

Self-Assembly of Organic–Inorganic Hybrid Amphiphilic Surfactants with Large Polyoxometalates as Polar Head Groups

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Amphiphilic surfactants are important in many fields due to their ability to self-assemble in selective solvents. Such surfactant molecules usually have a polar headgroup and one (or more) hydrophobic tail. Recently, various nanoscaled hydrophobic units such as fullerenes¹ and polyhedral oligomeric silsesquioxanes² have been used to form hybrid amphiphiles in an attempt to engineer surfactant molecules with new functionalities and physical properties. To build on this we have designed new types of inorganic–organic hybrids by tethering organic ligands to the surface of a large molecular metal-oxide cluster, e.g., polyoxometalate (POM)³ clusters, via covalent modification of the metal oxide cage.^{4,5} These hybrids are more stable than those complexes formed by electrostatic interactions between cationic surfactants and POM anions⁶ and contain hydrophilic POM clusters and long hydrophobic chains. Therefore these molecules can be treated as surfactants, yet with incorporation of polyoxometalate polar head groups, and as such these new hybrid materials allow the development of surfactant systems engineered with properties unique to the POM group, e.g., redox, catalytic, bistability, photochemical, and magnetic properties.^{3,4} Also, to the best of our knowledge, the self-assembly of inorganic–organic hybrids with large hydrophilic inorganic polar head groups in solution has never been reported.⁷

Recently, a POM-containing hybrid $[n\text{-Bu}_4\text{N}]_5[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{-CNHCO}-(\text{CH}_2)_{14}\text{CH}_3\}_2]$ (Mn-Anderson-C₁₆) (Figure 1) was synthesized^{5b} where the hydrophilic $\{\text{MnMo}_6\text{O}_{24}\}$ cluster has a plate-like structure with dimensions of $\sim 0.9 \times 0.9 \times 0.3 \text{ nm}^3$. One hydrophobic alkyl chain (C₁₅H₃₁) is covalently capped onto each side of $\{\text{MnMo}_6\text{O}_{24}\}$ via amide bonds, providing an amphiphilic property to the resulting hybrid. Compared to conventional surfactants, the hybrid “surfactant” has a much larger inorganic polar headgroup.

The Mn-Anderson-C₁₆ hybrid is insoluble in water but quite soluble in acetonitrile (MeCN) and MeCN/water mixed solvents to form stable and homogeneous solutions ($\sim 0.1 \text{ mg/mL}$). The formation of a supramolecular structure is observed in the mixed solvents of MeCN/water containing 35–60 v% MeCN, as studied by dynamic and static light scattering (DLS and SLS) techniques. As shown in Figure 2a, the scattered intensity increases with time in a Mn-Anderson-C₁₆ MeCN/water solution containing 40 v% MeCN. The initial scattered intensity is very low, close to the value for pure solvents, suggesting that there is no large structure formed. The scattered intensity continuously but slowly increases with time, indicating the continuous formation of supramolecular structures in solution.

DLS studies on the same solution show that large assemblies appear after several days (Figure 2b). The average hydrodynamic radius (R_h) of the assemblies obtained from the CONTIN analysis⁸

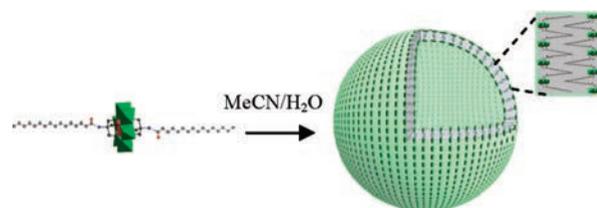


Figure 1. Schematic representatives of the Mn-Anderson-C₁₆ surfactant and their vesicle formation in MeCN/water mixed solvent. The inorganic Mn-Anderson structure is presented in a polyhedral model, and the organic part is presented in ball and stick model (Mn, pink; Mo–O polyhedral, green; C, gray; N, blue; and O, red).

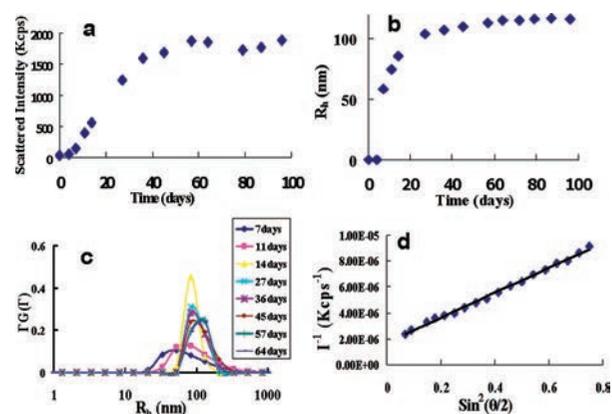


Figure 2. Change of scattered intensity (a) and hydrodynamic radii (R_h) (b) of a 0.1 mg/mL Mn-Anderson-C₁₆/MeCN/water solution containing 40 v% MeCN with time. (c) R_h distributions (from CONTIN analysis) of the assemblies at different times during the vesicle formation. (d) Zimm plot from SLS study on the same solution after reaching equilibrium (64 days).

at the scattering angle of 90° on day 7 is $\sim 58.5 \pm 1.8 \text{ nm}$ with a broad size distribution (Figure 2c). The size of the assemblies continues to grow during the following weeks, and the size distribution of the assemblies becomes narrower (Figure 2c). After 57 days, the assemblies stop growing at $R_h \sim 115 \text{ nm}$, indicating that the assemblies have reached equilibrium. The total scattered intensity from the solution also gradually stabilizes. The final scattered intensity ($\sim 1850 \text{ Kcps}$) is still not very high considering the large size of the assemblies and the initial concentration of the solute. This result indicates that the amount of assemblies in solution is not dominant and there is still a large amount ($> 80\%$) of discrete hybrid molecules in solution. Similar conclusions can also be drawn from TEM measurements as only a limited amount of large assemblies can be observed (see below).

The R_h value of the large assemblies almost has no angular dependence, suggesting that the assemblies are mostly spherical. After reaching equilibrium in solution, extrapolating the R_h value

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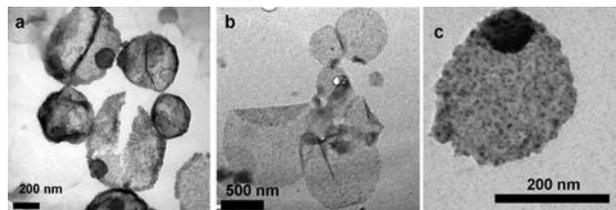


Figure 3. Typical TEM images of vesicular structure formed by Mn-Anderson- C_{16} in MeCN/water solution. Large burst vesicles are formed in 50 v% MeCN solution 2 (a) and 5 months (b) after sample preparation. Intermediate structures (c) during fusion and fission of vesicles were also observed in the same solution.

to zero scattering angle results in $R_{h,0} = 115 \pm 3$ nm. The radius of gyration (R_g) of the assemblies obtained from SLS measurement is 122 ± 6 nm (Figure 2d). For a solid spherical object, the ratio of R_g to R_h is 0.77. The relation of $R_g/R_h \sim 1.0$ suggests a hollow spherical shell with all mass distributed on its surface. Therefore, the assemblies formed by Mn-Anderson- C_{16} hybrids are likely to have a spherical vesicular structure.

TEM studies provide strong evidence that vesicles are formed in Mn-Anderson- C_{16} solution. As shown in Figure 3, the large particles have radii ~ 50 – 500 nm, and the relatively low electron density in bright-field images indicates their hollow nature. The small dark spots on the vesicle surface are due to POM clusters with higher electron density. The hollow shells likely have a typical bilayer structure with the hydrophilic Mn-Anderson POM facing outside and long hydrophobic alkyl chains staying inside to form the solvent-phobic layer. This is reasonable since the MeCN/water mixture is a good solvent for the POMs but a poor solvent for the alkyl chains. That is, the hybrids indeed demonstrate the nature of an amphiphilic surfactant. Intermediate structures (Figure 3c), which show that smaller vesicles (radii ~ 50 nm) are fused into the membrane of larger vesicles (radii ~ 200 nm), were observed. The reversible fusion and fission of vesicular structures are common but are seldom obtained for small surfactants because the fusion and fission of vesicles proceed simultaneously in equilibrated solutions.⁹ Here the intermediate structure seems to be trapped during the drying process of TEM sample preparation, revealing an unusually slow process toward equilibrium between the reversible process of fusion and fission.

Mn-Anderson- C_{16} surfactants in MeCN/water mixed solvents containing different amounts of MeCN (35–60 v%) show similar self-assembly behavior to that in 40 v% MeCN. The average R_h of the vesicles ranges from 50 to 120 nm. Increasing temperature accelerates the self-assembly process but has no obvious effect on the vesicle size. Vesicle formation is usually fast, but some exceptions exist. For example, the vesicle formation of a lipid surfactant 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine is complete within 1 week.¹⁰ The vesicle formation process of the current surfactant is indeed unusually slow.

We expect that the driving force for the vesicle formation in Mn-Anderson- C_{16} /MeCN/water systems is the solvent-phobic interaction, similar to conventional surfactants. For a lipid surfactant dipalmitoylphosphatidylcholine (DPPC) which possesses the same double alkyl chains as Mn-Anderson- C_{16} , smaller vesicles (the minimal radius ~ 10 nm) form in aqueous solution.¹¹ Compared to lipid molecules, Mn-Anderson- C_{16} has a much larger polar head-group, which can affect the packing of solvent-phobic alkyl tails on the vesicle surface. The Anderson cluster has a stiff plate structure, and one tail sticks out from each side of the plates. In order to form vesicular structure, the two long tails have to bend

into the solvent-phobic layer (Figure 1). Therefore, a high bending energy is needed, which favors a small curvature, i.e., large vesicles. Also, the high bending energy might be responsible for the fact that only a small fraction of hybrids self-assemble in solution. The vesicle formation of Mn-Anderson- C_{16} hybrids is completely different from the formation of vesicle-like blackberry structures by fully hydrophilic POM macroions, such as $\{Mo_{72}Fe_{30}\}$ ¹² and $\{Cu_{20}P_8W_{48}\}$ ¹³ as the driving forces of the latter case are not hydrophobic interactions or van der Waals forces, but the counterion-mediated effect and hydrogen bonds.

Vesicle formation was also observed in the water/MeCN solutions of $[n-Bu_4N]_3[MnMo_6O_{18}\{(OCH_2)_2CNHCO-(CH_2)_4CH_3\}_2]$ (Mn-Anderson- C_6 , see Supporting Information). The Mn-Anderson- C_6 hybrid has much shorter alkyl chains. It takes 1–2 months to reach equilibrium under light scattering studies, and vesicles with the radii 50–150 nm are also formed in solutions containing 35–60 v% MeCN. Compared with Mn-Anderson- C_{16} , fewer Mn-Anderson- C_6 hybrids form vesicles in the same type of solvent, due to their higher solubility and the shorter alkyl chains which makes the bending of alkyl chains more difficult. This result indicates that the vesicle formation is a quite general behavior for the new types of surfactants with large inorganic polar head groups.

In summary, we report the self-assembly of an unprecedented novel amphiphilic surfactant type with large polyoxometalate clusters being their polar head groups. The amphiphilic hybrid molecules can slowly assemble into membrane-like vesicles in MeCN/water mixed solvents. Due to the geometry of the surfactant, the two alkyl chains have to bend significantly in order to be incorporated into the solvent-phobic layer of the vesicles. This makes the vesicle formation more difficult compared to some conventional surfactants. Furthermore, the large and charged POM polar heads play a role in controlling the vesicle size.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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