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Research Article

Transition Metal Dodecyl Sulphates: Industrial Applications, Market Potential, and Future Perspectives

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Abstract: Transition metal dodecyl sulphates (TMDSs) are amphiphilic inorganic–organic salts in which a transition-metal cation is associated with dodecyl sulphate (DS^-), an anion combining a C12 hydrophobic chain with a strongly hydrated sulphate headgroup. The resulting materials occupy an interesting boundary between conventional surfactants, coordination chemistry and layered soft matter. Their behaviour is governed by metal charge and hydration, sulphate–metal association, hydrocarbon-chain packing, ionic strength, temperature and water content. Early work on sodium dodecyl sulphate (SDS) established the importance of micellization, critical micelle concentration (CMC), counter-ion binding and electrolyte effects, while later structural studies showed that trivalent metal dodecyl sulphates can form lamellar solids with metal-dependent hydration and thermal behaviour [1]. This review summarizes the chemical basis, synthesis, structural characterization, interfacial behaviour and emerging application opportunities of transition-metal dodecyl sulphates, with emphasis on Cu, Co, Ni, Zn and related divalent systems. Particular attention is given to the relationship between molecular structure and measurable properties such as CMC, phase behaviour, thermal stability, surface activity and morphology. The present scenario indicates that TMDSs are best viewed not simply as detergent-like salts but as tunable molecular materials capable of mediating interfaces and organizing inorganic species. Future opportunities include computationally guided metal selection, mixed-metal and mixed-surfactant systems, low-waste synthesis, nanostructure templating, electrochemical interfaces and application-oriented scale-up. A stronger connection between structure, performance, environmental fate and market requirements will be essential for translating laboratory observations into useful technologies.

Keywords: Transition Metals, Dodecyl Sulphate, Metallosurfactants, Micellization, Lamellar Materials

INTRODUCTION

Surfactants are amphiphilic molecules containing a hydrophobic domain and a hydrophilic or ionic domain. Their ability to accumulate at interfaces and to self-assemble into micelles, bilayers and liquid-crystalline phases underpins a wide range of technologies, from detergency and emulsification to mineral processing, drug delivery and materials synthesis [2,3]. Sodium dodecyl sulphate, commonly abbreviated SDS or SLS, is among the most extensively studied anionic surfactants. Its C12 chain provides hydrophobic association, whereas the sulphate headgroup remains strongly hydrated. In water, SDS undergoes concentration-dependent aggregation and exhibits a well-defined CMC whose measured value depends on temperature, electrolyte concentration and the method used [4-6].

Replacing the sodium counter-ion with a metal cation changes the electrostatic environment of the sulphate headgroup and can alter solubility, hydration, aggregation, phase equilibria and solid-state organization. For a divalent ion M^{2+}, a simplified stoichiometry is $M(DS)_2$, whereas a trivalent ion gives $M(DS)_3$. These formulae should be regarded as compositionally useful representations rather than universal descriptions of coordination geometry. Metal–sulphate

association can include electrostatic attraction, outer-sphere ion pairing and, depending on the metal and hydration state, more specific coordination interactions [1]. The scientific interest of TMDSs arises from this coupling of molecular amphiphilicity with metal-ion chemistry. Transition-metal centres contribute variable charge density, coordination preferences, redox activity and electronic properties, while the dodecyl sulphate component promotes interfacial adsorption and self-assembly. Such combinations can generate materials with properties that neither a simple metal salt nor SDS alone can provide. The concept is related to the broader family of metallosurfactants, in which transition metals are deliberately incorporated into amphiphilic architectures to create micelles, vesicles or lyotropic structures [7].

Chemical Basis and Scope

TMDS chemistry should be distinguished from two related but different systems:

- Conventional SDS solutions containing trace or deliberately added transition-metal ions and
- True metal dodecyl-sulphate salts isolated as solid compounds. In the first system, metal ions may bind to or adsorb onto SDS aggregates without becoming part of a stoichiometric crystalline salt. Molecular simulations and interfacial studies have shown that cationic species can be concentrated near the negatively charged SDS headgroups, influencing aggregate structure and adsorption [8,9]. In the second system, precipitation and drying can yield a distinct solid phase whose composition and lamellar structure are governed by the metal-to-sulphate ratio and hydration state.

Classical studies of SDS–metal dodecyl-sulphate mixtures already demonstrated that the counter-ion strongly affects micellization. For Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} systems, increasing the fraction of metal dodecyl sulphate lowered the CMC compared with pure SDS, consistent with a reduction in electrostatic repulsion at the aggregate surface [10]. Related phase-equilibrium studies showed that water content, temperature and sodium/metal composition control eutectic behaviour and the onset of micelle formation [11]. These results remain important because they demonstrate that metal substitution is not merely a change in chemical formula; it changes the thermodynamics of self-assembly.

Structural work on Al, Cr, La and Gd dodecyl sulphates provides a particularly useful model for understanding how metal identity affects the solid state. Pereira *et al.* [1] combined X-ray diffraction (XRD), FTIR, NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarized-light microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The products showed lamellar structures, metal-dependent hydration and characteristic thermal behaviour. A metal-to-sulphate ratio consistent with the expected trivalent composition was observed by SEM–EDS, while periodic surface features were consistent with layered organization. The Figure 1 is a conceptual schematic prepared for this review; exact coordination geometry depends on the metal ion and hydration state.

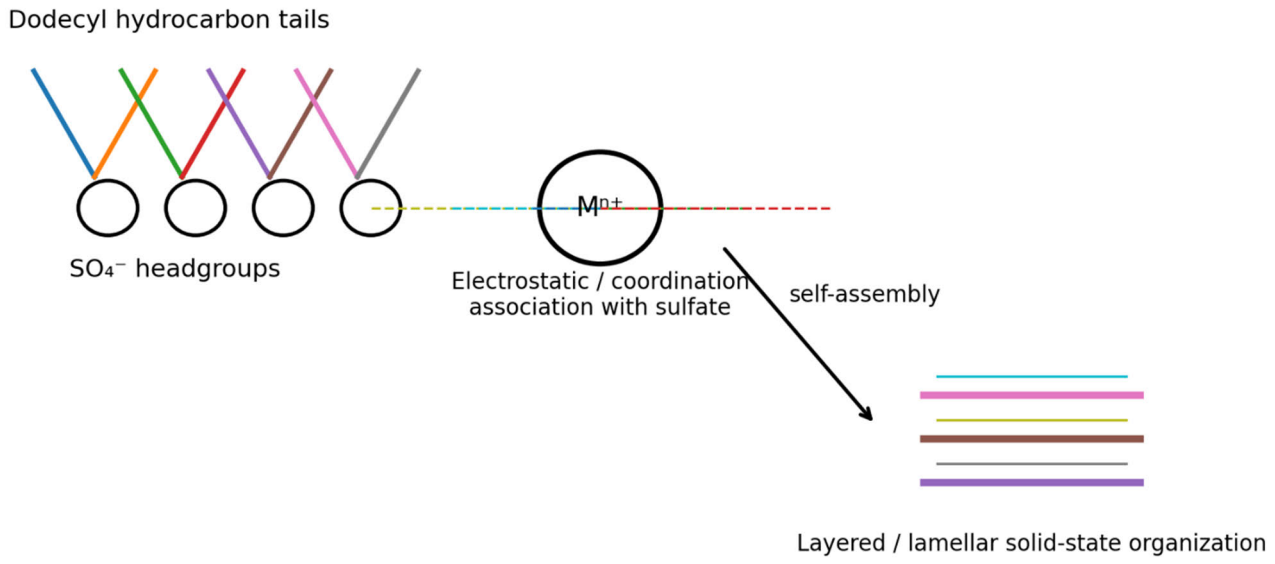

Figure 1: Simplified Structural Representation of a Transition-Metal Dodecyl Sulphate and Its Tendency Toward Layered Organization.

Present Scenario

Synthesis and Chemical Preparation

Most metal dodecyl sulphates can be prepared by metathesis or precipitation from an aqueous SDS solution containing the desired metal salt. A simplified reaction for a divalent metal is $MCl_2 + 2NaDS \rightarrow M(DS)_2\downarrow + 2NaCl$. For trivalent ions, $MCl_3 + 3NaDS \rightarrow M(DS)_3\downarrow + 3NaCl$. The practical product, however, depends on pH, temperature, concentration, mixing rate, counter-anion, hydration and washing efficiency. Pereira *et al.* [1] demonstrated preparation of trivalent metal dodecyl sulphates at near-neutral pH by adding metal salts to aqueous SDS. Direct metathesis has also been reported for copper and zinc dodecyl sulphates using SDS as the precursor surfactant [12].

Structural and Spectroscopic Characterization

XRD is central to identifying the layered character of metal dodecyl sulphates. Low-angle reflections can provide information on lamellar periodicity, while wide-angle features reveal hydrocarbon-chain packing and crystalline order. The long alkyl chain may adopt an extended conformation, although local disorder can occur close to the sulphate headgroup. Pereira *et al.* [1] found that differences in hydration and metal coordination were reflected in the lamellar structures and thermal transitions of Al, Cr, La and Gd derivatives.

FTIR spectroscopy is useful for monitoring the sulphate headgroup and the alkyl chain. Changes in sulphate stretching bands, together with CH_2 stretching and bending modes, can indicate changes in headgroup environment and chain packing. Importantly, spectral shifts should not automatically be interpreted as evidence for a specific inner-sphere coordination geometry; complementary XRD, elemental analysis and thermal data are required. NMR can provide information about molecular mobility and local environments, while DSC and TGA distinguish dehydration, structural transitions and decomposition. SEM and AFM provide morphological information and can reveal periodic or layered features at the surface [1].

Micellization, CMC and Electrolyte Effects

Micellization is a defining property of dodecyl sulphate systems. In water, increasing SDS concentration initially increases monomer concentration and interfacial adsorption; once the CMC is reached, additional surfactant preferentially enters aggregates. A frequently cited CMC for SDS in water at 25 °C is about 8.1 mM, although values vary with purity, temperature, ionic strength and measurement method [3]. Conductivity, surface tension, fluorescence probes, calorimetry and dielectric measurements can all be used, but they may detect different operational signatures of aggregation [4,13].

Metal dodecyl sulphates can reduce the electrostatic penalty associated with aggregation because multivalent counter-ions neutralize more sulphate charges per ion. Moroi *et al.* [10] reported a substantial decrease in CMC as the fraction of divalent metal dodecyl sulphate increased in SDS mixtures. Electrolytes can also compress the electrical double layer and modify micellar growth, aggregation number and phase behaviour. Studies with NaCl, acetate, propionate and butyrate demonstrate that the CMC and micellization thermodynamics of SDS are highly sensitive to the surrounding electrolyte.

These effects have practical implications. A TMDS formulation designed for an aqueous process must be evaluated under the actual ionic environment rather than in pure water alone. In industrial or biological media, pH, competing anions, hardness ions, dissolved organic matter and temperature can alter the aggregation state. Even the presence of solubilized molecules can shift apparent CMC and broaden the aggregation transition [4].

Phase Behaviour and Solid-State Organization

Phase behaviour is one of the most important links between molecular structure and application. Metal dodecyl sulphates can occur as hydrated crystalline solids, lamellar phases and mixed systems with sodium dodecyl sulphate. The balance between chain packing, headgroup hydration and electrostatic interactions determines the preferred morphology. The Krafft phenomenon is particularly relevant because surfactants may remain poorly soluble below a characteristic temperature, while micellization becomes favourable above it. In SDS–metal dodecyl-sulphate mixtures, the temperature at which micelles appear is not necessarily identical to the temperature at which a solid phase completely dissolves [11].

Transition-Metal Dependence

The transition-metal ion provides a major design variable. Cu^{2+} and Ni^{2+} possess distinctive electronic configurations and coordination preferences; Co^{2+} can support multiple coordination environments and oxidation states; Zn^{2+} is d^{10} and therefore lacks ligand-field stabilization effects associated with partially filled d orbitals. These differences can influence hydration, lattice energy, thermal behaviour and the kinetics of precipitation. It is therefore reasonable to expect that two compounds having the same nominal stoichiometry but different metals can exhibit markedly different

Table 1: Representative Structure–Property Considerations for Transition-Metal Dodecyl Sulphates

Metal / class	Nominal composition	Likely controlling factor	Useful characterization	Potential relevance
Cu^{2+}	$Cu(DS)_2$	Charge density, hydration, redox chemistry	XRD, FTIR, TGA/DSC, SEM	Interfaces, functional materials, catalysis
Co^{2+}	$Co(DS)_2$	Coordination/oxidation state, hydration	XRD, UV–Vis, FTIR, TGA	Redox-active or magnetic material platforms
Ni^{2+}	$Ni(DS)_2$	Coordination environment, chain packing	XRD, FTIR, DSC, SEM	Layered materials and interfacial chemistry
Zn^{2+}	$Zn(DS)_2$	d^{10} ion, hydration and lattice packing	XRD, FTIR, TGA, AFM	Surfactant-mediated materials synthesis
$Al^{3+}/Cr^{3+}/La^{3+}/Gd^{3+}$	$M(DS)_3$	Higher charge, hydration, lamellar packing	XRD, NMR, FTIR, DSC/TGA, SEM/AFM	Model lamellar and hybrid materials

solubility and thermal transitions. However, the available literature is uneven. The most detailed structural dataset for metal dodecyl sulphates concerns trivalent ions rather than the full series of first-row transition metals [1]. Older studies provide valuable thermodynamic evidence for Mg, Mn, Co, Ni and Cu systems, but modern structure–property investigations using standardized XRD, synchrotron scattering, surface analysis and computational modelling are comparatively limited [10,11]. This gap represents a significant opportunity for contemporary research (Table 1).

Interfacial and Materials-Relevant Behaviour

The dodecyl chain and sulphate headgroup make TMDSs naturally suited to interfacial phenomena. Adsorption of SDS at charged surfaces depends on surface charge, pH and counter-ion identity. Neutron-reflection studies at sapphire/solution interfaces have shown that counter-ions can substantially modify the hydration and packing of adsorbed dodecyl-sulphate layers [10]. The broader implication for TMDSs is that metal identity can become a handle for tuning the interfacial electrical double layer, although direct comparisons require carefully controlled experiments.

Metal-containing surfactant systems also offer routes to organized inorganic materials. Surfactant assemblies can concentrate ions, provide confined reaction environments and influence nucleation. The concept is consistent with surfactant-templated material synthesis, in which amphiphilic aggregates act as soft templates for inorganic structures. For TMDSs, the metal ion is not merely a guest within the template: it can become part of the amphiphilic salt itself, making the system attractive for hybrid organic–inorganic materials research.

Emerging Applications

Applications of TMDSs should be considered at the intersection of surfactant science and metal-based materials chemistry. First, they may function as surface-active additives in processes where multivalent ions are advantageous. Second, their layered solid-state structures make them candidates for controlled-release, adsorption or interfacial materials, provided stability and environmental fate are established. Third, metal-containing surfactant assemblies can serve as precursors or templates for inorganic nanostructures. Related work has demonstrated that surfactant monolayers can control the nucleation and thickness of inorganic nanosheets, illustrating the broader potential of ionic amphiphile–metal interfaces [14].

Fourth, TMDSs may be relevant to catalysis and electrochemistry when a redox-active metal is used. The surfactant layer can modify local polarity, mass transport and accessibility of active sites. Nevertheless, claims of catalytic performance should not be inferred solely from the presence of a transition metal; they require quantitative comparison with the parent metal salt, SDS, physical mixtures and appropriate controls. Fifth, the amphiphilic environment can affect the behaviour of metal complexes. Recent reviews of surfactant–metal-complex interactions emphasize that micellar microenvironments can change solubility, localization and biological or physicochemical behaviour [15].

Environmental and Safety Considerations

Future commercialization must account for the environmental profile of both components. Dodecyl sulphate is biodegradable under appropriate conditions, but surfactant concentration, formulation and treatment conditions influence aquatic effects and persistence. Transition metals add another dimension because toxicity and bioavailability depend strongly on oxidation state, free-ion activity, complexation and environmental chemistry. Therefore, the environmental assessment of a TMDS cannot be derived simply by adding the hazard profiles of SDS and the metal ion. An application-oriented evaluation should include acute and chronic aquatic toxicity, metal release, biodegradation or transformation, sediment interactions, ecotoxicity of degradation products, and life-cycle assessment. This is particularly important for Cu, Ni and Co systems, where regulatory and environmental concerns can be more significant than for less toxic or more biologically compatible ions. A design strategy based on minimum metal loading, recoverability and closed-loop processing would improve sustainability.

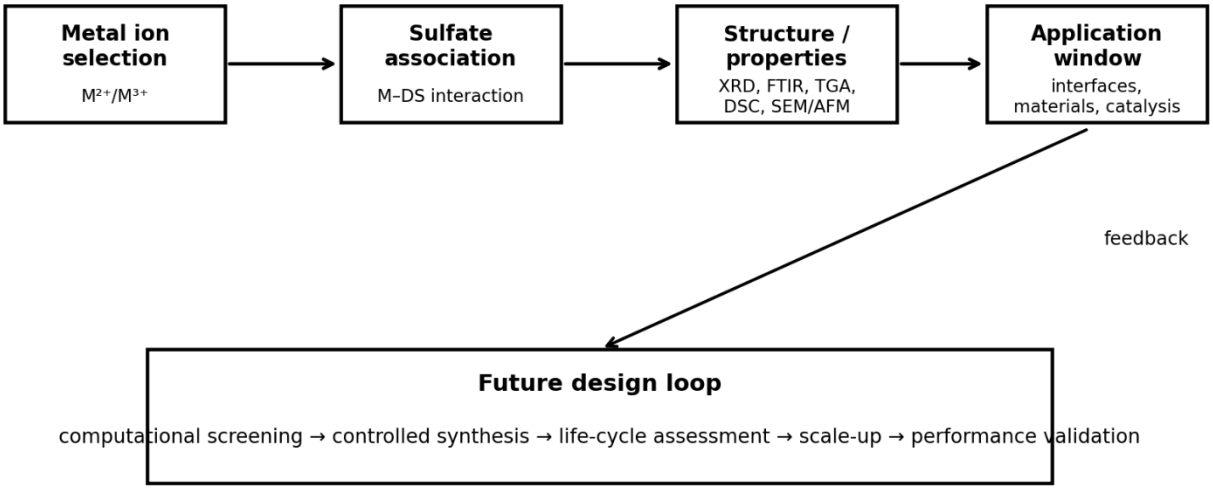

Figure 2: Proposed Research-To-Application Pathway for Transition-Metal Dodecyl Sulphates.

Research and Commercialization Landscape

From a research-translation perspective, TMDSs remain a relatively specialized class compared with conventional surfactants. Their commercial potential will depend on demonstrating a property that cannot be achieved economically with SDS, another alkyl sulphate, a conventional metal salt or a different metallosurfactant. The strongest opportunities are therefore likely to be niche, performance-driven applications rather than direct replacement of commodity detergents. A structure–property–performance loop can help connect laboratory synthesis with scale-up and sustainability requirements (Figure 2).

Future Perspective

The future of transition-metal dodecyl sulphates lies in moving from descriptive synthesis toward predictive materials design. Much of the earlier literature established that metal identity changes micellization and solid-state behaviour; the next stage should establish quantitative relationships between ionic radius, charge density, hydration enthalpy, coordination preference, chain packing and macroscopic performance. Such a framework would allow researchers to select metals rationally rather than screening ions empirically.

Molecular and Computational Design

Molecular dynamics, density-functional theory and coarse-grained simulations can be used to investigate metal–sulphate association, hydration shells, ion pairing, micelle structure and lamellar packing. Recent computational work on surfactant aggregation shows that specific ion effects can materially alter CMC and micellar organization, supporting the value of simulation-guided formulation [16]. A future TMDS workflow could combine predicted binding and hydration descriptors with experimental CMC, XRD spacing and thermal data to construct quantitative structure–property models.

Mixed-Metal and Mixed-Surfactant Systems

Mixed-metal dodecyl sulphates could provide a route to continuously tune hydration, charge density and electronic properties. Likewise, combining TMDSs with SDS, nonionic surfactants or biosurfactants may enable better control over phase behaviour. Studies of alkyl sulphate mixtures show that even small amounts of an ionic surfactant can strongly change microemulsion phase behaviour and interfacial structure [17]. Similar principles can be explored for TMDS-containing systems.

Advanced Characterization

Future studies should use complementary techniques rather than relying on FTIR alone. Synchrotron XRD or small-angle X-ray/neutron scattering could resolve lamellar periodicity and aggregate structures; cryo-TEM could visualize hydrated assemblies; solid-state NMR could probe local mobility; X-ray photoelectron spectroscopy could examine

surface composition; and operando spectroscopy could track changes during heating, hydration or redox cycling. Such datasets would help distinguish true coordination effects from simple electrostatic association.

Sustainable Synthesis and Circularity

Precipitation methods are attractive because they are simple and aqueous, but scale-up should address salt waste, water consumption, recovery of unreacted SDS and metal losses. Continuous precipitation, membrane-assisted washing, solvent-free drying and recovery of metal ions from process streams could improve sustainability. Where possible, abundant and comparatively low-toxicity metals should be prioritized, and the final material should be designed for recovery rather than uncontrolled release.

Application-Specific Development

Application development should begin with a clearly defined performance target—for example, lowering interfacial tension, increasing adsorption selectivity, controlling inorganic nucleation, improving dispersion stability or modifying electrochemical mass transfer. The appropriate TMDS can then be selected based on measurable structure–property relationships. This approach is more likely to produce meaningful value than broad screening without a defined end use.

An important future direction is the integration of TMDSs with advanced nanomaterials. The combination of an amphiphilic layer and a transition-metal centre may provide a route to hybrid structures with controlled interfacial chemistry. The demonstrated ability of ionic surfactant monolayers to regulate inorganic nanosheet growth suggests that metal–surfactant assemblies could be explored as self-limiting reaction environments [14]. Likewise, laser-ablation and surfactant-mediated processing have produced layered copper-containing organic–inorganic composites, illustrating how SDS can participate in the organization of metal-containing phases.

Another promising direction is the coupling of TMDSs to biological or pharmaceutical interfaces. Metal complexes are known to interact with surfactant micelles through electrostatic, hydrophobic and coordination-mediated pathways, and the micellar environment can alter apparent solubility and reactivity [15]. TMDSs could therefore be investigated as functional interfaces rather than simply as carriers. Such studies must, however, include rigorous cytotoxicity, metal-release and biodegradation measurements before biomedical claims are made.

Standardization is equally important. Reported CMC values can differ because of temperature, purity, electrolyte composition and measurement technique. The same issue applies to solid TMDSs because hydration state and drying history can change the observed XRD and thermal signatures. Future publications should report synthesis pH, ionic strength, metal-to-surfactant ratio, washing protocol, drying temperature, residual water content and analytical uncertainty. Such reporting would make datasets more comparable and facilitate meta-analysis.

From an industrial perspective, the strongest value proposition may be the ability to tune properties through the counter-ion rather than redesigning the entire amphiphile. This is conceptually attractive because dodecyl sulphate is inexpensive and well understood. However, the transition from laboratory material to commercial formulation requires a complete cost and performance assessment, including raw-material availability, metal recovery, process safety, storage stability, compatibility with other formulation components and regulatory requirements.

Overall, TMDSs should be positioned as functional interfacial materials rather than conventional surfactant commodities. Their scientific novelty comes from coupling self-assembly with transition-metal chemistry. Their practical value will depend on demonstrating reproducible advantages in a defined application. The next decade could therefore shift the field from isolated synthesis and characterization toward data-rich structure–property maps, predictive modelling and sustainable manufacturing.

CONCLUSION

Transition metal dodecyl sulphates represent a versatile class of amphiphilic inorganic–organic materials in which the C12 dodecyl chain and sulphate headgroup provide interfacial self-assembly while the metal ion controls charge density, hydration, coordination and, in selected cases, redox behaviour. Classical studies established strong metal-dependent effects on CMC and phase equilibria, while detailed structural investigations demonstrated hydrated lamellar phases and metal-dependent thermal properties [1,10,11].

The present literature supports the view that TMDSs can be useful as model systems for studying ion-specific micellization and as building blocks for layered or hybrid materials. Nevertheless, the field remains comparatively underdeveloped for systematic first-row transition-metal series. The most valuable future studies will combine rigorous synthesis and structural characterization with molecular simulation, interfacial measurements, environmental assessment and application-level benchmarking.

In conclusion, the scientific and technological opportunity is not simply to synthesize more metal dodecyl sulphates, but to establish a predictive relationship among metal identity, sulphate association, chain packing, hydration, self-assembly and functional performance. Such a structure–property–application framework can support the rational design of next-generation metallosurfactants and sustainable metal-containing interfaces.

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