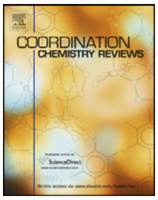
Coordination Chemistry Reviews 253 (2009) 2131–2132

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Preface

Although they had no idea of what an amphiphilic molecule or a micelle was, humans exploited the ability of micelles to include lipophilic molecules in their hydrophobic core since the discovery of soap, which dates back at least to 2800 BC. Surfactant science has developed enormously since then, and particularly in the 20th century, when the detergent industry expanded rapidly and the process of solubilization of hydrophobic molecules in micellar aqueous solutions was rationalized. With the late 60s, micellar chemistry received a strong impulse with the development of the concept that micellar aggregates may be models for biological membranes. Ten years later, attention was amplified by the mounting wave of supramolecular chemistry. A micelle is intrinsically a supermolecule, and it was soon realized that self-assembling a huge number of molecular units in the same supramolecular entity may bring many advantages, e.g. as regards cooperativity and catalysis.

Moreover, inclusion of a molecule in a micelle brings changes with respect to bulk water: solvation is lower, the palisade layer gives an overall excess charge (at least if surfactants are of the ionic type), local concentration rises as the volume in which the molecule is contained is in the nanometric range. These changes may be turned into advantages, if one reasons that the properties of the molecules included consequently vary and may be controlled by subtle variations of micelle's features: acidity and basicity constants change by several orders of magnitude, light absorption and emission is modified, reactions may be promoted or inhibited. In other words, it became clear that micelles are powerful tools, capable of tuning, amplifying, or even generating new molecular properties. It was soon understood also that coordination chemistry may advantageously participate in micellar chemistry: ligand coordination of metal cations and the reactivity of metal complexes is modified by micellar inclusion.

Catalysis promoted by metal coordination in micelles received a strong impulse and is still an important research field, as illustrated and discussed here by Bhattacharya et al., Tecilla et al. and Yu et al. Their papers deal mainly with metallomicelles, i.e. micelles in which the surfactant is a lipophilized metal complex. In metallomicelles the dramatic acceleration of the hydrolysis of activated carboxylate esters, phosphate esters and amides at ambient conditions and near neutral pH is observed. Micelles also bring the advantage that they can be easily modified and their properties tuned by subtle changes of the surfactant structure: Bhattacharya and Yu bring examples of metallomicellar catalysis applied to cycloaddition reactions, hydrogenation and phenolic oxidation in the presence of hydrogen peroxide. On the other hand, reverse micelles (formed by amphiphilic molecules in hydrophobic solvents, and containing an internal water pool) may also change the reactivity and catalyze the reaction of hydrophilic species included in the water pool. Metal complexes, in particular, may be affected by inclusion in reverse micelles, as Crans et al. illustrate in the case of oxovanadate and proton transfer reactions.

From a different perspective, micelles may be considered as a tool for attracting metal cations (e.g. by mere electrostatic interaction, using anionic surfactants) or for sequestrating them from aqueous bulk solutions, when the surfactant is also a ligand or lipophilic ligands are co-micellized with classical surfactants. Hebrant illustrates how this can be exploited for metal ion extraction, emphasizing how both kinetics and thermodynamics may be controlled to address the metal extraction processes with micelles and other microheterogeneous systems, especially when used in combination with ultrafiltration and cloud-point techniques.

Very recently, application of the knowledge and concepts of supramolecular chemistry to the booming area of nanotechnology has injected even more new blood into the use of micelles, e.g. in drug delivery (with polymeric micelles) and in the developments of vectors for contrast agents in imaging techniques. In these cases, the emphasis has been on the nanometric dimensions of micelles and on their ability to act as containers, in water, for several units of the same lipophilic species. Also with this viewpoint, coordination chemistry has brought fresh and creative contributions. Here Morelli et al. illustrate the possibility of using metallomicelles based on Gd^{3+} amphiphilic complexes as the surfactants, which are efficient contrast agents in magnetic resonance imaging. Gohy describes the use of metal complexes for the formation of supramolecular block-copolymer micelles, which may constitute a new strategy in the attainment of micelles for drug delivery, templating and nanofabrication. The controlled inclusion in nanosized micelles of more different molecular species, including metal complexes and fluorophores, promote their interaction and generate multi-molecular devices that cannot exist in bulk water or in larger containers, as Tecilla and Pallavicini et al. describe here. Fluorescent sensors for metal ions, for pH windows and for molecular lipophilicity are obtained by exclusive self-assembly into micellar nanocontainers, in the area of application to sensing, imaging and drug design.

This issue contains reviews covering a large spectrum of the many aspects of the use of metal coordination in micellar chemistry. I would like to express my thanks to all the contributors and especially to Professor Barry Lever for allowing such a stimulating and extensive collection, that provides a solid indication of how metal–ligand interactions can bring advantages, add properties and inject creativity even in a field – surfactant and micelles – that is

0010-8545/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2009.05.010

traditionally thought to belong to physical chemistry area with just some organic chemistry influences.

Piersandro Pallavicini[*]
Dipartimento di Chimica Generale, Università di Pavia, viale Taramelli, 12, 27100 Pavia, Italy

[*] Tel.: +39 0382 987336; fax: +39 0382 528544.
E-mail address: piersandro.pallavicini@unipv.it

15 May 2009