



Binding of divalent and higher valent metal ions to surfactants and polyelectrolytes



Beverly Stewart^a, Ksenija Kogej^b, M. Luísa Ramos^a, Artur J.M. Valente^a, Hugh D. Burrows^{a,*}

^a CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

^b Department of Chemistry and Biochemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 11 October 2017

Received in revised form 23 October 2017

Accepted 24 October 2017

Available online 31 October 2017

Keywords:

Metal-ion
Polyelectrolyte
Surfactant
Binding
Complexes
Ligand

ABSTRACT

Interactions between ionic organic systems, such as surfactants or polyelectrolytes, and divalent or higher valent metal ions have been studied extensively for many years, but still present challenges in understanding the type and nature of interactions involved and also the driving forces behind metal ion binding.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The behaviour of ionic surfactants and polyelectrolytes in solution depends on how the corresponding counter ions are bound. A variety of effects are involved in ion binding in these systems, including electrostatic interactions, and solvation. Theoretical treatments of the binding by polyelectrolytes of monovalent ions were developed independently over half a century ago by Oosawa [1], and Manning [2]. However, these assume predominantly nonspecific and nondirectional electrostatic interactions. We will discuss an important case where other effects, such as coordination behaviour of divalent and higher valent metal ions binding with anionic surfactants or polyelectrolytes, become significant. These are of importance in a wide variety of areas, including detergency [3], thickeners [4], froth floatation for metal ion recovery [5], and materials science. We will concentrate mainly on materials applications and readers are referred to two reviews which discuss some of the other applications, one on metal ion binding and coordination by long chain carboxylates, [6] and the other on interactions of trivalent ions with surfactants and polyelectrolytes [7]. These interactions are also of considerable importance in metal ion binding to biological systems such as proteins and nucleic acids [8].

The development of functional materials for applications in drug delivery [9], catalysis [10], sensing [11], and polymer nanocomposites [12], is also often the result of specific interactions taking place between such inorganic and organic species. Many interactions occur during

the formation of self-assembled systems, including hydrophilic-hydrophobic effects, electrostatic interactions, π - π stacking and van der Waals forces [13]. Additionally metals can coordinate with organic species; these bonds display strong and directional interactions [14,15]. The introduction of such metal-ligand bonds to organic systems can create new and interesting properties such as effects on luminescence [16] and thermochromism [17].

Another important feature the presence of metal ions can impart within ionic or coordinating organic systems is metal induced self-assembly. Examples of self-assembled supramolecules which have been studied in recent years are helicates, dendrimers and coordination polymers. Work carried out by Fraser in 1997 described the formation of metal centred star shaped polyoxazolines where Fe(II) and Ru(II) tris-bipyridine derivatives served as multifunctional initiators in metal-centred macromolecular structures [18] and in 2000 they demonstrated atom transfer radical polymerisation of poly(methyl methacrylates) by NiBr₂(PR₃)₂ complexes [19]. These studies led to the formation of systems where ligands are coordinated to metal centres with outward radial growth of polymer chains. In 2001, Schubert presented a simple, high yield pathway to a new class of α,ω -difunctionalised metal complexing polymers with terpyridine as metal binding units leading to the formation of extended metallo-supramolecular polymers [20].

However, the presence of metal ions can also be used to drive assembly of organic species in colloidal systems and as a result the interactions of metal ions with organic species in solution are of great relevance in a very wide range of chemical and biological applications [21].

The formation of supramolecular polymeric structures which are produced through coordination or non-covalent interactions

* Corresponding author.

E-mail address: burrows@ci.uc.pt (H.D. Burrows).

demonstrates significant progress in chemical, biological and materials science. The appeal of these systems is that they not only have the inherent properties of polymers, but they also possess the potential to have new and novel characteristics.

The most important aspect of molecular self-assembly is the seemingly low activation energy for the coordination or non-covalent interactions, which in many cases have a strong entropic contribution. This, in turn, results in highly dynamic systems which have the potential to possess novel properties. This self-assembly approach allows for the creation of systems with unique stimulus responsive behaviour [22,23].

Additionally, the wealth of metal-ions available, comprising almost half of the periodic table, provides a wide and flexible range of possibilities when it comes to the design of coordinating polymers around a metal-ion. They may also possess various oxidation states, extending still further their potential for producing novel structures. There are many different properties of metal ions which can be utilized, for example charge, colour, redox behaviour and catalysis, and they can be incorporated into polymer networks, leading to the development of multi-functional materials [24]. The appropriate combination of ligands and metal ions can be used to engineer the binding strength, for instance, the binding strength of polydentate ligands is higher than that of monovalent ligands.

Many factors influence the thermodynamic and kinetic stability of metal ions for example those with second and third row transition metal ions such as palladium and ruthenium display kinetic stability whereas those with first row transition metals may display kinetic lability and can dissociate upon changes in the surrounding chemical and physical environments such as pH, temperature and solvent [25–28].

Many studies have been performed on systems where the focus has been the dynamic behaviour of coordination polymers in organic media. This however imparts a limitation to their applicability as many systems for example biological systems require self-assembly to take place in water.

In this review we aim to discuss recent advances in divalent and higher valence metal ions and, in particular, the role that they play in the formation of self-assembled system comprising polymers, polyelectrolytes and surfactants.

2. Some thermodynamic and kinetic considerations

Both kinetic and thermodynamic factors are involved in the binding of oppositely charged ions in solution. Metal ions never exist “free” in solution, but are always surrounded by a primary coordination sphere [29], which in turn, may be surrounded by second and outer spheres of solvent molecules. Generally, binding involves exchange of ligands (such as water) in the primary coordination sphere by anionic groups of the surfactant or polyelectrolyte. With monovalent ions, this process is very fast, and these metal ions are considered “labile”. Binding in these systems is commonly treated largely as an electrostatic interaction [30], considering water as dielectric continuum [31]. With polyelectrolytes, this is normally discussed in terms of the Manning condensation theory [2]. Quantitative studies on ion binding by poly(styrenesulfonate) show that the cation charge plays a dominant role in the interaction, in agreement with the importance of electrostatic interactions [32]. However, even with monovalent ions there are indications that loss of water molecules plays a role in the binding [33]. With higher valent metal ions interacting with surfactants and polyelectrolytes there is clear evidence for loss of coordination water upon binding [34]. With divalent and higher valent ions, a variety of factors have been shown to be involved in binding. However, the binding of both Ca(II) [35] and Al(III) [34] with polyelectrolytes is endothermic, meaning that it is entropy controlled. The entropy increase results, in part, from exchange of monovalent ions by higher valent ions. However, there is good evidence that changes in cation hydration on binding are also involved, notably from the contrasting behaviour on interaction of the

kinetically inert chromium(III) ion with that of the labile aluminium(III) [36] with surfactants [37] and polyelectrolytes [34].

Interactions of metal ions with ligands can be treated with Pearson's Hard-Soft Acid-Base (HSAB) concept [38]. Divalent and higher valent metal ions frequently behave, like the proton, as hard acids, such that their tendency to bind to surfactants or polyelectrolytes frequently depends on the ligand acid strength. This can be seen in the relatively stronger binding of trivalent ions with polyelectrolytes containing carboxylate groups than those with sulfates or sulfonates [7].

In the following sections we will apply some of these ideas to recent examples of interaction of high valent metal ions with polymers and surfactants, with particular relevance to the use of colloids in the development of advanced materials.

3. Hierarchical assembly of polydiacetylene microtube biosensors mediated by divalent metal ions

Jiang and Jelinek describe polydiacetylenes (PDAs) which comprise a family of conjugated amphiphilic polymers that possess unique colour and fluorescent properties [39]. The paper discusses the hierarchical assembly of micrometre sized tubes comprised of melamine-substituted PDA derivative. The transformations from nano- to microscale amphiphilic building blocks were induced by the addition of divalent metal ions.

The colour and fluorescence transformations associated with topo-polymerisation of the diacetylene monomers provide promising chemo- and biosensing properties [40]. PDA systems are known to display spontaneous association of monomers into well-defined structures through non-covalent interactions and form complex supramolecular nanostructures. As a result there is considerable interest in obtaining and studying self-assembled nanostructures derived from diacetylene [41].

Functionalisation of diacetylene monomers has proven to be a valuable tool for controlling self-assembly; varied architectures such as nanorods, nanowires and helical nanoribbons have been created through varying the head group substituent of diacetylene [42]. It is supposed that hydrogen bonding, hydrophobic interactions and π - π stacking constitute the primary driving force for self-assembly. The authors demonstrate that a mixture of carboxylic acid displaying diacetylene monomer 10,12-tricosadiynoic acid (TrCDA) and a diacetylene monomer in which the head group is substituted with melamine (*N*-[2-(4,6-diamino-1,3,5-triazin-2-ylamino)ethyl]tricosadiynamide) (TMN) forms long nanotubes upon addition of Zn^{2+} ions and slow evaporation. This formation is based upon a hierarchical assembly process in which the vesicles that are produced initially assemble into elongated nanotubes which then undergo cross-linking onto microscale tubular morphologies. These microtubes also exhibit highly sensitive fluorescence/colour responses in bacterial solutions which makes them a promising avenue to possible sensing applications.

It was found that PDA microtubes were formed upon a slow evaporation of an aqueous preparation of the two diacetylene mixture at a ratio of 9:1 (TrCDA:TMN) and exposed to room lighting. The addition of Zn^{2+} ions one day after incubation played a critical role in the formation of nanostructures as the PDA microtubes underwent slow self-assembly and appeared to the naked eye as bundles of visible fibres within around 30 days. Scanning electron microscopy (SEM) revealed the formation of abundant and extremely long microtubes which exhibit a thickness of 3–5 μm and several millimetres long. Optical microscopy and corresponding fluorescence microscopy show the tubular organisation of the tubes and confirm that they are made up of PDAs.

To clarify the kinetic and structural details of microtube formation, the diacetylene solution was examined by SEM at different points during incubation of the two monomers, Fig. 1. This data underlined the hierarchical assembly of the microtubes. Upon dissolving the monomers, nanosized vesicular particles were formed. Within six days of addition of Zn^{2+} thin nanofibres were observed which then grew in length and

Download English Version:

<https://daneshyari.com/en/article/6984674>

Download Persian Version:

<https://daneshyari.com/article/6984674>

[Daneshyari.com](https://daneshyari.com)