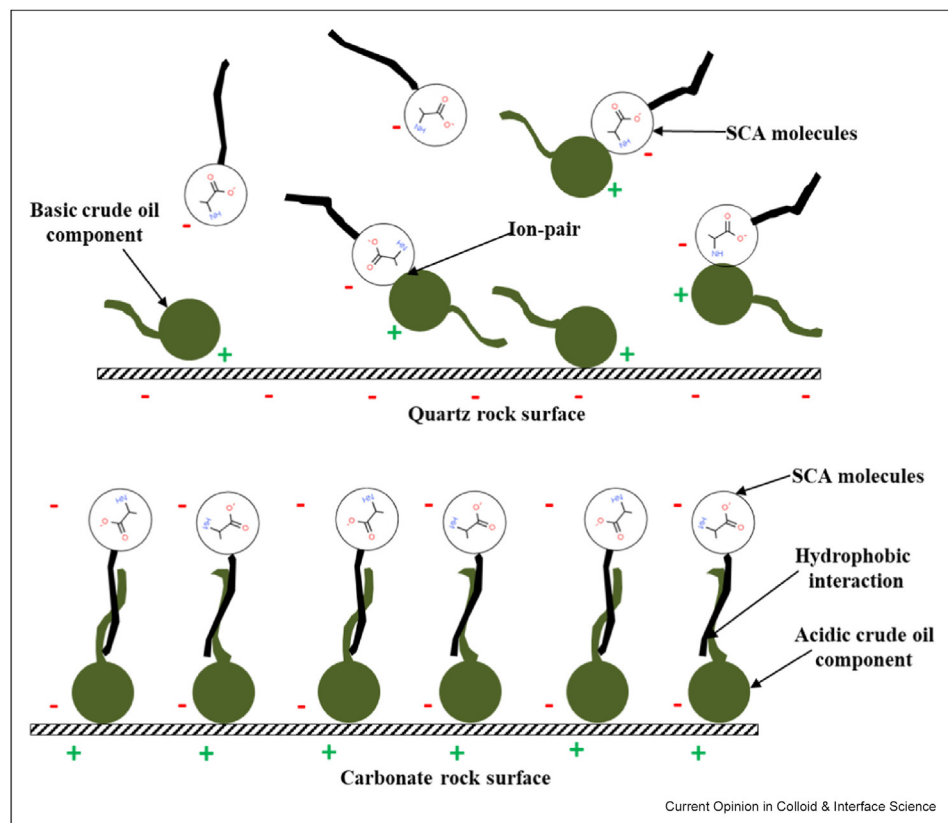
water-crude oil interfacial tension, modify the wettability of reservoir rocks (from oil or intermediate wetness to more water wetness), and mobilize trapped oil by improving sweep efficiency (i.e., the fraction of reservoir invaded by the displacement fluid) is utilized. By specific interactions with metal ions present in reservoir fluids, formation minerals, or crude oil components, chelating surfactants offer a possibility for further increased efficacy in oil recovery applications. In particular, amino acid-based chelating surfactants have been explored in EOR. The biodegradability and non-toxicity of amino acid-based surfactants have often been reported as motives for introducing them in this field, even if some studies have shown less satisfactory performance than conventional surfactants regarding their EOR application [51–53].

A few recent studies have demonstrated the potential of chelating surfactants in improving oil recovery in various reservoir conditions, including sandstone and carbonate rock. Tackie-Otoo and Mohammed reported the advantages of using the amino acid-based surfactant sodium cocoyl alaninate (SCA) in EOR [54]. SCA proved to be more surface active than the conventional anionic surfactant sodium dodecyl sulfate (SDS) in terms of surface and interfacial tension reduction.

Furthermore, SCA showed a superior ability to modify wettability on both quartz and carbonate surfaces. The quartz surface was altered from intermediate wet to water-wet, while the carbonate surface was changed from oil-wet to water-wet. The researchers explained the modified wettability on quartz by ion-pairing, whereas in the case of carbonate rock surfaces, it could be explained by hydrophobic interactions, as illustrated in Figure 6.

SCA was also more effective than SDS in emulsifying crude oil-brine mixture [55]. For both surfactants, the researchers found that the adsorption at the aqueous–rock interface was best described by the Langmuir isotherm, implying the formation of a surfactant monolayer at the interface. The core flood data confirmed the better EOR potential of SCA, with an additional oil recovery of 29.5% compared to 23.8% for SDS. Tackie-Otoo et al. continued to investigate amino acid-based surfactants for oil recovery applications by examining N-lauroyl sarcosine (NLS) and lauroyl glutamic acid (LGA) [56]. They found that NLS was more surface active than LGA, showed superior crude oil/water interfacial tension reduction capacity (as low as 0.07 mN/m), and stronger wetting on quartz surfaces. The difference between the two structures was

Figure 6



Proposed mechanism of the amino acid-based surfactant sodium cocoyl alaninate (SCA) for modifying wettability on quartz by ion-pairing (upper part) and hydrophobic interactions in the case of carbonate rock (lower part). Reprinted from Ref. [54], with permission from Elsevier.

explained by the additional carboxylate group in the LGA headgroup compared to NLS. Therefore, NLS showed better emulsifying power, although LGA produced more stable emulsions. Both surfactants exhibited high tolerance to salt and hardness and showed improved interfacial tension reduction at high salinity. Furthermore, NLS and LGA yielded significant additional oil recovery after waterflooding, 43% for NLS and 25% for LGA.

### Corrosion inhibition

Corrosion of metals due to chemical reactions with the environment presents a challenge across numerous industries ranging from infrastructure to manufacturing, with reduced lifespan of metallic structures, costly repairs, and safety hazards as potential consequences. Using surfactants as anticorrosion agents is one of the established effective actions to mitigate the consequences, and surfactants as biodegradable sustainable inhibitors for corrosion control has recently been reviewed [57]. Surfactants inhibit metal corrosion by adsorbing onto the metal surface, forming a protective layer that blocks corrosive agents. This barrier prevents the diffusion of harmful species. At the same time, some surfactants may also modify the surrounding pH, providing conditions less favorable for corrosion and exhibiting self-healing properties that extend the protective film's durability. Chelating surfactants offer the possibilities of enhanced interactions with metal surfaces through coordination of surface metal ions. Studies have shown promising results from using amino acid-based surfactants for this purpose [58,59], even though the number of recent publications on the topic is somewhat limited. Some related studies on corrosion inhibition are also reviewed in the next section on metallosurfactants.

The amino acid-based surfactant Sodium Cocoyl Glycinate (SCG) was examined by Ganjoo *et al.* as a corrosion inhibitor for protecting mild steel (MS) from corrosion in 1 M HCl [60]. From weight loss and electrochemical tests, the inhibition efficiency (IE) was found to increase with increasing concentration of SCG up to 0.28 mM, slightly above the CMC of 0.21 mM (reported in another study by Zhang *et al.* [61]). Ganjoo *et al.* investigated the IE at different temperatures from 30 to 60 °C and reported the highest IE of 95% at 30 °C and decreasing IE to 73% at 60 °C [60]. Furthermore, from polarization curves, the researchers found that the Langmuir adsorption isotherm best described the adsorption of SCG on MS. Calculated values of Gibbs free energy of adsorption, in the range between  $-30$  and  $-40$  kJ mol<sup>-1</sup>, indicated mixed adsorption (i.e., both chemisorption and physisorption). Two possible adsorption mechanisms were suggested: interactions between the delocalized electrons of the C=O double bonds in SCG and the unoccupied d-orbital of the iron

atoms, leading to physisorption, and interactions between the lone pairs of electrons in heteroatoms (N and O) and the vacant d-orbital of metal surface atoms, resulting in chemisorption.

Fawzy *et al.* investigated the three amino acid-based surfactants sodium N-dodecyl asparagine (AS), sodium N-dodecyl tryptophan (TS), and sodium N-dodecyl histidine (HS) concerning their ability to protect copper from corroding in 1.0 M H<sub>2</sub>SO<sub>4</sub> at 298 K [62]. From weight loss measurements, in the presence of a fixed surfactant concentration (500 mg/L), the researchers reported IE of 81, 83, and 88 % for AS, HS, and TS, respectively. The order of efficiency among the three studied surfactants was confirmed with potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). The researchers found that the studied surfactants behaved like mixed-type inhibitors with slight anodic priority, and the inhibition of copper corrosion was proposed to take place by the formation of two protective layers: solidly adsorbed film and formation of precipitate on the copper surface. Additionally, the three investigated surfactants were reported to exhibit a strong broad-spectrum antimicrobial activity against pathogenic bacteria and dermatophyte fungi.

### Metallosurfactants

Metallosurfactants (MS), a relatively new class of surfactant molecules, are characterized by a polar headgroup that contains a metal center as an integral structural component. Some of these metallosurfactants are chelating but not the main part; nonetheless, we include this metallosurfactant sub-section in our review. These amphiphilic molecules possess, in other words, both organometallic and surface chemistries and offer a route to concentrate these metal ions and their associated functionality at interfaces. The term "metallosurfactant" was first reported by Scrimin in 1989 [63]. However, the concept of metallosurfactants had been discussed earlier in the context of metallomicelles, as seen in the study on phosphate ester hydrolysis catalyzed by metallomicelles by Menger *et al.* [64]. The research field of MSs is growing, focusing on developing and synthesizing new MSs for fundamental research questions and exploring future application areas from a broad perspective. Some recent reviews in the area of metallosurfactants are the comprehensive review of Kumari *et al.* focusing on MS aggregate interactions with biomolecules, synthesis of nanoparticles, and an extensive part on biomedical applications [65] and the review by Schattschneider on the biological activity of metallosurfactants in the fields of biology and medicine focuses on MS binding to biomolecules, cleaving DNA and proteins, and in the field of life science [8]. Incorporating metal ions in the surfactant structure opens up possibilities, leading to additional functionalities such as

catalytic activity. This is exemplified in a recent review for sustainable catalysis in water, which focuses on catalyst recovery, organic solvent replacement, selectivity, and activities of these self-assembling MS catalysts [7]. Furthermore, coordination-driven self-assembly [66], nanoparticle fabrication [67,68] polymerization catalysts [69], and even specific interactions with biomolecules such as DNA [70–72], RNA [73], proteins [74], and bacteria [75–77] are recent fields of research interest. We can conclude from the literature that this sub-class of surfactants is broad and appears in many different guises and contexts.

An example of the specific influence different metal ions could have on coordination-driven self-assembly is the study of Au(I), Ag(I), and Pd(II)- coordination to NHC-based amphiphiles where it is shown that different structures occur depending on the transition metal when increasing concentration. Au-MS and Ag-MS develop hexagonal packing at higher concentrations, whereas Pd-MS transforms into a lamellar structure, see Figure 7. Another observation in this study is the time dependence of surface tension at the air/water interface on dissolving the MSs, Au-MS, and Ag-MS, which shows significant changes; however, Pd-MS shows no time dependence [66]. Significant time dependence has been shown earlier in the chelating surfactant work by Svanedal et al., arguing that the time

dependence is due to rearrangements at the surface [14].

Borras et al. have synthesized a new lipophilic zinc complex (ZnC) containing two dithiocarbamate ligands with palmitoyl groups for further preparation of rhenium and technetium metallosurfactant complexes [78]. The synthesized rhenium complex is shown to self-aggregate and could be integrated into preformed liposomes. The second route combined the Zinc complex, a polar monodentate ligand, and the radionuclide Tc-99m, forming the Tc-99m complex. The Tc-99m labeled complex could be integrated into the liposome bilayer, making it a radio-labeled liposome.

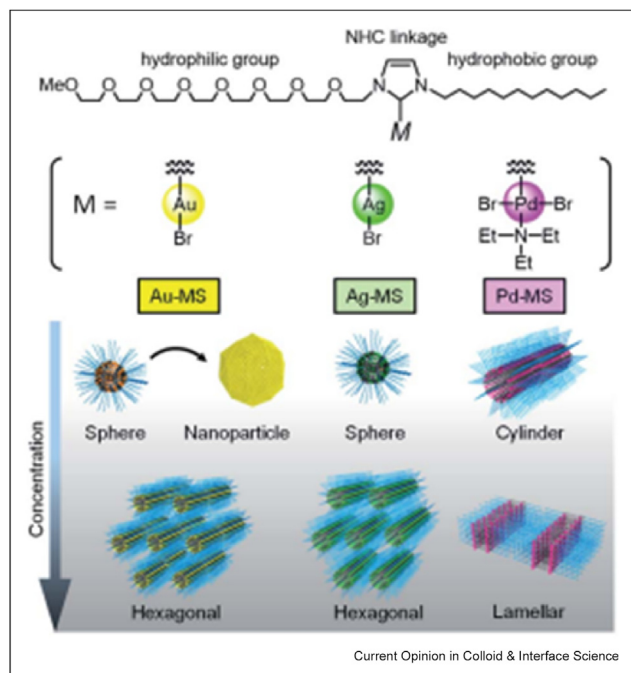
Some reviewed articles in this section have been clustered in shorter sub-sections.

#### *Metallosurfactants support various nanoparticle formations.*

Using MSs in the synthesis of nanoparticles is common in the recent literature [67,68]. For example, Nagaraj and co-workers used MSs to stabilize Ag/ZnO nanoparticles to prevent agglomeration, and the size of the nanoparticles could be controlled by varying pH and the MS concentration [68]. Donner and co-workers have developed two novel NHC-metallosurfactants bearing Cu(I) and Fe(II) as polymerization catalysts. The MS complexes act as emulsifiers, active catalysts, and stabilization agents simultaneously during the polymerizing of poly(methyl methacrylate) (PMMA) colloids and PMMA-polystyrene (PS) core-shell particles (colloids) in water, see Figure 8, with the MSs as catalysts located at the surface during the polymerization [69].

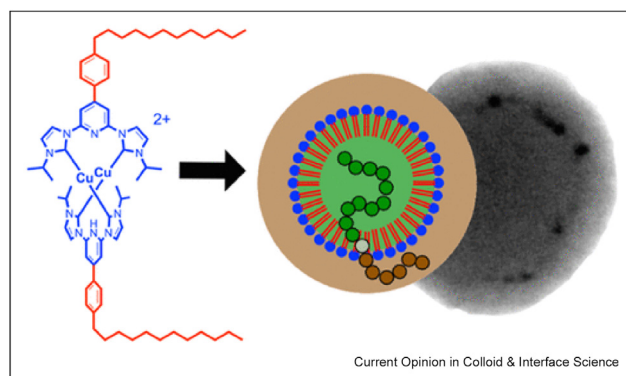
*Biomolecular interactions and Toxicity.* Nehru and co-workers have used a group of surfactant-ruthenium(II)-complexes, differing in head and tail groups, exploring the biophysical impact and developing

Figure 7



Coordination to metal-NHC-based amphiphiles shows that different structures evolve depending on the transition metal and concentration. Reprinted from Ref. [66] with permission from the Royal Society of Chemistry.

Figure 8



To the left is the metallosurfactant, N-heterocyclic carbene (NHC) bearing Cu(I). In the middle is a scheme of the PMMA-PS core-shell particle, and to the right is a TEM micrograph. Reprinted from Ref. [69] with permission from the American Chemical Society.

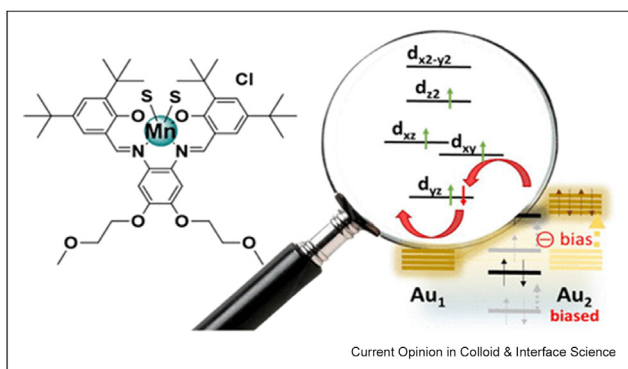
strategies for designing effective metallodrugs for biomedical applications [70,74]. The MS complexes effectively interacted with DNA [70] and, in Reference [74], with bovine and human serum albumins, concluding that HSA has a higher binding affinity than BSA to the MS. In other words, these studies showed that tuning the structural parts as head groups and tail groups of the metallosurfactants could influence the pharmacokinetics of metallodrugs for therapeutic applications. Furthermore, Nagaraj and co-workers studied the interactions binding of Co(III)-MS complex with calf thymus-DNA that occurred due to the insertion of the alkyl chain between the base pairs of DNA [71]. A second study showed that ionic liquids could enhance the interactions of MS to calf thymus-DNA [72]. Yue *et al.* [73] studied lanthanum complexes of four long-chained tridentate imidazole derivatives, where the complexes promoted efficient transesterification of HPNP as a model system for RNA. Dogra and co-

workers have made nanoparticles from different metallosurfactants, focusing on profiling toxicity assessments. Groups of Palladium oxide nanoparticles (PdO NPs) and ruthenium and ruthenium oxide (RuO<sub>2</sub>) NPs were synthesized using palladium-based [79] and ruthenium-based metallosurfactants [80]. The PdO NP nanosuspensions study concluded that all three suspensions are toxic to cells and the genome. The second study confirmed that the NPs have damaging effects on the genomic DNA studied. Bearing in mind that the function of a protein can be altered by binding with a surfactant and that a protein can be stabilized or denatured by the surfactant association to the protein.

**Corrosion inhibition.** Mehta and co-workers have conducted a series of recent studies in the area of corrosion inhibition, and we can see that releasing metallosurfactant coatings in a marine environment could mitigate bacterial fouling on carbon steel surfaces. It is leading to bio-corrosion resistance and durability under seawater media [75]. In the following studies, it is shown that Hafnium-based metallosurfactant acts as a novel corrosion inhibitor on iron surfaces and exhibits the highest inhibition efficiency at its surface aggregation concentration [76], and cobalt-based MSs act as corrosion resistant, anti-bacterial, and non-cytotoxic biomaterial on 316L stainless steel surfaces [77].

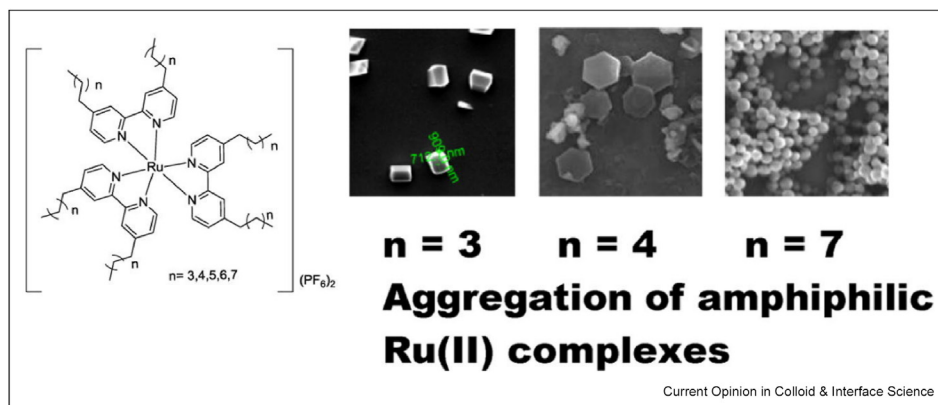
**Electron transfer calculations and characterization.** Combining the design of new MSs, experimental techniques, and quantum mechanical methods as the density functional theory, both Verani and co-workers [81,82], Amunugama *et al.* [83] and Nagaraj *et al.* [84] have studied electron transfer phenomena. Verani and co-workers used three distinct phenylenediamine-bridged phenolate-rich ligands where the metal ions are incorporated. In Ref. [81], 3d<sup>4</sup> manganese(III) ions were used to compare earlier studies from the group, focusing on directional electron transport responses, see Figure 9, and in the

Figure 9



To the left is one 3d<sup>4</sup> manganese(III) metallosurfactant studied, and to the right, the scheme shows an idealized stepwise sequence for electron transport, Reprinted from Ref. [81] with permission from the American Chemical Society.

Figure 10



An example of synthesized ruthenium(II) complexes is shown to the left, and to the right, three different forms of regular nanostructures evolve from the different ruthenium(II) complexes. Reprinted from Ref. [85], with permission from Elsevier.

second study [82], two new MSs containing vanadyl(IV) and chromium(III) were explored.

Secondly [83], focused on developing a new class of metallosurfactants with unidirectional electron transfer properties, a (terpyridine) ruthenium complex containing a semiquinone derivative  $L^2$ , namely  $[Ru^{III}(L^{terpy})(L^2)Cl]PF_6$ . The complex's redox and electronic behavior were studied experimentally, and theoretically studied using DFT methods. Last, Nagaraj and co-workers focused on the kinetics of the electron transfer reactions and could explain the differences due to the ligands in the metallosurfactant complexes [84]. Bhand and co-workers have synthesized five ruthenium(II) complexes and studied the aggregation behavior in aqueous and non-aqueous media, exploring the aggregates formed by Field Emission Scanning Electron Microscopy (FESEM), obtaining theoretical calculations, and discussing electron density transfer from ligand orbitals to the orbital of the metal ion, see Figure 10 [85].

## Conclusions

Chelating surfactants exhibit complex dissociation behavior, leading to varying headgroup charges with pH. Determination of CMC using traditional techniques like tensiometry can be ambiguous, and complementary techniques such as NMR diffusometry, neutron reflectivity, and pH measurements are necessary for accurate CMC determination. Neutron and X-ray reflection measurements provide insights into chelating surfactant organization at interfaces. Techniques such as extended X-ray absorption fine structure (EXAFS) and potentiometry are valuable for studying complex formations and determining stability constants. Addition of specific salts can influence the aggregation behavior of chelating surfactants, leading to transitions between different aggregate structures. Small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and electron paramagnetic resonance (EPR) spectroscopy are important instruments for studying these transitions.

Chelating surfactants offer versatile solutions for the remediation of heavy metals, organic pollutants, and radionuclides from wastewater and soil. Recent studies demonstrate the effectiveness of chelating surfactants like Sodium N-lauroyl ethylenediamine triacetate (LED3A) in removing various contaminants, including copper, lead, zinc, cadmium, petroleum, and phenanthrene from contaminated soils, especially when applied in electrokinetic remediation of co-contaminated soil.

The unique ability of chelating surfactants to form stable complexes with metal ions enables selective modification of valuable mineral surfaces. Recent studies highlight the advantages of chelating surfactants such as 5-heptyl-1,2,4-triazole-3-thione (HpTT) and 2-dodecanoylamino-

pentanedioic acid (DPA) in selectively separating minerals like malachite, rhodochrosite, fluorite, and scheelite from gangue materials. Innovative approaches utilize the pH-responsiveness of chelating surfactants for stepwise separation of multicomponent mineral systems.

Amino acid-based chelating surfactants have been explored for their potential in enhanced oil recovery applications. Recent research has demonstrated increased surface activity, wettability modification, and additional oil recovery using the amino acid-based surfactant sodium cocoyl alaninate (SCA). SCA effectively modified wettability on quartz and carbonate surfaces, enhancing water wetness and improving emulsification of crude oil-brine mixtures. Amino acid-based surfactants like Sodium Cocoyl Glycinate (SCG) have also been applied as efficient corrosion inhibitors for metallic structures.

We can conclude from the literature that metallosurfactants as a sub-class of surfactants are broad and evolving fast in many different directions, such as coordination-driven self-assembly, nanoparticle fabrication, polymerization catalysts, and specific interactions with biomolecules and biomedical applications.

As the demand for sustainable and effective chemical solutions grows, chelating surfactants will expand as an important research and application development area. However, as Eivazihollagh et al. [13] pointed out in an earlier review, this will take time as long as the costs for using chelating surfactants are not competitive with other solutions, and research in the field has been limited in recent years.

## Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT3.5 to edit the text. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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