



## Amphiphilic hybrids containing inorganic constituent: More than soap



Sebastian Polarz <sup>\*</sup>, James Arthur Odendal, Stefanie Hermann, Alexander Klaimer

Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany

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### ABSTRACT

Amphiphiles and surfactants are indispensable compounds in industry, scientific research and everyday life, such as emulsification agents, detergents, etc. The vast majority of currently used amphiphiles are organic in nature, and are composed of two molecular parts joined together, one hydrophilic and one hydrophobic. The current article highlights some of the recent developments in the emerging field of hybrid amphiphiles, focusing on systems with at least one inorganic constituent. Different classes of amphiphiles can be defined, depending on if the inorganic entity is molecular or has particle character, and depending on the strength of interaction between the inorganic and organic phase. It is seen that in addition to typical amphiphilic properties, most importantly the formation of self-assembled structures like micelles or lyotropic liquid crystals, the hybrid amphiphiles exhibit additional, functional features like special magnetic or catalytic properties. Ultimately, systemic features can be observed, leading to the emergence of new properties which none of the constituents of hybrid amphiphile could have on its own.

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### 1. Introduction and background

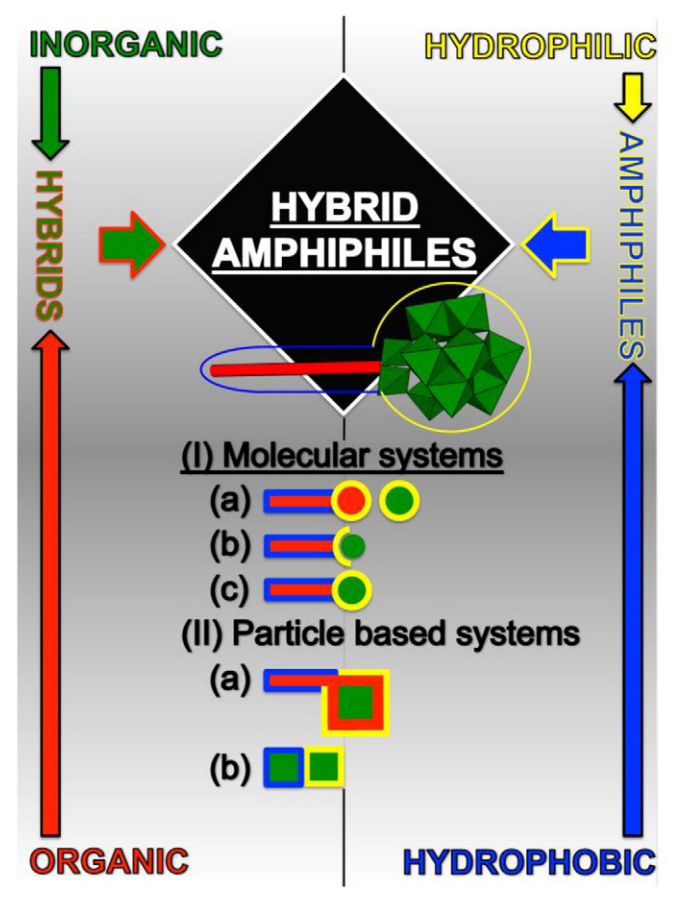
The persistent, general question in materials science is, how novel materials with unique and ultimately unprecedented properties can be found. A strategy, proven to be quite successful, is to combine seemingly opposite entities, hoping for systemic features. A very superficial description of systemic features is that the whole is more than the sum of its parts, found for instance in swarms of certain ensembles e.g. particles [1]. A very obvious choice for joining opposites is to combine organic and inorganic constituents, and this has resulted in the vast field of ‘organic–inorganic hybrids’ with numerous examples of synergistic properties [2]. Another prominent case for a chemical antagonism joined together in one system is represented by surfactants, the latter term representing an abbreviation for surface active agents.

Surfactants are defined as molecular compounds containing one water-compatible, hydrophilic part, the so-called head group, and a water-incompatible, hydrophobic part covalently linked to each other. The hydrophobic unit of a classical surfactant is typically a simple alkyl-chain, whereas the hydrophilic part can be cationic (e.g. ammonium), anionic (e.g. carboxylic acid, sulfonic acids) or neutral (e.g. oligoethylene glycol) in nature. The resulting amphiphilic nature of surfactants leads to a range of fascinating and valuable properties for applications in industry and nanotechnology [3], which are connected to their ability to occupy interfaces and with that lowering surface energy. For instance, for ternary systems (water, organic solvent, surfactant) they are known to effectively stabilize different kinds of emulsions. A fascinating property of surfactants

and amphiphiles is their ability for self-organization above a certain threshold concentration, the so-called cmc (critical micelle concentration). The observed structures, micelles, liquid crystals and inverse phases, are also a function of the so-called packing parameter introduced by Israelachvili et al. more than 30 years ago [4]. In the meantime more advanced theories for the self-assembly of surfactants and other amphiphiles such as amphiphilic block-copolymers have been developed [5], and they consider the modes of intermolecular interaction to explain the formation of the structures. Therefore, one can eventually expect new and exciting self-assembled structures, if additional interaction modes come into play.

The latter is only one argument, why amphiphiles containing inorganic parts are thrilling, e.g. thinking of magnetic interactions due to paramagnetic species. There are many more reasons, why it could be highly tempting to combine amphiphilic design and the concept of organic–inorganic hybrids (see also Scheme 1). The incorporation of metal cations to the head group of an amphiphile i.e. metallosurfactant [6<sup>\*\*</sup>], now gives interfacial surfactant systems a means to link the associated metal ion functionality to its amphiphilic structure. Inorganic matter provides numerous features (magnetism, redox variety, catalytic properties, higher electronic contrast, etc.), which are hard to realize for organics, but which would be highly desirable, if e.g. a surfactant/amphiphile has them [7<sup>\*\*</sup>]. Thus, surfactants with inorganic constituents (I-SURFs) can be seen as belonging to the larger class of so-called metallomesogens [8]. The term metallomesogens was introduced by Bruce et al. for molecular species showing the ability to form liquid crystalline (LC) phases comprising coordination complexes as building blocks [9]. In most of this early work one has concentrated on systems with thermotropic LC-characteristics, for instance rod-like or plate-like

<sup>\*</sup> Corresponding author. Tel.: +49 7531 884415; fax: +49 7531884406.  
E-mail address: [sebastian.polarz@uni-konstanz.de](mailto:sebastian.polarz@uni-konstanz.de) (S. Polarz).



**Scheme 1.** Classification and genesis of the emerging field 'hybrid surfactants and amphiphiles'.

metal compounds [10]. In the meantime, also some metal-containing polymers and even inorganic particles forming LC phases or some supracrystals can be seen as belonging to metallomesogens [11].

However, this area still stands at the beginning and will be highlighted in the current article. In this sense, it should be noted that the aim of our manuscript is not to give a comprehensive overview here, but we have selected some of the most important, recent developments in this emerging research field dating back to the last decade. For further discussion, it makes sense to differentiate between two classes of amphiphilic hybrids (see scheme 1), dependent on, if the system has pure molecular character (class I), or, if constituents with nanoparticle characteristics are involved (class II). Three scenarios can be discussed for class I. The simplest strategy is to start from a conventional surfactant system (Scheme 1; Ia) and just add a metal component to it. The metal component is at most weakly bound to the surfactant. Typically, the inorganic metallic species is the counter-ion of the surfactant head group (see also Section 2.1 of this paper). In alternative (Ic) the metal-containing unit is the hydrophilic head-group covalently linked to the hydrophobic tail. Thus, it has become an integral part of the surfactant (see Section 2.3). The situation in scenario (Ib) is somehow in between, and is best represented by a metal cation coordinated by a ligand linked to a hydrophobic chain (see Section 2.2). Hybrid amphiphilic systems can also be achieved when inorganic nanoparticles are combined with suitable molecular species as shown in Scheme 1/IIa. Another interesting case is realized, when two different nanoparticles with different solvent compatibilities can be joined together like shown in Scheme 1/IIb, or as a result form particles with Janus-type characteristics [12]. The latter two topics will be highlighted in Section 3 of this article. It should also be noted that the assignments of the cases discussed in the

following to the defined classes are not absolutely strict, but the junctions from one area to the other are rather smooth.

## 2. Molecular hybrid amphiphiles

### 2.1. Surfactants with weakly bound metallic species

It is obvious that anionic surfactants with metal cations as counterions represent the imaginable simplest I-SURF system (see Scheme 1) [13]. The first examples for I-SURFs (type-Ia) were presented by Mirnaya et al. back in 1989, when the LC-formation of alkali metal alkanoate ( $M(OOCC_nH_{2n+1})$ ) ionic melts was discovered [14]. An interesting case was reported by Weber about the influence of self-organization/packing on spin-transition on Fe(II) I-SURFs [15]. However, also cationic or neutral surfactants in combination with metal species deserve attention. The interaction of the cationic cetyltrimethylammonium surfactant with anionic, silicate species has led to the development of ordered mesoporous materials via the so-called synergistic co-assembly mechanism [16]. The hybrid surfactant/inorganic phase forms a lyotropic liquid crystal, which acts as a template for the generation of pores. Mesoporous materials have then defined an entirely new field by themselves.

Another interesting area is the combination of anionic metal species like palladates, aluminates etc. with cationic surfactants ions [17]. These form molecular systems that are very similar to surfactants with large, cationic heads. A nice demonstration of how the properties of the amphiphilic systems are enriched by inorganic constituents, comes from the area of ionic liquids (ILs) with metal-containing counterions [18]. Particular impressive examples have been published, when a magnetic counter-ion was present [19]. For example, Eastoe showed in a nice paper in 2012 how magnetic ILs could be used to establish responsive surface properties [20]. Also other, less common counterions like ferrocenyl anions can be used [21]. Some spectacular results, which deserve special attention, could be obtained by using the so-called polyoxometalates (POMs) as negative counter anions for cationic ammonium surfactants [22].

POMs consist of multinuclear metal oxide building blocks  $[MO_x]$  and are widely known for their interesting properties in catalysis and magnetism [23]. Because polyoxometalates as a class includes thousands of specific compounds, it is beyond the scope of the current paper to give a comprehensive overview of the POM field [23a]. POM-SURF hybrid systems represent excellent examples for so-called surfactant-encapsulated clusters (SECs). Kurth and co-workers created SECs by replacing the counter cations of anionic molybdovanadate POMs by long alkyl-chained cationic ammonium surfactants [22b,24]. A close packing of the alkyl chains was observed, and it was concluded that there is a compact shell around the POM. The surfactant shell improves the stability of the embedded POM and its solubility in nonpolar, aprotic organic solvents. Our group presented a unique system [22e], which was some years later "adapted" by Cronin and coworkers [25]. Giant, donut-shaped POMs were treated with a cationic, double-tailed surfactant. It was found that the surfactant binds exclusively on the periphery of the inorganic POM cluster. A novel species forms with special, quadrupolar amphiphilic properties (hydrophilic, hard, inorganic core and hydrophobic, soft, organic shell). Self-organization into columnar lyotropic liquid crystal (LLC) phases was reported. Noro et al. used a very similar system to demonstrate gas and vapor adsorption and catalytic properties in addition to the self-organization properties [25]. In recent time surfactant complexes with smaller POM-cores like the Keggin structure have moved into the focus of research. Zhang reported in 2013 the reversible redox-controlled switching of the morphology of a SEC containing the  $[Mo_6O_{19}]^{2-}$  (see Fig. 1) [26]. This example gives an idea of the complex self-assembly characteristics and opens the door for manifold adjusting for tailor made liquid crystal phases, as not only the encapsulating surfactant but also the core can have an impact on self-assembly behavior. Wu and Wang contributed extensively on this topic with their

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