

Surfactant-Induced Trans-Interface Transportation and Complex Formation of Giant Polyoxomolybdate-Based Clusters

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The interaction and complex formation between cationic surfactants dimethyldioctadecylammonium Bromide (DODA-Br) and a polyoxomolybdate (POM)-based giant cluster $\{\text{Mo}_{72}\text{Fe}_{30}\}$, in its both single cluster (in aqueous solution, these clusters exist as anions) format and supramolecular format in aqueous solution, are studied by using laser light scattering (LLS) techniques. DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ complexes containing basically single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ clusters are observed when the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aqueous solution is freshly prepared and contains mainly unimer or oligmer $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions. The $\{\text{Mo}_{72}\text{Fe}_{30}\}$ clusters tend to form supramolecular vesicle structures slowly in solution. At high surfactant concentrations, the DODA cationic surfactants can break the vesicle structure and form single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ /DODA complexes. At low surfactant concentrations, complexes containing the whole vesicles coated by a layer of DODA is formed and transferred into the organic phase. For the surfactant concentrations in between, the vesicles are partially destroyed, leading to the formation of complexes with large size distribution. Studying the behaviors of the interaction between DODA and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anionic structures will help to further explore the complicated mechanism of the POM vesicle formation, which was recently discovered but still not fully understood. Such unique complex structures may also have potential applications as nanoreactors or nanocontainers.

KEY WORDS: Polyoxomolybdate; supramolecular structure; vesicle; surfactant; complex; trans-interface.

Dedicated with sincere regards to Professor Achim Müller on the occasion of his 65th birthday.

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INTRODUCTION

Recently, inorganic chemists have made significant progress in synthesizing nanometer-scale inorganic molecules and clusters, with most of which belonging to the family of polyoxometallate: “By different types of linking of oxygen polyhedra with metal centers an extreme diversity of structures of molecular systems is generated showing an overwhelming variety of exciting and unusual properties, even leading to the largest known structurally characterized inorganic species” [1]. The most noticeable success so far is the synthesis of giant polyoxomolybdate (POM) molecules (sometimes called clusters), to which Professor Achim Müller’s group at University of Bielefeld has made very critical and substantial contributions [2–7]. By partially reducing Mo^{VI} to Mo^{V} via simple inorganic-synthesis approaches in acidic solutions, they synthesized many new POM molecules with large sizes (several nanometers) and hundreds to even thousands of atoms. Some of these POM molecules have astonishingly beautiful geometrical shapes, such as the “giant wheel” structures (e.g., $\text{Na}_{15}[\text{Mo}_{126}^{\text{VI}}\text{Mo}_{28}^{\text{V}}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]_{0.5}[\text{Mo}_{124}^{\text{VI}}\text{Mo}_{28}^{\text{V}}\text{O}_{457}\text{H}_{14}(\text{H}_2\text{O})_{68}]_{0.5}\text{ca.}400\text{H}_2\text{O}$, $(\{\text{Mo}_{154}\})$ [4] and $\text{Na}_{16}[\text{Mo}_{144}^{\text{VI}}\text{Mo}_{32}^{\text{V}}\text{O}_{528}\text{H}_{16}(\text{CH}_3\text{OH})_{17}(\text{H}_2\text{O})_{63}] \cdot 600\text{H}_2\text{O} \cdot 30\text{CH}_3\text{OH}$, $(\{\text{Mo}_{176}\})$ [5] and the C_{60} -like hollow spherical “Keplerate” structures (e.g., $(\text{NH}_4)_{42}[\text{Mo}_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}\text{H}_{16}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}] \cdot \text{ca.}300\text{H}_2\text{O} \cdot \text{ca.}10\text{CH}_3\text{COONH}_4$, $\{\text{Mo}_{132}\}$ [6], Fig. 1a). Moreover, the 60 Mo^{V} in $\{\text{Mo}_{132}\}$ can be replaced by 30 Fe^{III} ions, leading to the formation of giant molecules ($\text{Mo}_{72}^{\text{VI}}\text{Fe}_{30}^{\text{III}}\text{O}_{252}\text{L}_{102}$

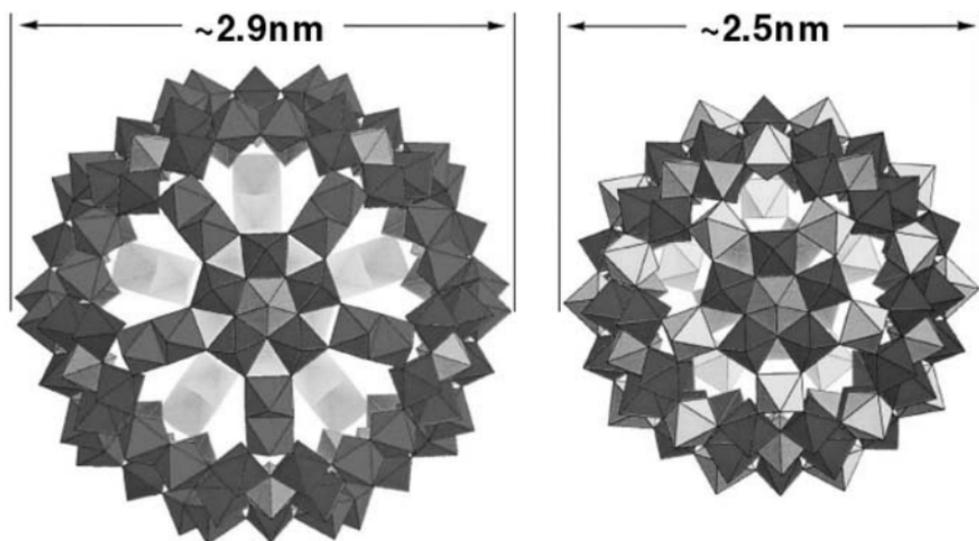


Fig. 1. Structures of $\{\text{Mo}_{132}\}$ (1a) and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ (1b) “Keplerate” giant molecules. Reprinted from Ref. 2, p. 198, Fig. 5, copyright 2001, with permission from Elsevier Science.

ca. $180\text{H}_2\text{O}$ with $L = \text{H}_2\text{O}/\text{CH}_3\text{COO}^-/\text{Mo}_2\text{O}_{8/9}^{n-}$, $\{\text{Mo}_{72}\text{Fe}_{30}\}$ [7], Fig. 1b) with novel magnetic properties [8]. Such complicated molecules usually contain a large number of ligands (both water and small organic species) in their crystals.

There is no doubt that the discovery of these giant POM molecules is an important achievement in inorganic chemistry. Moreover, the impact of these works to the scientific community is far beyond the boundary of inorganic chemistry itself. Scientists in other fields are also benefiting from this progress. These POMs represents the first group of available inorganic molecules with nanometer sizes. Studies are underway to explore their “exciting and unusual” physical and chemical properties, as well as their potential applications.

An important example is the unique solution behavior of these giant POM anions. The various giant POM molecules are highly soluble in polar solvents including water, ethanol and acetone [9]. It is known that in aqueous solution, the main parts of the POM clusters exist as anions, balanced by small cations such as Na^+ or NH_4^+ . These charged, highly soluble large clusters can be easily dissolved in polar solvents, but they do not stay as single ions in solution for very long, which contradicts our common knowledge on inorganic compounds. On the contrary, they tend to self-assemble into larger, highly uniform, spherical structures. Recently, we proposed that such supramolecular structures could be vesicle-like, with the POM anions forming a single layer on the vesicle surfaces [10–12]. The POM anions do not directly touch each other, but certainly within a very short distance. In the vesicles, the giant anions do not show any long-range orders, but some local short-range orders were observed [12]. The POM vesicle structures are the first type of supramolecular structures formed by hydrophilic inorganic ions. There are still many unclear phenomena associated with this new solution system, such as the unusually slow self-assembly process in dilute solution [11]. It takes several months for all the giant single anions to form vesicles at room temperature, while we have the common idea that the thermodynamic equilibrium in dilute solution should be quickly reached.

The POM anions can further interact with various cationic surfactants to form complex structures, mainly developed by Volkmer and Kurth *et al.* [13–16]. It was observed that cationic surfactant dimethyldioctadecylammonium Bromide DODA-Br could strongly interact with the POM-based anions in aqueous solution by means of electrostatic interactions [13, 14], and transfer the POM anions into an organic phase (e.g., chloroform) due to the hydrophobic nature of the long DODA double tails. Averagely as many as 40 DODA cations surround with each $\{\text{Mo}_{132}\}$ anion and form complex structure that has an obvious hydrophobic nature [13]. They

suggested that such trans-interface transportation and the formation of DODA-POM complex could lead to the development of nanocontainers and nanoreactors in the future.

In this paper, I report a more detailed study on the trans-interface transportation process of the POM supramolecular vesicles achieved by DODA-Br surfactants. Such explorations on the POM vesicle systems will provide deeper understanding on such novel systems. The vesicles are found to be able to interact with cationic surfactants, while different physical phenomena were observed under different external conditions, e.g., the molar ratio of DODA/POM. Understanding of such process will not only provide fundamental knowledge on the POM vesicles and organic/inorganic complex structures, but also highlight potential possibilities of using such complex systems as nanoreactors or nanocontainers with the unique advantages of uniform, spacious (with cavity size up to 300 nm) and stable.

EXPERIMENTAL CONDITIONS

POM-based cluster ($\text{Mo}_{72}^{\text{VI}}\text{Fe}_{30}^{\text{III}}\text{O}_{252}\text{L}_{102} \cdot \text{ca.}180\text{H}_2\text{O}$ with $\text{L} = \text{H}_2\text{O}/\text{CH}_3\text{COO}^-/\text{Mo}_2\text{O}_{8/9}^{n-}$, $\{\text{Mo}_{72}\text{Fe}_{30}\}$), which can be obtained in extremely pure form that has been proven by sophisticated magnetic experiments [8], was synthesized by following the descriptions in literature [7]. Single crystals of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ with $R\bar{3}$ structure were dissolved in deionized water at room temperature with stirring [17–19]. The clear solution was stored for a long time to wait for the growth of the vesicle supramolecular structures. A warm temperature (e.g., 30°C) is helpful to accelerate the process. The above-mentioned $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aqueous solution was then mixed with CHCl_3 solution containing cationic surfactant DODA-Br. The cationic DODA surfactants were able to interact with the POMs in water phase and continuously drag them into the CHCl_3 phase, by showing that the color of the water phase due to the existence of the POMs faded till colorless while the CHCl_3 phase became colorful (yellow). All the basic chemicals were purchased from Sigma-Aldrich Co. and used without further purification.

Laser light scattering (LLS) techniques were applied to study the DODA-POM complexes in CHCl_3 . A commercial Brookhaven Instrument laser light scattering spectrometer was used for the LLS experiments. It is capable of making measurements of both the angular dependence of absolute integrated scattered intensity (static light scattering, SLS), and the photon correlation (DLS and depolarized DLS, DDLS). SLS experiments were performed at scattering angles between 10 and 150°, at 2° intervals. DLS measurements were made by means of a BI-9000 AT digital correlator. The CONTIN method [16] was used to analyze the first-order field

correlation function $g^{(1)}(\tau)$ as determined by DLS. Then, the hydrodynamic radius (R_h) of the particles can be calculated from the characteristic linewidth Γ . DLS measurements also provide information on the particle-size distribution in solution from a plot of $\Gamma G(\Gamma)$ versus R_h . The basis of the SLS data analysis is the Rayleigh–Gans–Debye equation: $H \cdot c / R_\theta = 1 / M_w (1 + q^2 \langle R_g^2 \rangle / 3) (1 + 2A_2 c)$ with $H = 4\pi^2 n^2 (dn/dc)^2 / N_A \lambda_0^4$ and $q = (4\pi n / \lambda_0) / \sin(\theta/2)$ where the Rayleigh ratio R_θ depends on the scattered intensity at different scattering angles θ , c , q , $\langle R_g^2 \rangle$, A_2 , n , N_A , and λ_0 being the solute concentration, the magnitude of the scattering wave vector, the mean square radius of gyration of the particles, the second virial coefficient, the refractive index of the solvent, the Avogadro constant and the wavelength of incident light in a vacuum, respectively.

RESULTS AND DISCUSSIONS

{Mo₇₂Fe₃₀}/DODA Complex Formation in a Fresh-Prepared Solution

It is known that it takes a very long time (up to several months at room temperature) to complete the vesicle formation in dilute solutions. Almost all the {Mo₇₂Fe₃₀} clusters exist as single anions in a fresh-prepared solution, as proved by earlier studies [11]. Small amount of oligomers may also exist. In solid state, {Mo₇₂Fe₃₀} clusters are charged neutral. However, the {Mo₇₂Fe₃₀} aqueous solutions are acidic as a result of partial deprotonation of the H₂O ligands attached to the Fe centers [7]. Consequently, the {Mo₇₂Fe₃₀} clusters are negatively charged. For a 1 mg/ml {Mo₇₂Fe₃₀} aqueous solution, pH ~ 3.4. That is, in 1 l solution, there are $\sim 5.4 \times 10^{-5}$ mol {Mo₇₂Fe₃₀} clusters which totally release $\sim 4 \times 10^{-4}$ mol H⁺, i.e., each {Mo₇₂Fe₃₀} cluster has ~ 7 net negative charges. Mixing such {Mo₇₂Fe₃₀} solution with CHCl₃/DODA-Br solution (with molar ratio DODA : {Mo₇₂Fe₃₀} > 500) leads to the formation of POM/DODA complex with only one POM in each complex, as reported before by Volkmer and Kurth *et al.* on a similar system (DODA/{Mo₁₃₂} complex) [13]. The water phase became colorless when all {Mo₇₂Fe₃₀} anions were transferred into the CHCl₃ phase, which turned to yellow, the color of {Mo₇₂Fe₃₀}. Our recent results based on {Mo₇₂Fe₃₀} solution also confirmed their observation, by noticing that only very weak scattered intensity was detected from SLS measurements and there was no large particles detected from DLS measurements. A schematic plot is shown in Fig. 2 to illustrate the formation of DODA/{Mo₇₂Fe₃₀} complex at water/CHCl₃ interface and the trans-interface transportation process that transfer and stabilize {Mo₇₂Fe₃₀}

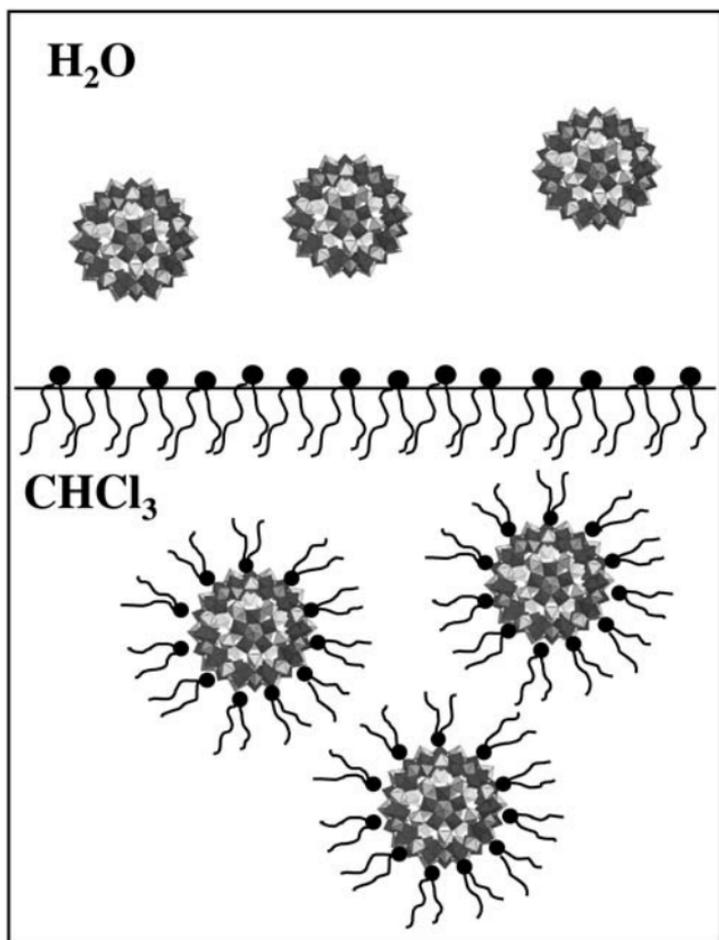


Fig. 2. Schematic plot showing the DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ complex formation at the water/ CHCl_3 interface and the trans-interface transportation process in order to stabilize $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions in CHCl_3 solution.

anions in CHCl_3 . Due to the smaller number of net charged on each $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anion (compared to that of $\{\text{Mo}_{132}\}$ or other POMs), it is much more difficult for DODA cations to interact with $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions. Consequently, larger amount of DODA surfactants was needed to transfer all $\{\text{Mo}_{72}\text{Fe}_{30}\}$ into CHCl_3 phase; and it takes much longer time to complete the whole process.

$\{\text{Mo}_{72}\text{Fe}_{30}\}$ /DODA Complex Formation in an Aqueous Solution Containing $\{\text{Mo}_{72}\text{Fe}_{30}\}$ Supramolecular Vesicles: Low DODA Concentration

Contrast to the regular soluble inorganic ions, which tend to distribute homogeneously in a good solvent, reaching the minimum free energy and

maximum entropy simultaneously, the highly soluble POM and POM-based giant ions such as the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions tend to further self-assembly into vesicle-like hollow spherical supramolecular structures slowly. It is very easy to detect and monitor the vesicle formation by LLS, with the observation of a drastic and continuous increase in the total scattered intensity from the solution by SLS and the appearance of a slow mode that corresponds to large particles in DLS measurements [11]. Figure 3 shows the CONTIN analysis of a DLS study on a dilute $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aqueous solution. Two modes can be clearly identified: a fast mode represents particles with an average R_h of ~ 1.3 nm, which should be attributed to single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions; another more dominant slow mode appears at R_h of ~ 55 – 57 nm, which should be corresponding to the vesicles. Due to the existence of the large vesicles, the scattered intensity recorded from such solution is hundreds times higher than a fresh-prepared solution containing the same concentration of $\{\text{Mo}_{72}\text{Fe}_{30}\}$. For vesicles prepared from different batch of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ single crystal, their R_h shows some discrepancies, in a range from 20 to 55 nm [11]. It could be due to the fact that for different batch of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ crystals, the giant anions carry different amount of net charges; or it could be due to the different amount of

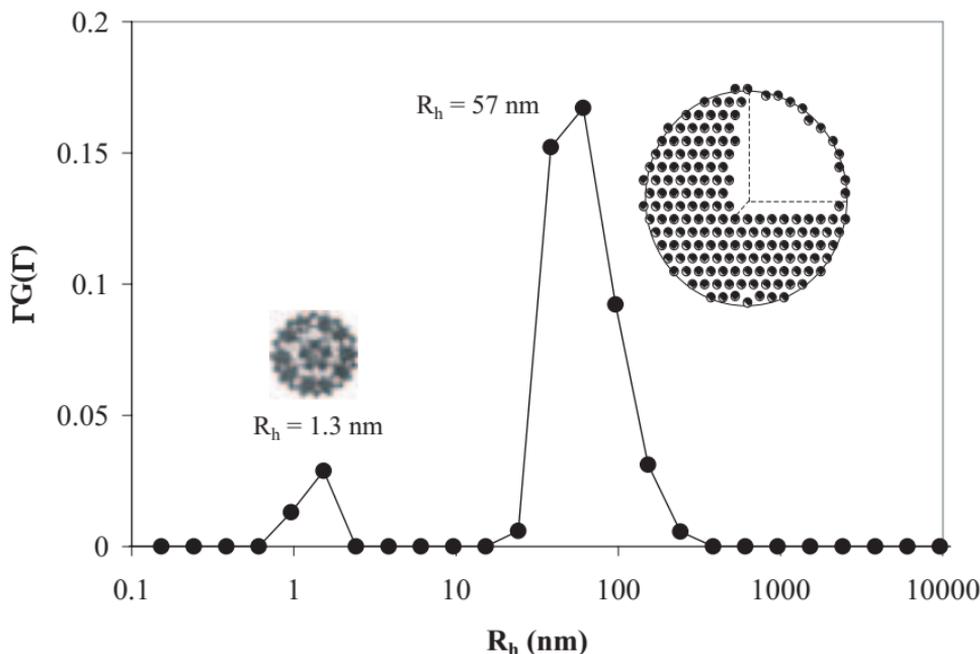


Fig. 3. A typical CONTIN analysis of DLS study on $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aqueous solution. Two modes can be identified: the single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions and the spherical vesicle supramolecular structures.

salts (NaCl) remained within single crystals after synthesis. It is also observed that dissolving $\{\text{Mo}_{72}\text{Fe}_{30}\}$ crystals with heating when stirring would lead to the formation of larger vesicles. There is still no firm explanation on this issue.

The 50 ml 1.5 mg/ml $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solution same as above was mixed with 40 g DODA/ CHCl_3 (DODA concentration in CHCl_3 was ~ 1 mg/g). The mass ratio of DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ was about 1:1.8, corresponding to a molar ratio of $\sim 20:1$. After several days, the upper layer (water phase) became nearly colorless while the bottom layer (CHCl_3 phase) turned to yellow, suggesting that almost all the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions had been transferred into the CHCl_3 phase. A CONTIN analysis on a DLS study performed at both 45° and 60° scattering angles on the CHCl_3 solution is shown in Fig. 4, where again two modes can be identified, with the average R_h values of ~ 2.5 nm and ~ 60 nm, respectively. Considering that the length of DODA C_{18} double-tail cationic surfactants in a good solvent (e.g., CHCl_3) is about 1 nm, the first peak (2.5 nm) should be attributed to

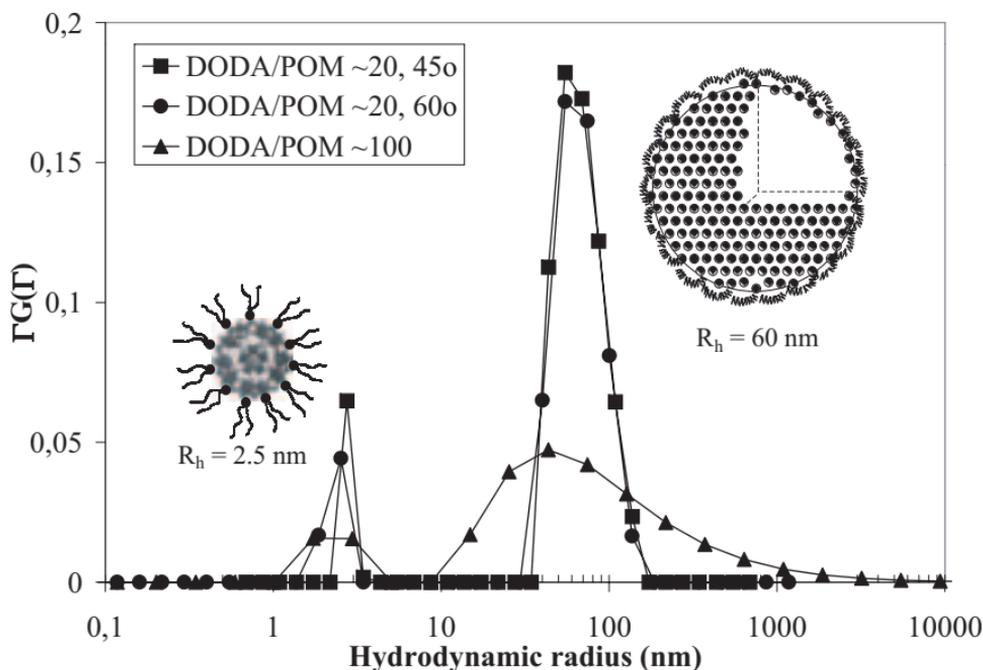


Fig. 4. Typical CONTIN analysis of DLS study on DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ complex in CHCl_3 solutions. (●) and (■): measured on a solution with low DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ molar ratio (~ 20); (▲): measured on a solution with medium DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ molar ratio (~ 100). Two modes can be identified on each analysis: the DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ complexes each containing individual $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions and the complexes each containing a whole or partial of a vesicle.

the DODA-coated single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions, as shown schematically in Fig. 4. The second mode at $\sim 58\text{--}60$ nm should be related to the vesicle supramolecular structures in aqueous solution, which has an average of ~ 57 nm. I propose that the aggregates were transferred into the CHCl_3 phase as a whole by forming unique complexes, with each containing a DODA-coated soft single layer, a hard shell of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions as well as water encapsulated in the vesicles. The strong scattered intensity from SLS studies also indicated the existence of large structures in CHCl_3 solution. Considering that the interaction between DODA cations and POM species is obviously electrostatic interaction, we can conclude that the vesicles formed by $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions in aqueous solution are also negatively charged, i.e., the vesicles overall can be considered as “giant anions.” The charges on the vesicles should come from the charges on each individual $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anion.

It seems that the electrostatic interaction between $\{\text{Mo}_{72}\text{Fe}_{30}\}$ in the vesicles, which at least partially contributes to the vesicle formation, remains undisturbed in the presence of additional electrostatic force contributed from the DODA cations. It could be attributed to the relatively low concentrations of DODA, i.e., larger amount of cations and stronger interaction is needed to break the supramolecular structure.

In an earlier report, we suggested that the water assemblies between adjacent POM anions in the vesicles could play an important role to help maintain the supramolecular structure [12]. The DODA-manipulated trans-interface transportation further suggests that the vesicles have quite rigid outer shells. The vesicle structure remains unchanged when external electrostatic force is introduced, suggesting that the driving force of the vesicle formation is certainly not *only* due to the electrostatic interaction.

$\{\text{Mo}_{72}\text{Fe}_{30}\}$ /DODA Complex Formation in an Aqueous Solution Containing $\{\text{Mo}_{72}\text{Fe}_{30}\}$ Supramolecular Vesicles: Middle DODA Concentration

Increasing the amount of DODA surfactant will change the complex structure in CHCl_3 . By using the same $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aqueous solution as above. At a higher DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ molar ratio (e.g., 100:1), it is easier to transfer $\{\text{Mo}_{72}\text{Fe}_{30}\}$ into the organic phase. However, a LLS study on such a CHCl_3 solution indicates that the scattered intensity is much lower than that of the original aqueous solution containing $\{\text{Mo}_{72}\text{Fe}_{30}\}$ vesicles, suggesting a (at least) partial dissociation of the vesicle structures. At the same time, obvious change is also observed from DLS measurements. The fast mode (curve with filled triangles in Fig. 4) represents particles with R_h of 2.5 nm, as same size as the fast mode detected in Section 2, which should

also be attributed to the DODA/single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ complexes. The slow mode, representing the complex containing multiple $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions, has an obviously broader size distribution than before. The peak area of the slow mode also becomes smaller, suggesting that the vesicle-containing complexes are less dominant in solution, i.e., some vesicles might have been totally dissembled into single anions. The broad size distribution could be partially due to the low scattered intensity, which leads to poorer data points collected by the correlator. This is more likely to be the case for the very large size portion. Another important possible reason is that the vesicles could be partially broken, so that complexes with different sizes are formed with DODA surfactants interacting with various fractions of the original vesicles. This result is also similar to the reports of Volkmer and Kurth *et al.* [13]. They observed that a broad size distribution for the DODA/ $\{\text{Mo}_{132}\}$ complex in CHCl_3 , while they originally expected uniform complex containing single $\{\text{Mo}_{132}\}$ anion.

$\{\text{Mo}_{72}\text{Fe}_{30}\}$ /DODA Complex Formation in an Aqueous Solution Containing $\{\text{Mo}_{72}\text{Fe}_{30}\}$ Supramolecular Vesicles: High DODA Concentration

In the last experiment, totally 20 g of 5 mg/g DODA/ CHCl_3 was mixed with 40 ml of 0.15 mg/ml $\{\text{Mo}_{72}\text{Fe}_{30}\}$ aqueous solution, corresponding to a mass ratio of $\text{DODA}/\{\text{Mo}_{72}\text{Fe}_{30}\} = 17:1$, or a molar ratio of $\text{DODA}/\{\text{Mo}_{72}\text{Fe}_{30}\} = 560:1$. In the presence of excessive amount of DODA, most of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions have formed vesicles in water before the experiment. With the presence of such dominant amount of DODA surfactants, all the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ species were quickly transferred into the CHCl_3 phase. Surprisingly, SLS studies indicated that the CHCl_3 solution only showed very weak scattered intensity, not much higher than that of the CHCl_3 solvent only containing DODA surfactants. This is the situation very similar to that of the first section in our discussion, where DODA/ $\{\text{Mo}_{72}\text{Fe}_{30}\}$ complexes with single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions were observed. The ~ 57 -nm-radius large aggregates in aqueous solution have obviously been disassembled by the large amount of surfactants. This is another indirect evidence that the electrostatic interaction plays an important role in the vesicle formation. Strong external electrostatic interaction, such as the presence of large amount of DODA cationic surfactants, is able to break the supramolecular structure into discrete $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions. Due to the low scattered intensity, CONTIN analysis could not provide reasonable results for the DLS study. Therefore, it cannot be excluded that some complexes having a number of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions instead of one.

CONCLUSIONS

Combining the results in the above experiments, we are able to provide a general picture of the formation of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ -DODA complex via water-to- CHCl_3 trans-interface process. The original solute state of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and the relative molar ratio of $\text{DODA}/\{\text{Mo}_{72}\text{Fe}_{30}\}$ play important roles on determining the complex structure. $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions slowly form large vesicles in aqueous solution, but the introduction of DODA in CHCl_3 will interrupt this process. For the aqueous solutions mainly containing $\{\text{Mo}_{72}\text{Fe}_{30}\}$ vesicles, they can be transferred into CHCl_3 phase as a whole at low DODA concentrations by forming giant $\{\text{Mo}_{72}\text{Fe}_{30}\}$ vesicle/DODA complexes. The presence of larger amount of DODA starts to partially dissemble the vesicles into smaller pieces so that smaller and irregular complexes form. With sufficiently amount of DODA surfactants, all the vesicles are broken down into discrete $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions before complex formation. Understanding such complicated processes will help us to design potential applications of such systems as nano-containers or nano-reactors. It also provides important information to further elucidate the nature of the fascinating self-assembly of giant POM anions in solution.

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