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Towards functional nanostructures: Ionic self-assembly of polyoxometalates and surfactants

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Abstract

Major recent advances in the field of POM-surfactant ISA complexes are the extension of the studies into both thermo- and lyotropic phase behaviour, and the use of the vesicle motif for the production of novel hybrid vesicle structures. The use of metal-coordinating functional surfactants has led to the expression of synergistic functionality in POM-based materials.

Keywords: Ionic self-assembly; ISA; POMs; Surfactants; Nanostructured materials; Functional materials

1. Introduction

The production of nanostructures, nanoparticles and, generally, nanostructured materials has become part of everyday scientific life, whether in the research or undergraduate laboratory, and published as a matter of course in most journals related to this fast-growing field of research. This would therefore imply and very strongly suggest that not only is the synthesis of materials with features in the nanometer range (i.e. nanostructured materials) becoming less challenging, but the emphasis in the laboratory, and finally also in the published literature, must shift to the reporting of functionality in (nano-structured) materials. Even more so, materials possessing addressable or switchable functionality seem to be where the real challenge is lying — not only for basic research, but for the development of applications where addressability is of crucial importance.

In this review we wish to present an overview of the publications focusing on the preparation of nanostructured materials using noncovalent interactions by applying the principles of ionic self-assembly [1••]. More specifically, the scope of the review will be narrowed to only assess the use of polyoxometalate-surfactant systems for the production of hybrid nanostructured bulk materials with function, as published mainly since 2004. This would therefore exclude any work done using the layer-by-layer (LBL) technique, or any investigations of Langmuir–Blodgett films for the preparation of polyoxometalate (POM)-based materials. The readers are referred to other reviews [2,3] that cover these areas.

*I*onic *s*elf-*a*ssembly (ISA) is a noncovalent synthesis strategy that makes use of the electrostatic interactions between charged surfactants and oppositely charged oligo- or polyelectrolytes. Owing to the incompatibility of the surfactant alkyl tails and the oligo- or polyelectrolytes on the one hand, and the ionic connection of these incompatible parts on the other hand, phase separation is achieved on a molecular scale, leading to the formation of nanostructured materials. This is analogous to the situation found in block copolymers and H-bonded amphiphile-polymer systems [4••]. One further aspect that drives the formation of new materials, for the general case of ISA materials, is the cooperative nature of the binding of the surfactants to the oppositely charged tectons (or building blocks). This concept, initially developed for helix-coil transitions, was expanded for the case of small ions binding to polyions (and

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then also applied to polyelectrolyte-surfactant systems) [5–7]. This cooperative process (also shown to be the case for low molecular weight oligoelectrolytes [8•]) causes a fast and high degree of binding of the surfactants to the oppositely charged binding sites, ensuring that new materials with new properties are formed. Factors that influence the binding and binding parameters include the concentration of the surfactant (i.e., ensuring that the critical aggregation concentration is exceeded), the nature of both the surfactants (size and hydrophobicity) and the existing counterions, and the energetic gain experienced from their release into the surrounding solvent medium.

As the ISA process consists of the binding of two moieties, careful choice of these molecular tectons enables the inclusion of a variety of different functionalities and properties into the resulting nanostructured material [9–11]. Other than polyoxometalates (POMs), other inorganic tectons have also been used in the ISA approach [12]. As it is possible to tune the phase properties of such ISA materials through variation of the length, number and degree of branching of the surfactant alkyl tails, both thermotropic [9] and lyotropic [13] liquid–crystalline materials can be prepared in a facile way. As will be shown later, this new avenue has recently also been opened for POM-surfactant systems. A broad overview of the field of ionic liquid crystals (LC) can be found in a recent review by Binnemans [14••].

Several recent extensive reviews [15••,16••] and books [17] exist and focus solely on the topic of POMs — we will not try and duplicate these works, but only strive to highlight a few issues and characteristics that will be relevant to this discussion. POMs are a fascinating class of inorganic mixed (transition) metal oxide supramolecular materials that exhibit a large variety of structural, compositional and chemical types, and can be organised into three main classes (after Cronin [15••]): a) heteropolyanions (metal oxide clusters containing hetero anions and atoms, the most well-known class, includes the Keggin and Wells–Dawson types), b) isopolyanions (metal-oxide frameworks, no heteroatoms or -anions), c) Mo-blue and Mo-brown reduced POM clusters (including high nuclearity Mo_{154} clusters).

These large nanostructures are now widely hailed for their use in catalysis, medical applications and photochemistry. For in-depth treatment of the topic of POMs the readers are referred to the above-mentioned reviews and books. Other studies [18] focus on the covalent modifications of POMS and fall outside the scope of this review paper.

The following points seemed worthy to be highlighted in relation to the use of POMs in functional nanostructured materials.

Properties which are especially attractive for their use in (soft) nanostructured functional materials:

- Diverse chemical compositions and possibilities to alter the composition, especially with the inclusion of transition metals
- Defined molecular size and shape
- Stability (thermal, chemical)
- Redox properties (and diverse electronic states of existence) and pH sensitivity
- Photo activity
- Varied possibilities for surface modifications (especially noncovalent) exist

In a critical assessment of the issues to be addressed for investigations concerning POMs and catalysis, Hill [16••] has highlighted several points, several of which the authors feel are of similar importance for the future use and development of POM-surfactant-based materials for the production of novel nanostructured materials with function: a) the role and nature of the counterion (in this case surfactants); b) presence of multiple reactive forms, rearrangements and isomerisations of the POMS especially in the hydrophobic environment in POM-surfactant materials, and c) insight into the electronic structures of POMs, and the ability to control these states more carefully for applications.

Keeping these highlighted issues in mind, we turn our discussion to the surfactants, the other component or tecton utilised in these hybrid materials. Surfactants are the prototypical examples of self-assembly and rich phase behaviour in soft matter [19,20]. It seems, however, that the possibilities that are present for tuning phase behaviour, phase structure and even function by molecular design of the surfactant headgroup, the number, architecture and chemical nature of the hydrophobic tails, and inclusion of functional groups, have only been explored on a very limited basis. Very closely connected to this is fact that liquid–crystalline (LC) phase behaviour (lyotropic phase behaviour was only found relatively recently for the first time) has not been actively investigated for POM-surfactant systems. As liquid crystallinity is controlled and induced by the size of the alkyl volume fraction surrounding the POM tecton [21••], the lack of focus is not surprising seen in the light of the absence of molecular design of the surfactant counterions.

Finally, for the case of POM-surfactant materials: reviews [22,23•] in recent years have focussed mainly on structure, and structure elucidation of very interesting materials, with functionality given only minor attention. In this review we therefore endeavour to focus on the opportunities that exist for future studies for the development of materials with real function, as this seems to never be fully addressed in many of the published studies, but only hinted at.

2. Discussion

As structure formation and elucidation still forms a major part of the published work in recent years, part of the discussion will focus on this topic. However, function (and possibilities for applications) and novel approaches through use of different surfactants will also be discussed.

2.1. Formation and structure

2.1.1. General remarks on cooperativity and the formation of well-defined (stoichiometric) complexes

A very good empirical description was provided by Jia et al. of the preparation of a Mo154-tetradecyltrimethylammonium complex from aqueous solution [24]. The authors provided a full and detailed description of the phase behaviour of this system