Metallosurfactants Consisting of Amphiphilic Ligands and Transition Metals: Structure, Bonding, Reactivity, and Self-assembling Property

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Abstract: Metallosurfactants are emerging as a relatively new class of surfactants whose ligand moieties bind to various transition metals. Because transition metal centers are incorporated into the surfactant frameworks, they can form various self-assembled structures with metallic interfaces such as micelles, vesicles, and lyotropic liquid crystals. To reduce the lability of transition metal complexes under aqueous conditions, various amphiphilic ligands have been developed as surfactant frameworks. This review discusses some aspects of the design and chemical structures of amphiphilic ligands, as well as focus on various functions and types of chemical bonds present in metallosurfactants.

Key words: metallosurfactants, transition metals, self-assembly, coordination complex, organometallic complex

1 Introduction
Surfactants are substances that contain both hydrophilic and hydrophobic groups. They are amphiphilic molecules and have ability to adsorb the interface between a solution and a different phase. Conventional surfactants mainly consist of ionic (cationic, anionic, and zwitterionic) or non-ionic head groups together with hydrophobic groups. They are widely used as detergents, emulsifiers, forming agents, and dispersants. They also serve as building blocks in the fabrication of diverse nanostructures. Equipping surfactants with an enhanced set of properties is a highly attractive method to synthesize nanostructures with various functions. Thus, there is a need for the rational design of surfactants with desired functionalities.

Metallosurfactants (MSs) are a relatively new class of surfactants whose ligand moieties bind to various metal ions. The term "metallosurfactant", first reported by Scrimin in 1989, is commonly used to designate surfactants that contain a metal atom in their molecular structure. Owing to various functions derived from their metal centers and surface activity, MSs have potential for use as catalysts, electronic materials, medicines, templates for mesoporous materials, and precursors for nanoparticles. There are several reviews that have dealt with the different properties and applications of MSs; however, it is beyond the scope of the current review to discuss all of them. In the present review, we briefly explore some aspects of the design and chemical structures of amphiphilic ligands, as well as focus on various functions and types of chemical bonds present in MSs.

For this purpose, we further define an MS as an amphiphile in which transition metals are bound to a surfactant framework via coordination or metal-carbon bonds. Therefore, we draw a distinction between the MSs and surfactants in which transition metal ions are bound to a surfactant framework via ionic bonds, such as the studies of ionic-type MSs with double-tailed structures, where two dodecyl sulfates are bound to divalent Ni, Co, Cu, and Mg12, 13, Lewis acid-surfactant combined catalysts (LASCs) such as scandium tris(dodecyl sulfate), which works both as a Lewis acid to activate the reactants and as a surfactant to form stable colloidal dispersions14, 15, Ferrum laurate[Fe(OOCC11H23)3] with triple-tailed structures, which spontaneously form reverse vesicles in organic media such as CHCl3 and a mixed solvent of CHCl3 and CH3OH16.
Metallic atoms have the ability to act as Lewis acids that form complexes with Lewis bases. Most of the elements in the periodic table are metals, and almost all metals form coordination complexes where a metal center is bound to one or more ligands (known as Werner complexes). Organic ligands bind the metal through a heteroatom. Depending on the combination of metals and ligands, MSs with coordination bonds can realize a variety of molecular shapes. To date, nitrogen-based ligands such as amine, pyridine, imidazole, triazole, phenanthroline, bipyridine, and terpyridine have typically been used as ligands for MS synthesis.

Scrmin and Tonellato et al. synthesized amphiphilic pyridine ligands with different hydrophilic/hydrophobic balances (1a-d), as shown in Fig. 1.17,18 1a with a methyl group (R = CH₃) dissolved in water and did not form any self-assembled structures. 1b with short alkyl chains (R = C₆H₁₃) self-assembled to form micelles in water, while 1c (R = C₁₀H₂₁) and 1d (R = C₁₆H₃₃) with long alkyl chains formed larger aggregates of vesicles. Although 1b showed complexation with Cu(II) at the micellar interface, no complexation with Cu(II) was observed at the vesicular interface of 1c and 1d. These results indicate that the aggregate structure and ligand location significantly influence the ability of the ligands to bind Cu(II).

Osakada et al. employed N-alkyl bipyridinium ligands [4,4′-bpy-N-(CH₂)ₓOC₆H₅-3,5-X₂][NO₃] (2: X = tBu, 3: X = OMe), as shown in Fig. 2.19 The authors synthesized a series of Pd- and Pt-containing MSs.20 The reaction of 3 with M(NO₃)₂ (M = Pd, Pt, en = ethylenediamine) yielded [M(4,4′-bpy-N-(CH₂)ₓOC₆H₅-3,5-(OMe)ₙ]₂(en)] [NO₃]₄ (M = Pd) and 5 (M = Pt) with double-tailed structures. Although Pd- and Pt-containing MSs have the same bipyridinium ligands, they self-assembled to form metallic micelles with different sizes. The average hydrodynamic diameters were estimated to be 5.9 nm for 4 (M = Pd) and 27 nm for 5 (M = Pt). A single-tailed MS with one bipyridin-
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It is well-known that the Pd–N coordination bond is more labile than the pyridine ligands because of its positive charge. Thus, 4 with bipyridinium ligands showed dynamic behavior in water at ambient temperatures based on the reversible liberation of the ligand. The addition of \( \alpha \)-cyclodextrin (\( \alpha \)-CD) to a \( \text{D}_2\text{O} \) solution of 4 led to form \( [n] \) rotaxanes via a slippage reaction (Fig. 3)\(^{20,21-25} \). In this reaction, 4 was equilibrated with a mixture of 3 and [Pd(\( L \))(\( \text{D}_2\text{O} \))(en)] \( [\text{NO}_3]_\gamma \) (\( L = 3 \)) via the partial dissociation of 3 and its coordination. Once liberated, 3 and \( \alpha \)-CD produced pseudorotaxanes \( [3(\alpha \text{-CD})]_\gamma \) (\( m = 1, 2 \)), which were end-capped by [Pd(\( L \))(\( \text{D}_2\text{O} \))(en)] \( [\text{NO}_3]_\gamma \) to form the \( [n] \) rotaxanes (\( n = 2-5 \)). Each step in the reaction is reversible, although the high stability of the \( [n] \) rotaxane structure arises from the hydrophobic interaction between the cavity of \( \alpha \)-CD and alkylbipyridinium ligands, making the reaction formally irreversible in \( \text{D}_2\text{O} \).

A similar reaction of the Pt-containing MS shown in 7 with \( \alpha \)- and \( \beta \)-CDs in aqueous media produced the corresponding \( [2] \) rotaxanes with 1:1 stoichiometry\(^{22} \). \( \gamma \)-CD and 7 formed a rotaxane with components in a 1:1 or 2:1 molar ratio. The addition of NaBH\(_4\) to the rotaxanes in aqueous media formed Pt nanoparticles with diameters of 1.3–2.8 nm. The Pt nanoparticles formed from the rotaxanes showed higher thermal stability than those obtained from the reduction of the cyclodextrin-free Pt complex of 7.

Phosphines are often used as ligands for homogeneous catalysis. The combination of hydrophilic and hydrophobic substitutes results in amphiphilic phosphine ligands (Fig. 4). Suades et al. reported the amphiphilic phosphine ligands \( \text{Ph}_n\text{P(CH}_2)_m\text{SO}_3\text{Na} \) (8a: \( n = 2, 8b: n = 6, \) and \( 8c: n = 10 \)), in which sulfonate was linked to the ligands\(^{26} \). The ligands allow the metal atom to be located in a hydrophobic environment. Similar amphiphilic phosphine ligands (9a-f)\(^{27} \), whose coordination sites were located at the end of the hydrophilic moiety, were synthesized in two steps, starting from the corresponding commercial nonionic surfactants. Other series of amphiphilic phosphine ligands 10a-f were also synthesized\(^{28} \). The reaction of amphiphilic phosphine ligands 8a-c with \( \text{PtCl}_2\text{(dmsol)} \) (\( \text{dmsol} = \text{dimethyl} \text{ sulfoxide} \)) gave cis-[\( \text{PtCl}_2\text{L}_2 \)] (\( L = 8a, 8b, \) and \( 8c \))\(^{29} \). The surface properties of the amphiphilic phosphine ligands 8a-c and their respective MSs were studied using the Wilhelmy plate method. The comparison between free phosphines and their respective Pt (II)-containing MSs demonstrated that CMC values were substantially lower for cis-[\( \text{PtCl}_2\text{L}_2 \)] (\( L = 8a, 8b, \) and \( 8c \)).
The ratio between the CMC of MSs and their free ligands was almost five for compounds 8a and 8b, and nearly ten for 8c. The authors considered that the PtCl2 fragment acts as a linker between the two hydrophobic chains, and the MSs cis-[PtCl2L2] (L = 8a-8c) can be seen as bolaform surfactants. The study of self-assembled structures using dynamic light scattering spectroscopy and cryo-transmission electron microscopy showed the formation of vesicles in all cases. Pd(II)-containing MSs were also found to form vesicles in water. Two families of molybdenum carbonyl MSs with single- and double-tailed structures, Mo(CO)4L2 and Mo(CO)6, were also synthesized from the same amphiphilic phosphine ligands. The authors found that the CMCs of the molybdenum carbonyl MSs were significantly lower than those of the respective amphiphilic phosphine ligands. In all cases, the MSs formed multilamellar vesicles rather than micelles in water.

Van Leewan et al. reported amphiphilic phosphine ligands consisting of rigid Xantphos ligands. Rh-containing MSs were prepared by the reaction of the amphiphilic phosphine ligands with [RhH(CO)(PPh3)]. The MS formed vesicles with a particle size of 140 nm in water. Incorporation of 1-octene into the vesicle led to the formation of a large aggregate with a particle size of approximately 500-600 nm. Because 1-octene was in close proximity to Rh in the membrane, the hydroformylation reaction proceeded, and the corresponding linear aldehyde was obtained in high yield. The product can be separated with an extraction procedure, and the vesicular Rh catalysis remains in the aqueous phase and can be used repeatedly.

As described above, some transition metals with coordination bonds reversibly dissociate via ligand exchange reactions with water. To reduce lability, macrocyclic ligands, which can encapsulate transition metals within the inner cavity, have been employed. The azacycloalkane ligand is poorly soluble in water and readily dissolved upon the addition of Ni(II) and Cu(II) salts because of the formation of their MSs. The CMCs of the MSs were determined by the Du Noüy platinum ring method. The lower CMC value of the Cu(II)-containing MS is attributed to the tendency of Cu(II) to adopt five-coordinate geometries, resulting in a marginally smaller head group. The ligand structures were expanded in order to reveal the structure-function relationship for the interfacial properties.

Cyclic peptides are also known to act as ionophores, wherein metal ions can be encapsulated within the inner cavity. The cyclic lipopeptide surfactin, which is abundantly produced by microorganisms such as Bacillus subtilis, is regarded as a promising biosurfactant. Owing to two carboxylate groups, 15 can bind divalent transition metals such as Ni2+, Zn2+, and Cd2+ and form large aggregates in water. Because the cyclic peptide moiety provides an ideal coordination number and cavity size for Cs+ encapsulation, 15 selectively encapsulates Cs+ among the...
other alkaline metals\(^{35}\). High binding affinity and effective removal of Cs\(^+\) from water were achieved through micellar-enhanced ultrafiltration.

### 3 Metallosurfactants Having Metal-carbon Bonds

Organometallic compounds are chemical compounds that contain at least one direct metal–carbon bond. The metal–carbon bonds in organometallic compounds are generally highly covalent. Thus, metal atoms can be strongly attached to the surfactant frameworks. However, organometallic MSs are still rare, likely due to the difficulty of synthesizing non-symmetric structures, preferentially with distinct amphiphilic character.

Uozumi et al. designed amphiphilic pincer-type ligands and their MSs (16-19)\(^{36-40}\), in which a chelating agent binds tightly to three adjacent coplanar sites of Pd (Fig. 6). The Pincer ligands permit the labile ligands to be firmly bound, and thus endow their metal complexes with exceptional thermal stability. Owing to oligoethylene glycols and alkyl chains, Pd-containing MSs spontaneously form vesicles in water. The vesicles formed from 16 with concentrated Pd centers within the vesicular interface facilitate the Miyaura-Michael reaction in a highly selective manner. It should be noted that when the same reaction was carried out in an amorphous state, the reactivity decreased significantly. Therefore, the organized membrane structure of vesicles contributes to the expression of excellent catalytic functions. Vesicular reactive environments are applicable to various reactions, such as allylic arylation of allyl acetates with sodium tetraarylborates, cyclization, and the arylation of terminal alkynes.

N-Heterocyclic carbenes (NHCs), which are derived from imidazolium salts, have attracted significant interest as ligands for transition metal-catalyzed reactions in water. Glorius et al. reported a combination of an NHC ligand and a structurally simple surfactant (20) with an Au (I) complex,
found that mixing a co-surfactant such as sodium dodecyl sulfate (SDS) with the Au(I)-containing MS generated metallic micelles whose interface was covered with Au(I) atoms. Under these conditions, the hydration of 1,2-diphenylacetylene was facilitated through the solubilization of the reactants within the metallic micelles. Poliarz et al. reported the synthesis of chelating ligands (21a and 21b) in which two NHC moieties were attached to a pyridine, resulting in a tridentate amphiphile. The CMC of 21a was estimated to be $7.9 \times 10^{-5}$ M. Above the CMC, 21a formed spherical micelles. The authors synthesized Pd(II)-, Fe(II), Cu(I)-, and Ag(I)-containing MSs, in which one or two NHC ligands (21a) were coordinated to the metal centers. The Pd(II)-containing MS not only exhibited Suzuki-Miyaura cross-coupling reactions, but its amphiphilic design also proved to be advantageous for coupling hydrophobic and hydrophilic compounds, likely because the Pd center at the interface facilitated the reactions between reagents with opposite solubility preferences. Cu(I)- and Fe(II)-containing MSs with two NHC ligands can be used for emulsion polymerization under atom transfer radical polymerization. Polymerization of methyl methacrylate yielded...
stable poly(methyl methacrylate colloids in water). Cu(I)-containing MS spontaneously formed vesicular structures in water.

Amphiphilic NHC ligands 20 and 21 have NHC moieties at the end of the hydrophilic part. In the case of NHC ligand 22, the NHC moiety was placed at the linkage of hydrophilic and hydrophobic parts, which allowed the transition metals to be located at the air-water interface. The reaction of 22 with Pd(OAc)$_2$ in water resulted in Pd-containing MS. In situ generation of MS reduced the CMC value compared to that of 22 (3.9×10$^{-3}$ M). MS forms micelles in water, with an interface covered with Pd(II). When oily substrates such as iodobenzene and styrene were added to the micellar solution, the mixture provided emulsion droplets. The addition of triethylamine as a base facilitated the Mizoroki-Heck reaction to give the cross-coupling product of stilbene. The detailed surface and self-assembly properties were found via synthesis of Pd-containing MS[PdBr$_2$(L)(NEt$_3$)] (25: L = 22) with triethylamine as a co-ligand.

Owing to the capability of MSs to bond a broad spectrum of metals, Au(I) and Ag(I)-bonded MSs [MBr(L)] (23: M = Au(I), 24: M = Ag(I)) were also synthesized. Compared to the self-assembling behavior of the MSs, the identity of the transition metal had a significant effect on the entire system, setting the self-assembly direction of the NHC-based amphiphile, as shown in Fig. 8. The CMCs of the MSs were lower than those of 22, indicating that metal coordination promotes self-assembly in water. Moreover, the CMC of 23 (1.3×10$^{-3}$ M) was one order of magnitude lower than that of 24 (7.3×10$^{-4}$ M), even though they consisted of the same NHC and bromide ligands. In addition, the CMC of 25 (1.4×10$^{-4}$ M), bearing triethylamine as an additional hydrophobic ligand, was similar to that of 24. The lowest CMC seen in 23 can be attributed to the distinctive role of Au(I), such as Au(I)–Au(I) interactions. The γcmc of 23 (44.9 mN/m) was higher than those of 24 (29.6 mN/m) and 25 (36.7 mN/m). Therefore, the alignment of the Au(I) atom at the air/water interface may hamper the disruption of the hydrogen bonds present in water, resulting in the aforementioned difference in γcmc. In a diluted aqueous solution, 23 and 24 formed spherical micelles with an average diameter estimated to be 5.1 ± 0.9 nm for 24 and 5.7 ± 1.1 nm for 23. On the other hand, 25 formed cylindrical micelles with a maximum dimension of 20 nm.

Interestingly, 23 spontaneously formed not only spherical micelles, but also gold nanoparticles (AuNPs) in water. The AuNPs spontaneously formed when 23 was dissolved in water above the CMC. Control experiments revealed the role of the surface activity of 23 in AuNP formation. The mixing of β-CD with 23 in water inhibited AuNP formation. The apparent rate of AuNP formation in the presence of β-CD was approximately two times lower than that in its absence. As is the case with 4, β-CD formed pseudorotaxane with 23, inhibiting the formation of spherical micelles. Moreover, the reaction of 23 in ethanol, whose interfacial tension was lower than that of water, did not produce AuNPs. These results suggest that AuNPs were formed from 23, which was adsorbed at the air/water interface. The formation of [n]pseudorotaxane and the use of ethanol as a solvent inhibited the adsorption behavior of 23.

The difference in the transition metals also induced geometrical transformation at high concentrations. Although 22 did not display an optically anisotropic phase at any concentration, 23-25 exhibited such phases. In the case of 23, the micellar solution became increasingly viscous with increasing concentration. The phase transition from the isotropic micellar phase to the anisotropic phase occurred above 46 wt%, where hexagonal phases were observed. In the case of 24, micellar and hexagonal phases were also observed. These self-assembled structures differed from those of 25, wherein the hexagonal phase was not observed, while sponge and lamellar phases were detected. The formation of the lamellar structure suggests that the curvature of 25, bearing a triethylamine as an additional co-ligand, is considered to be close to zero. In contrast, 23 and 24, which did not contain triethylamine, exhibited positive curvatures, resulting in the formation of hexagonal structures.

4 Conclusion

In this review, we briefly explore some aspects of the designate amphiphilic ligands and their MSs with coordination and metal–carbon bonds. Owing to the varied electronic configurations and bonding patterns of transition metals, MSs exhibit diverse structures and properties that are typically difficult to realize using commonly used organic surfactants. MSs have the ability to program both physical and chemical functionalities, including catalytic functions. Furthermore, in most cases, metal coordination induces unusual self-assembly, such as the formation of vesicles and liquid crystals in water. Self-assembly via metal coordination is beyond the conventional concept of the critical packing parameter (CPP). Therefore, the use of MSs may prove critical in the rational design of nanostructures with various functional interfaces.

Conflicts of Interest

There are no conflicts of interest to declare.

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