

Synthesis and Characterization of Surfactant-encapsulated Polyoxoanions: $[(C_nH_{2n+1})_2N(CH_3)_2]_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]$ ($n = 12, 18$)

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By employing electrostatic interaction as driving force, an organic/inorganic composite with positively charged dimethyl dialkyl-chain ammonium surfactants encapsulating negatively charged $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}] \cdot 33H_2O$ polyoxoanion was prepared. The structure of the novel organic/inorganic hybrid particle with hydrophilic core and hydrophobic shell in a defined stoichiometric ratio was confirmed by element analysis, ¹H NMR and FT-IR spectra. The property of the polyoxoanion was changed due to the encapsulation and it can be dissolved in organic solvent such as chloroform, benzene and toluene, but not dissolved in water.

Keywords surfactant, polyoxoanion, encapsulation, core-shell structure

Introduction

Supramolecular self-organization as a controllable technique for the artificial supramolecular architecture at molecular and/or nanosized level is showing fascinating perspectives in the field of the molecular materials design, due to that organic and inorganic components can be facilely assembled together.¹⁻³ It is well known that the driving force of layer-by-layer assembly is based on electrostatic interaction between anions and cations.⁴ This makes alternative polyelectrolyte multilayers quite stable and no longer dissolve in water through ionization due to

the loss of their counter ions. With this method, many water-soluble materials such as CdTe semiconductor nanoparticles⁵ and other inorganic salts can be transferred into organic media with surfactants.^{6,7} Polyoxoanions are intriguing inorganic building blocks to form functional materials because they possess both well-defined molecular weight and nano-structure, and furthermore display a lot of interesting conducting, magnetic, electronic, photonic and catalytic properties.⁸⁻¹³ Generally, the polyoxoanion is only soluble in water, based on the naked anion surface. This can limit versatile applications of polyoxometalates. In order to tailor compatibility of polyoxometalates with organic materials and biological organism, it is necessary to modify their surface properties by electrostatic self-assembly. Some polyoxometalates have been successfully canned¹⁴⁻¹⁶ and used for the multilayer film fabrication.^{17,18}

With the aim of fabricating functional films, we herein report the encapsulation of a polyoxoanion, $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}] \cdot 33H_2O$,¹⁹ with dialkyldimethylammonium bromide to form a novel organic/inorganic hybrid material. The surfactant-enwrapped polyoxoanion (SEP-1, 2), $[(C_nH_{2n+1})_2N(CH_3)_2]_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]$ ($n = 12, 18$), possesses the structure with a hydrophobic dialkyldimethylammonium shell and an encapsulated hydrophilic polyoxoanion core of a

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defined stoichiometric ratio in organic media. The driving force for this encapsulation is proposed to be electrostatic binding. SEP-1 and SEP-2 are water insoluble, but can be dissolved in organic media such as chloroform, benzene and toluene. In the present research, polyoxoanions can be phase-transferred into organic medium and their existing states have been improved, as shown in Fig. 1. This can lead to a series of catalytic materials for organic compounds because of the compatibility between SEP and substrates.

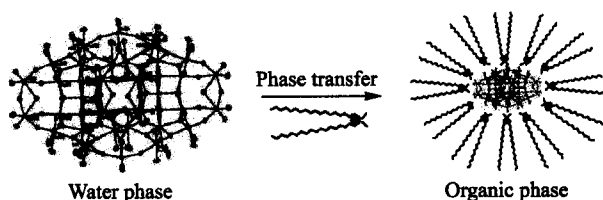


Fig. 1 Schematic drawing of the chemical structures of polyoxoanion (left) and SEPs (right).

Experimental

General

^1H NMR spectra (TMS) and two-dimensional H-H cosy spectra were recorded on a Bruker UltraShieldTM 500 MHz spectrometer. Fourier Transformation Infrared measurements were performed on a Bruker IFS66V FT-IR spectrometer equipped with a DTGS detector for solids. The element analysis was measured on a Flash EA1112 from ThermoQuest Italia S. P. A.

Synthesis of SEP-1 and SEP-2

A polyoxoanion, $[\text{NH}_4]_{12}[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}] \cdot 33\text{H}_2\text{O}$ (**1**), freshly prepared according to the known procedures¹⁹ was dissolved in aqueous solution (pH = 1) and then stirred with a chloroform solution of surfactants dimethyl dioctadecyl ammonium bromide (DODA·Br, for SEP-1) or didodecyl dimethyl ammonium bromide (DDDA·Br, for SEP-2). The two surfactants, DODA·Br (99%) and DDDA·Br (99%), were purchased from Acros Organics and used as received. The structure of polyoxoanion (**1**) was confirmed by single crystal X-ray diffraction experiments. The initial molar ratio of surfactants to **1** was controlled at 12:1. The aqueous phase became almost colorless showing that the polyoxoanion was

extracted and transferred into chloroform solution. The red organic phase was separated and SEPs were obtained by evaporating the chloroform to dryness. Then the sample was further dried *in vacuo* until the weight remained constant.

For SEP-1, ^1H NMR (CDCl_3 , 500 MHz) δ : 0.88 (t, $J = 7$ Hz, 6H, CH_3), 1.26 (m, 52H, CH_2), 1.34 (s, 8H, CH_2), 1.64 (s, 4H, CH_2), 3.27 (s, 4H, NCH_2), 3.34 (s, 6H, NCH_3); IR (KBr) ν : 2955, 2919, 2850, 1635, 1467, 1380, 944, 911, 871, 804, 775, 721, 645, 613, 573 cm^{-1} . Anal. calcd for $\text{C}_{456}\text{H}_{992}\text{N}_{16}\text{O}_{128}\text{Mo}_{36}$ (12205.50): C 44.89, H 8.19, N 1.84; found C 45.17, H 8.28, N 1.91.

For SEP-2, ^1H NMR (CDCl_3 , 500 MHz) δ : 0.88 (t, $J = 7$ Hz, 6H, CH_3), 1.26 (m, 52H, CH_2), 1.34 (s, 8H, CH_2), 1.64 (s, 4H, CH_2), 3.24 (s, 4H, NCH_2), 3.35 (s, 6H, NCH_3); IR (KBr) ν : 2955, 2924, 2852, 1635, 1467, 1380, 944, 911, 871, 804, 775, 721, 645, 613, 573 cm^{-1} . Anal. calcd for $\text{C}_{312}\text{H}_{704}\text{N}_{16}\text{O}_{128}\text{Mo}_{36}$ (10184.76): C 36.79, H 6.97, N 2.20; found C 36.81, H 7.20, N 2.30.

Results and discussion

Preparation

It is well-known that the polyoxoanion **1** is only soluble in water. However, the SEP-1 and SEP-2 are no longer soluble in water, and they are just dissolved in organic media such as chloroform, benzene and toluene. This indicates that the surface of polyoxoanion becomes hydrophobic, which implies that the hydrophobic encapsulation of polyoxoanion **1** with dialkyl-chain ammonium surfactants is successful. Therefore, based on the exact elemental analysis and the detailed characterization of **1**, the SEP-1 and SEP-2 should correspond to the formulas: $(\text{DODA})_{12}[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]$ and $(\text{DDDA})_{12}[\text{Mo}_{36}(\text{NO})_4\text{O}_{108}(\text{H}_2\text{O})_{16}]$, respectively. The surfactants (DODA, DDDA) replace the ammonium ions of the polyoxoanion, and neutralize its charge, which lead to a neutral assembly and make SEPs soluble in organic media. Herein, amphiphilic molecules (DODA, DDDA) play an essential role in the packing of the polyoxoanion, a solvophilic moiety (alkyl chains) orients toward solvent while the solvophobic moiety (polyoxoanion) are capped inside the supramolecular assembly, *i. e.*, SEPs, as

shown in Fig. 1.

^1H NMR Spectra

^1H NMR spectra of SEP-1 (CDCl_3 solution) as shown in Fig. 2, confirms the presence of surfactants in the encapsulated cluster. In contrast to those of neat DODA, the resonance signals of DODA in SEP-1 are changed as pointed in following. (1) The resonance signals due to *N*-methyl proton are significantly broadened and shift to high field by δ 0.06. (2) Proton signals of α -methylene should be split into triplet. However, they turn into a considerably broadened singlet, and shift toward high field by δ 0.24. (3) Proton signals of β -methylene vary from five peaks in DODA·Br to singlet in SEP-1, and shift toward high field by δ 0.06. (4) The similar broadening and shifting toward high field of the resonance signals of γ , δ -methylenes are also observed, but the extent is relatively low of δ 0.03. The other proton signals change little.

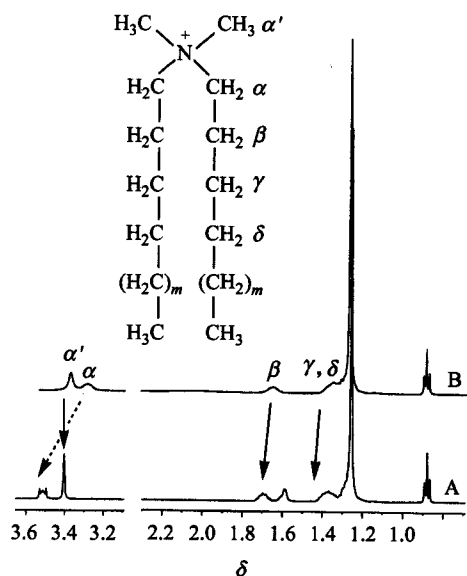


Fig. 2 ^1H NMR spectra of DODA·Br (A) and SEP-1 (B).

For DDDA surfactant-encapsulated polyoxoanion, SEP-2, the similar broadening of ^1H NMR signals of DDDA surfactants can also be observed. But the extent of their shifts toward high field exhibits different values, for example, *N*-methyl, δ 0.07; α -methylene, δ 0.28; β -methylene, δ 0.05; γ , δ -methylene, δ 0.02. The resonance signals at δ 2.07 are attributed to coordinating water molecules in the polyoxoanion. The integrated area,

31.77, is in excellent agreement with the number (16) of water ligand in the polyoxoanion. These assignments have been confirmed by ^1H - ^1H NMR correlation spectra of SEP-1 and SEP-2. Our results are different from those in literatures,¹⁴⁻¹⁶ which pointed out a high-field shift (δ 0.2) of *N*-methyl. This may be attributed to the different polyoxoanion used in the SEPs.

The broadening and shift of resonance signals should be due to the strong electrostatic interaction between surfactants and the polyoxoanion, as suggested in literatures.¹⁴⁻¹⁶ That is, surfactants are immobilized on the surface of the polyoxoanion in organic phase, and, to some extent, their mobility is confined, especially to the head part of it. The shift and broadening of resonance signals are ascribed to the different chemical microenvironment.

FT-IR spectra

Fig. 3 presents the IR absorption bands of **1** and the SEP-1. The bands at 2919 and 2850 cm^{-1} are attributed to the asymmetric and symmetric CH_2 stretching modes, respectively. Comparable with solid DODA·Br at 2918 and 2850 cm^{-1} , the alkyl chains in SEP-1 are well ordered. Other bands concerning the alkyl chains appear at 2955, 1467, 1482, 1379 and 721 cm^{-1} . As compared to the IR absorption bands of the polyoxoanion, the peaks at 3180 and 1400 cm^{-1} , due to the asymmetric stretching modes and scissor modes of NH_4^+ , respectively, disappear in the SEP-1. This means that DODA surfactants have completely replaced ammonium ions. And the IR spectrum also displays the characteristic modes of the polyoxoanion, for example, 1635 ($\text{N}=\text{O}$ asymmetric

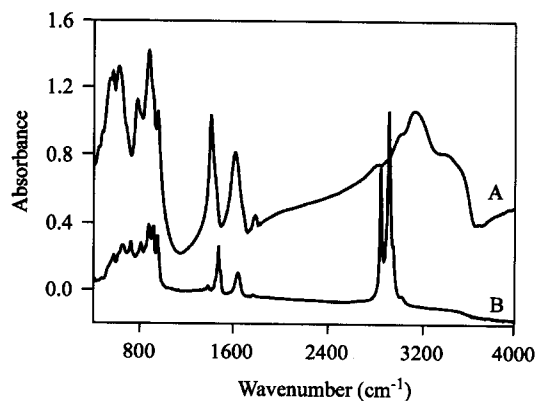


Fig. 3 Infrared spectra for (A) the polyoxoanion (**1**) and (B) SEP-1.

stretching), 944, 911 (W-O_d asymmetric stretching), 871 ($\text{W-O}_b\text{-W}$ asymmetric stretching), 804, 775 ($\text{W-O}_c\text{-W}$ asymmetric stretching) cm^{-1} . The IR absorption bands of asymmetric and symmetric CH_2 stretching modes of SEP-2 appear at 2924 and 2852 cm^{-1} , respectively. Comparing with CH_2 stretching modes (2918, 2850 cm^{-1}) of solid DDDA·Br, the alkyl chains of DDDA in SEP-2 are more disordered. The other peaks are consistent with those in SEP-1. The detailed assignments were summarized in Table 1.

Table 1 Assignments for characteristic infrared bands of SEP-1 and SEP-2

Wavelength (cm^{-1}) for SEP-1	Wavelength (cm^{-1}) for SEP-2	Assignment
2955	2955	CH_3 asymmetric stretching
2919	2924	CH_2 asymmetric stretching
2850	2852	CH_2 symmetric stretching
1635	1633	$\text{N}=\text{O}$ asymmetric stretching
1467	1465	CH_2 scissor mode
1482	1482	CH_2 scissor mode
944	949	Mo-O_d asymmetric stretching
911	911	Mo-O_d asymmetric stretching
871	872	$\text{Mo-O}_b\text{-Mo}$ asymmetric stretching
804	803	$\text{Mo-O}_c\text{-Mo}$ asymmetric stretching
775	775	$\text{Mo-O}_c\text{-Mo}$ asymmetric stretching

Conclusion

Based on the above analysis, the polyoxoanion has been successfully encapsulated with dialkyl dimethyl ammonium salts, and the cationic head points toward the cluster surface. The molar ratio of dialkyl dimethyl am-

monium and the polyoxoanion is proposed to be 12:1, which is confirmed by the element analysis. Dialkyl dimethyl ammonium cation displaces the ammonium cation, which means the successful encapsulation for polyoxoanion. This SEP structure model is consistent with the solubility of SEPs in organic solvents, such as benzene, chloroform and toluene. The amphiphilicity-directed method has been applied to form various supramolecular assemblies, for example, surfactant-encapsulated cluster,¹⁴⁻¹⁶ lipid-packaged one-inorganic nanowire^{6,7} and micelle containing heteropolyoxoanion.⁹ The driving force for these complexes is the electrostatic interaction.

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