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 fullerenes and polyhedral oligomeric silsesquixoxanes 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) clusters, via covalent modification of the metal oxide cage. These hybrids are more stable than those complexes formed by electrostatic interactions between cationic surfactants and POM anions 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. 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.

Recently, a POM-containing hybrid[n-Bu4N][MnMo6O18(OCH2)3-CNHO- (CH2)14CH3]2- (Mn-Anderson-C16) (Figure 1) was synthesized where the hydrophilic [MnMo6O24] cluster has a plate-like structure with dimensions of ~0.9 × 0.9 × 0.3 nm2. One hydrophobic alkyl chain (C15H31) is covalently capped onto each head group 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 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 (~0.1 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 (Rh) of the assemblies obtained from the CONTIN analysis.

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 (Rh) of a 0.1 mg/mL Mn-Anderson-C16/MeCN/water solution containing 40 v% MeCN with time. (c) Rh 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 ~58.5 ± 1.8 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 Rh ~115 nm, indicating that the assemblies have reached equilibrium. The total scattered intensity from the solution also gradually stabilizes. The final scattered intensity (~1850 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 Rh value of the large assemblies almost has no angular dependence, suggesting that the assemblies are mostly spherical. After reaching equilibrium in solution, extrapolating the Rh value...
particles have radii on the vesicle surface. The Anderson cluster has a stiff plate group, which can affect the packing of solvent-phobic alkyl tails observed in the same solution.

The vesicle size. Vesicle formation is usually fast, but some interaction, similar to conventional surfactants. For a lipid surfactant mixture is a good solvent for the POMs but a poor solvent for the charged POM macroions, such as {Mo72Fe30}12 and {Cu20P8W48}13 as the driving forces of the latter case are not hydrophobic interactions or van der Waals forces, but the countereion-mediated effect and hydrogen bonds.

Vesicle formation was also observed in the water/MeCN solutions of [Bu4N][MnMo6O18{(OCH2)3CNHCO-(CH2)4CH3}2] (Mn-Anderson-C6, see Supporting Information). The Mn-Anderson-C6 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-C16, fewer Mn-Anderson-C6 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.

Acknowledgment. T. L. gratefully acknowledges support of this work by the NSF (CHE-0545983), ACS-PRF 46294-G3, and Lehigh University. L.C. and Y.S. thank the University of Glasgow, WestCHEM, and the EPSRC for funding. We thank Mr. Joe Pigga for creating images in Figure 1.

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

References


