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A Complete Macroion−"Blackberry" Assembly−Macroion Transition with Continuously Adjustable Assembly Sizes in $\{Mo_{132}\}$ Water/Acetone Systems

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Abstract: A complete, continuous transition from discrete macroions to blackberry structures, and then back to discrete macroions, is reported for the first time in the system of $\{Mo_{132}\}$/water/acetone, with $\{Mo_{132}\}$ (full formula $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot ca.300H_2O\cdot ca.10CH_3COONH_4$) as the C_{60}-like anionic polyoxomolybdate molecular clusters. Laser light scattering studies reveal the presence of the self-assembled $\{Mo_{132}\}$ blackberry structures in water/acetone mixed solvents containing 3 vol % to 70 vol % acetone, with the average hydrodynamic radius (R_h) of blackberries ranging from 45 to 100 nm with increasing acetone content. Only discrete $\{Mo_{132}\}$ clusters are found in solutions containing $<$3 vol % and $>$70 vol % acetone. The complete discrete macroion (cluster)−blackberry−discrete macroion transition helps to identify the driving forces behind the blackberry formation, a new type of self-assembly process. The charge density on the macroions is found to greatly affect the blackberry formation and dissociation, as the counterion association is very dominant around blackberries. The transitions between single $\{Mo_{132}\}$ clusters and blackberries, and between the blackberries with different sizes, are achieved by only changing the solvent quality.

Introduction

Recent developments in inorganic chemistry have led to the synthesis of a large series of giant metal-oxide-based polyoxometalate (POM) molecular clusters. Such nanoscaled, structurally well-defined species represent a class of inorganic compounds that display a wide variety of molecular and electronic structures. POM molecular clusters exhibit unparalleled structural, magnetic, and electronic properties as compared to many other inorganic compounds, and they offer unique opportunities for both fundamental studies and practical applications in many different fields.[1−10] In particular, some types of hydrophilic, soluble POM macroanions show unique solution behavior. It is widely expected that soluble inorganic ions should distribute homogeneously in dilute solutions. However, this is no longer true for very large anionic POM clusters in polar solvents,[11−22] such as wheel-shaped $\{Mo_{154}\}$ and $\{Mo_{176}\}$, hollow, spherical "Keplerate" $\{Mo_{132}\}$, and lemon-shaped "hedgehog" $\{Mo_{368}\}$.[23−33]

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The high solubility of POMs in polar solvents is due to the external water ligand layer and the negative charges of the POMs, which are balanced by small counterions, such as Na^+ and NH_4^+. We found that for such POM macroions, which are fully hydrophilic and highly soluble in polar solvents, will self-assemble into large, relatively uniform, single layer, "blackberry"-type structures in very dilute solutions as proven by static and dynamic laser light scattering (SLS and DLS), TEM, SEM, and AFM studies.[11−22] The "strong electrolyte" type and "weak electrolyte" type macroions show different self-assembly mechanisms.[17]

The monodispersed large POM anions are valuable model systems for studying the fundamental behavior of macroionic solutions, which connect simple ionic solutions and colloidal suspensions, but are different from both. A key issue for the blackberry structure is the driving force behind the blackberry formation. Previous work based on a weak electrolyte-type, 2.5-nm-diameter polyoxometalate $\{Mo_{72}Fe_{30}\}$ macroanions has unveiled that the driving force behind the blackberry formation process is not primarily due to van der Waals forces (the dominant attractive force among large, hydrophobic colloidal particles), hydrophobic interactions (responsible for the self-assembly of amphiphilic surfactants), or chemical interactions.[14,15] The blackberries show unusual properties, such as an obvious soft nature that would not be expected for inorganic species;[11] and unlike common inorganic ions in solution which quickly reach equilibrium in dilute solutions, the blackberry formation may require months to reach an equilibrium state.[13]

The driving forces behind the blackberry formation can be clarified by studying the transition between blackberry structures and discrete ions, i.e., whether the transition between these two states is observed by simply changing the solvent quality or the charge density of macroions. The negative charges on POM macroions seem to be important for the solution behavior of the POMs. As indicated in our previous work, $\{Mo_{72}Fe_{30}\}$ macroions stay as discrete ions (or molecules) when they are almost neutral. However, the macroanions tend to strongly attract one another when they carry enough charges. This indicates that an increase of charge density on macroions leads to a more significant attraction between the macroions and encourages blackberry formation, although the electrostatic repulsion is expected to be more significant.[14,15,20]

A critical question is whether or not the blackberry structure is still the free-energy-favored structure when the macroanions carry a large amount of charge. We speculate that, in this case, the electrostatic repulsion would become dominant and, therefore, the macroions would remain as discrete ions in solution. However, until now there is no direct experimental evidence of the electrostatic repulsion dominance on POM macroions which leads to the dissociation of blackberries. $\{Mo_{72}Fe_{30}\}$ macroions are not suitable for this study because $\{Mo_{72}Fe_{30}\}$ has a low charge density in aqueous solutions (7−8 charges per cluster). As a weak acid, the $\{Mo_{72}Fe_{30}\}$ charge density depends on solution pH; thus, a higher charge density can be expected at higher pH. However, $\{Mo_{72}Fe_{30}\}$ macroions are not stable at pH > 7. To understand the process that occurs in solutions of highly charged macroions, we chose to study $\{Mo_{132}\}$ in a series of water/acetone mixed solvents.

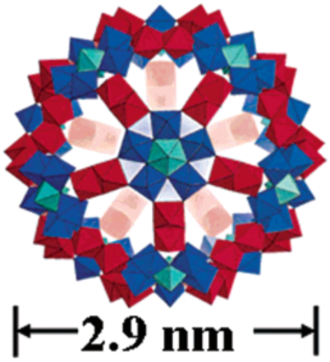

Figure 1. Structure of $\{Mo_{132}\}$ "Keplerate" giant cluster (full formula $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot ca.300H_2O\cdot ca.10CH_3COONH_4$). Reprinted with permission from ref 2, p 198, Figure 5. Copyright 2001 Elsevier Science.

$\{Mo_{132}\}$ (full formula $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot ca.300H_2O\cdot ca.10CH_3COONH_4$) is a type of molybdenum brown "Keplerate" anion showing I_h symmetry with a diameter of ~2.9 nm and charge of −42. It has a similar structure to $\{Mo_{72}Fe_{30}\}$, by using 30 Mo^V_2 linkers to replace the 30 Fe^{III} linkers in $\{Mo_{72}Fe_{30}\}$.[23,33,34] $\{Mo_{132}\}$ is a type of highly charged, "strong electrolyte" macroanion, as well as a type of "molecular insulator" POM. Cammers et al. have studied $\{Mo_{132}\}$ in highly concentrated aqueous solutions (mother liquor) and found the formation of large, hollow, spherical objects in solution.[21,22] We believe that those observed supramolecular structures may be the "blackberries" referred to in other macroionic systems. Here, we will choose to work with very dilute $\{Mo_{132}\}$ solutions due to the limited solubility of $\{Mo_{132}\}$ in organic solvents (Figure 1).

Another important issue is the status of the small counterions in POM solutions. Different from small ions which distribute homogeneously in diluted solutions, some long-chained organic macroions (polyelectrolytes) and charged colloidal particles are able to bind to a large fraction of small counterions found in close proximity to the charged polyelectrolytes or colloidal particles. The ability of the macroions to bind to small counterions is important for understanding the properties of macroions in solution. POM anions are much smaller than colloids. Therefore, the size disparity between cations and anions is less significant, though still existent. Hill and Weinstock et al. showed that the cations in Keggin-type (1-nm size POM) anionic solution exchange quickly between "free ions" and "cation-Keggin ion pairs", suggesting that the solution still follows the Debye−Hückel equation.[5] Here we present a systematic study to clarify the issue of the small counterions in large POM macroionic solutions and "blackberry"-containing solutions.

Finally, exploring the relationship of the blackberry size and the solvent quality is of interest. It is also important to determine whether the transition from discrete clusters or macroions to blackberries and vice versa can be achieved by only adjusting solvent quality, and whether the size of the blackberries is changed by changing solvent quality after blackberry formation, or if the blackberries are so inert that their size does not change once formed in solution. Positive results will strongly confirm that the unique blackberry formation is a thermodynamically favored process.

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Experimental Section

Sample Preparation. {Mo_{132}} single crystals were synthesized according to the literature[33] and then dissolved in different solvents of water, acetone, and their mixtures for study. A series of 1.0 mg/mL {Mo_{132}} solutions were prepared in water/acetone mixed solvents with different percentages of acetone ranging from 0% to 100% acetone by volume. The solubility of {Mo_{132}} in pure acetone is less than 1.0 mg/mL; therefore, a less concentrated solution was prepared. The newly prepared solutions were tightly sealed in glass vials to prevent the slow oxidation of {Mo_{132}} clusters in air. Additional amounts of acetone or water were added to the solutions, if changing solvent quality was required for the experiment.

pH and Conductivity Measurements. An Orion pH-meter is used for pH measurements, and an Oaklon Conductivity meter is used for conductance measurements. NaCl solutions (0.125 mg/mL) are used as standard solutions for calibrating the decrease of solution conductance when the solution contains a higher percentage of acetone. At this concentration, sodium chloride completely ionizes in each water/acetone solvent; thus, the number of charges will remain equal in each solution. Dialysis experiments were performed on aqueous {Mo_{132}} solutions to remove possible impurities (small electrolytes attached to {Mo_{132}} crystals during synthesis) before conductivity measurements, by using semipermeable Spectra/Por Membrane (1000 MWCO). A Genesis-10UV UV−vis spectrometer was used to determine the accurate concentration of POM solutions after dialysis.

Static and Dynamic Laser Light Scattering. A commercial Brookhaven Instrument light-scattering spectrometer was used for both the DLS (with a BI-9000AT digital correlator) and the absolute integrated scattered intensity (SLS) measurements. The CONTIN method[35] was used to analyze the DLS data and to calculate the hydrodynamic radius (R_h) of the particles. DLS measurements further provide information on the particle-size distribution in solution from a plot of $\Gamma G(\Gamma)$ versus R_h. SLS experiments were performed at scattering angles between 20° and 100°, at 5° intervals. The basis of the SLS data analysis is the Rayleigh−Gans−Debye equation,[13] which is used to obtain the radius of gyration (R_g) and the weight-average molecular weight (M_w) of the particles in solution.

Scanning Electron Microscopy (SEM). A Philips XL30 ESEM was used for SEM studies of the sample solutions. The ESEM was used in SEM mode and set to an accelerating voltage of 25.0 kV, with a spot size of 3.0, under high vacuum conditions. {Mo_{132}} samples were dried onto SEM stubs and then analyzed.

Small-Angle X-ray Scattering (SAXS) Experiments. SAXS experiments were performed at the CMC-XOR, 9-ID, Advanced Photon Source (APS), at Argonne National Laboratory (ANL). The incident X-ray wavelength (λ) was tuned at 0.154 nm. A 2-D CCD camera was used as the detector.

ζ Potential Analysis. A Brookhaven Instruments commercial *ZetaPALS* analyzer was used to measure the ζ potential of the particles in sample solutions. The analyzer was equipped with a 35-mW solid-state laser operating at 660 nm. The sample chamber was held at 25 °C and could be controlled to within ± 0.1 °C. According to the instrument design, ζ potentials ranging from −150 to +150 mV could be measured, and the data accuracy and repeatability were ± 2% for dust free samples.

Results and Discussion

{Mo_{132}} Clusters in Dilute Aqueous Solutions. {Mo_{132}} single clusters are highly soluble in water (>10 wt % at room temperature) and exist as macroions, showing no signs of self-association in dilute solutions. SLS studies show that dilute {Mo_{132}} aqueous solutions (<10 mg/mL, or 1 wt %) have very weak scattered intensities, suggesting that there are no large supramolecular structures formed in such solutions. DLS measurements also confirm this observation, as no peak corresponding to large structures is identified by the CONTIN analysis. However, this study is not sufficient in determining whether {Mo_{132}} stays as discrete ions, or forms small associates in aqueous solution.

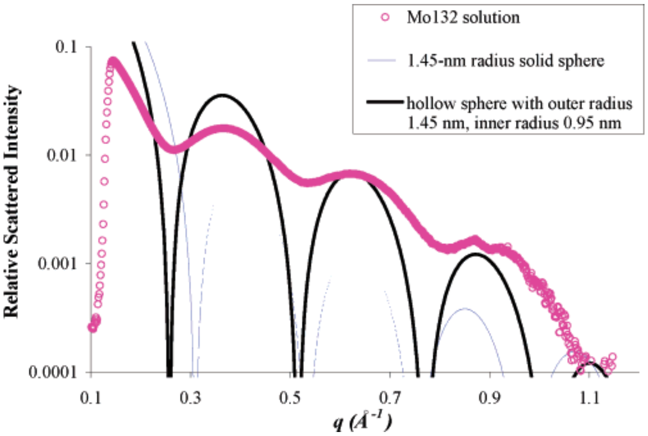

Figure 2. Diffraction pattern (pink circles) of 10 mg/mL {Mo_{132}} aqueous solution, measured by SAXS. The experimental curve can be fit with the theoretical diffraction pattern from a single {Mo_{132}} cluster (1.45-nm-radius hollow sphere).

SAXS was used to further determine the state of {Mo_{132}} macroions in aqueous solutions. Figure 2 shows a typical profile of SAXS measurement of 10 mg/mL {Mo_{132}} solution at 25 °C. The solution had been kept at 30 °C for several months before the experiment, in order to ensure that the solution was at equilibrium. In Figure 2, the *y*-axis is the normalized scattered intensity while the *x*-axis denotes the magnitude of the scattering wave vector q with

$$q = 4\pi\cdot\sin(\theta/2)/\lambda \tag{1}$$

where θ is the scattering angle, λ is the X-ray wavelength, and q is in units of Å^{-1}. The diffraction pattern (pink circles) represents the experimental data, which clearly shows three maxima at ∼0.37, 0.62, and 0.87 Å^{-1}, respectively. The scattered intensity I of SAXS measurements is determined by two factors: the form factor $I(q)$ and structure factor $S(q)$. The former is determined by the size and shape of the particles, while the latter is determined by the interaction between solute particles. Considering that the concentration of {Mo_{132}} solution is very low, its diffraction pattern should be determined by $I(q)$.

The calculated diffraction pattern from hollow spheres with an outer radius of 1.45 nm and inner radius of 0.95 nm (very similar to the structure of {Mo_{132}} single clusters) is also presented in Figure 2. It is obvious that the diffraction pattern has very similar shape and maxima positions (at least three peaks can be identified), and fits nicely with the experimental result. The diffraction patterns provide strong evidence that {Mo_{132}} clusters stay as single ions in dilute aqueous solutions. The experimental curve has a less ideal shape than that of theoretical calculation (solid line), which is due to the smearing effect. Comparing the diffraction pattern from a 1.45-nm-radius solid sphere (dashed blue curve in Figure 2) to the experimental curve there is a significant difference in the peak positions.

However, {Mo_{132}} macroions may self-assemble into single-layer vesicle-like “blackberry” structures in highly concentrated aqueous solutions. The groups of Cammers and Selegue at the

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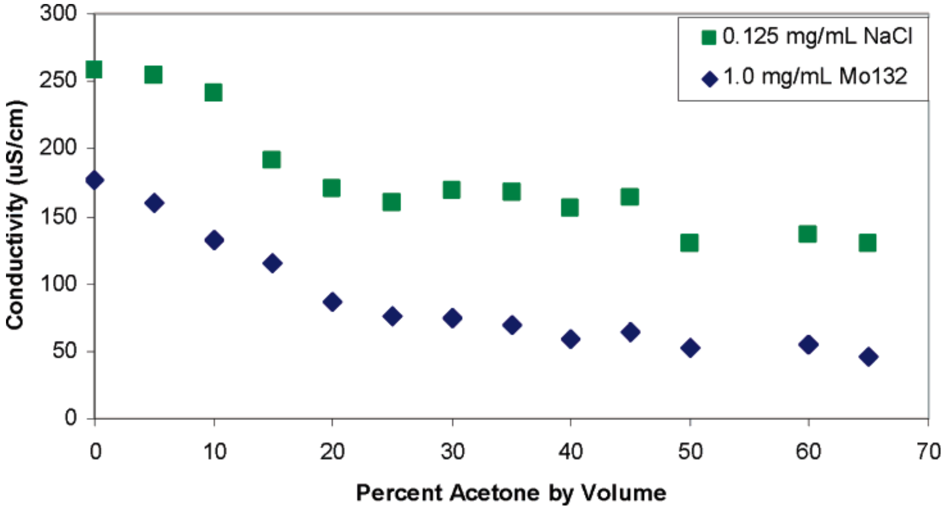

Figure 3. Conductivity of 1.0 mg/mL $\{Mo_{132}\}$ and 0.125 mg/mL NaCl solutions vs percent of acetone by volume. By assuming that Na^+ and Cl^- ions are free in all NaCl solutions, it is obvious that more cations are closely associated with $\{Mo_{132}\}$ macroanions with increasing acetone volume.

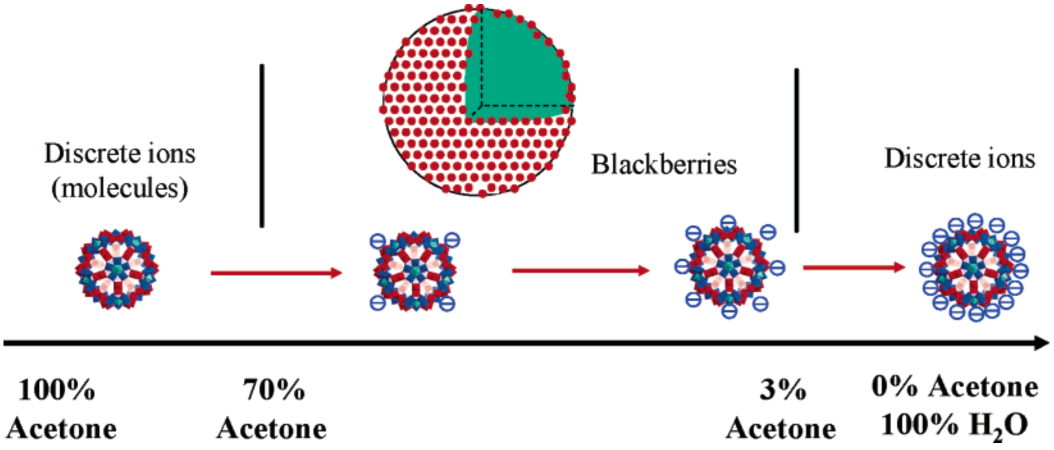

Figure 4. Complete transition of single macroanions—blackberry structures—macroanions is achieved by simply adjusting the solvent quality of the $\{Mo_{132}\}$/H_2O/acetone system.

University of Kentucky observed the formation of hollow, spherical, ∼20−40 nm diameter objects formed in highly concentrated $\{Mo_{132}\}$ solutions (including mother liquor) by TEM.[21,22] We believe that the structures Cammers et al. observed were the blackberry structures we refer to, as the results were very similar to those of other self-assembled POMs. The reason blackberry formation in dilute solutions was not observed may be due to the fact that the $\{Mo_{132}\}$ blackberry formation has a very high critical association concentration (CAC) in aqueous solutions. A high CAC value is quite possible since each $\{Mo_{132}\}$ anion can carry many charges. In comparison, each $\{Mo_{72}Fe_{30}\}$ macroanion only carries ∼7 localized charges in aqueous solution, leading to a very low CAC value.[15]

Status of Counterions in $\{Mo_{132}\}$/H_2O Solutions by pH and Conductivity Measurements. We speculate that the small counterions play an important role in determining the fascinating behavior of POM macroionic solutions. If this is true, some counterions could be closely associated with the macroions at very low concentrations, as observed in polyelectrolyte (including biomacromolecules such as proteins) solutions, which is called counterion condensation or counterion association.[16,36−44]

A major difference between POM macroionic solutions and most common polyelectrolyte solutions is that POM macroionic solutions do not contain additional small electrolytes, which provides an opportunity to use simple conductivity measurements to determine how many counterions are free in solution and how many are effectively associated with macroions.

After dialysis, the only anions in $\{Mo_{132}\}$ aqueous solutions are $\{Mo_{132}\}$, which are balanced by small cations including NH_4^+ (dominant) and H^+ released from the POM clusters. pH measurements directly determine the concentration of free H^+ ions, from which the contribution from H^+ ions to the total solution conductance can be accounted. Thus, the determined conductance value should be due to free NH_4^+ ions and $\{Mo_{132}\}$ macroanions. In previous work, it was determined that most NH_4^+ cations are free in very dilute $\{Mo_{132}\}$ solutions;[16] however, more NH_4^+ cations tend to associate with $\{Mo_{132}\}$ as

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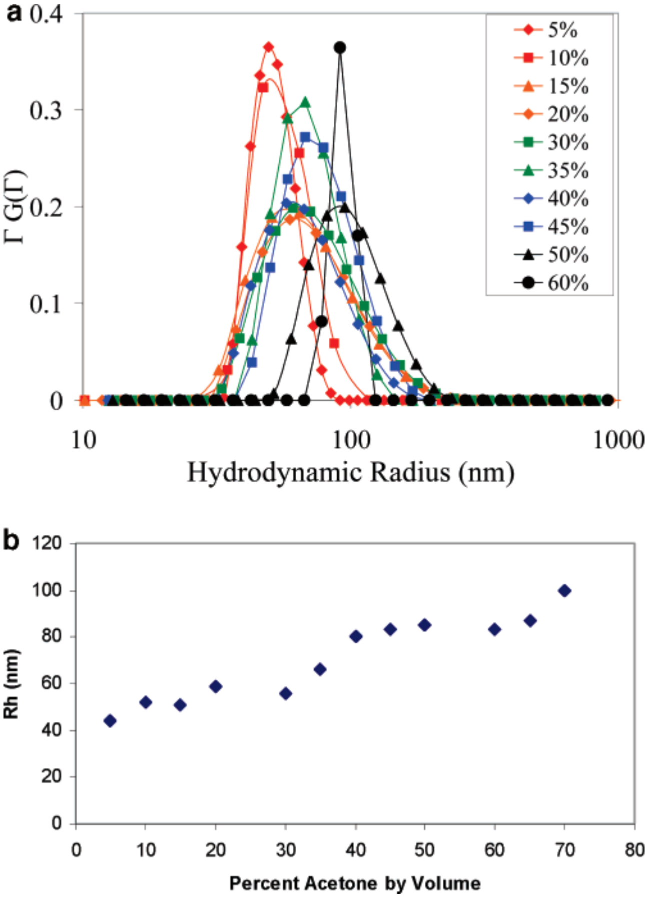

Figure 5. (A) CONTIN analysis of DLS study on 1.0 wt % {Mo_{132}} aqueous solutions of 5−60 vol % acetone. Experiments were performed at 90° scattering angle. (B) Average hydrodynamic radius (R_h) of the {Mo_{132}} blackberries in water/acetone mixed solvents measured by DLS (same experiments as those in part A).

macroionic concentration is increased. The observation of the increase of bound NH_4^+ is reasonable since we speculate there exist two extreme cases. First, all the cations are closely bound to the macroanions in {Mo_{132}} single crystals (concentrated “solution”). Second, in an infinitely dilute solution, all the cations are expected to be free.

Hill and Weinstock et al. used NMR to show that, in solutions of Keggin-type macroanions (∼1 nm size), all the small cations can be considered as “free ions” since the cation exchange between free ions and cation−macroanion pairs was very fast.[5] In our current case, the {Mo_{132}} anions are larger in size and carry more charges than the Keggins; therefore, it is reasonable to see stronger counterion association effect.

Status of Counterions in Water/Acetone Mixed Solvents. In less polar solvents (e.g., acetone), the association of counterions to {Mo_{132}} macroions could become more significant. To confirm this, the solution conductance of a series of 1.0 mg/mL {Mo_{132}} solutions in the mixed solvents of water and acetone with water content ranging from 10 to 100 vol % was studied. The conductivity of the {Mo_{132}} solutions decreased from 176.9 to 46.0 μS/cm, when solvent concentration of acetone is increased from 0 to 65 vol %, as shown in Figure 3. However, the molar conductance of ions usually becomes lower in a less polar solvent due to lower ionic mobility. This effect must be excluded in order to obtain the actual degree of counterion association. To achieve this, a series of 0.125 mg/mL NaCl solutions in mixed solvents was studied. NaCl is a strong electrolyte and expected to fully dissociate into discrete ions in dilute solutions of water/acetone mixed solvents. The conductance of 0.125 mg/mL NaCl solution decreases with increasing acetone content. If the degree of counterion association in {Mo_{132}} solution does not change with solvent quality, the same rate of conductivity decrease can be expected. However, a more significant decrease of {Mo_{132}} conductance than that of NaCl is obtained (Figure 3), which implies that, with higher acetone content, more NH_4^+ cations are associated with {Mo_{132}} and do not contribute to solution conductance. The measured solution conductance is mainly attributed to the presence of free cations, because the anions are excessively large and their contribution for the solution conductance is negligible.

Further calculations allow for the determination of both the associated and the free cations present on each {Mo_{132}} cluster. As the acetone content increases in {Mo_{132}} solution, the number of free cations decreases from 32.2 per {Mo_{132}} anion at 5 vol % acetone to 18.3 at 65 vol % acetone. When the solvent contains 70 vol % of acetone, the solution conductance is mainly from the free ammonium acetate ions in solution (10 per macroion, see the chemical formula in Figure 1, which results in a total conductance equivalent to 16 free NH_4^+ ions; no dialysis was performed for solutions of water/acetone mixtures). Thus, the {Mo_{132}} species are almost chargeless; i.e., counterions are almost stoichiometrically closely associated with {Mo_{132}} and move together. Correspondingly, the observed range for {Mo_{132}} blackberry formation was from ∼3 to 70 vol % acetone, as shown in the following text.

Self-Assembly of {Mo_{132}} Macroanions in Water/Acetone Mixed Solvents. LLS is a powerful tool for monitoring the formation of supramolecular structure in solution,[13−17] such that a continuous increase in scattered intensity by SLS and a new mode (usually with narrow distribution) identified by DLS indicate the blackberry formation. Blackberry formation in dilute {Mo_{132}} aqueous solutions was not observed, as confirmed by SAXS (Figure 2), SLS (very low scattered intensity from such solutions), and DLS (no mode corresponding to species with R_h > 10 nm).

At 1.0 wt %, {Mo_{132}} is not completely soluble in 100% acetone, but is soluble in solvents of <90 vol % acetone. Blackberry supramolecular structures of {Mo_{132}} were observed for dilute solutions between 3 vol % and 70 vol % acetone, based upon SLS and DLS results (Figure 4). A {Mo_{132}} solution shows a drastic increase in the scattered intensity when the large blackberries form. The average radii of gyration (R_g) of the blackberries can be obtained from SLS measurements. Likewise, CONTIN analysis of DLS measurements on such solutions shows a mode with average hydrodynamic radius (R_h) of approximately 25−100 nm, depending upon the solvent quality. The concentration effect on blackberry size (R_h) is negligible; therefore, an extrapolation of R_h and R_g values to zero concentration is not critical.

{Mo_{132}} macroions in solutions containing less than 3 vol % acetone do not show blackberry formation over a long period of time. In such solutions, the {Mo_{132}} macroanions are highly negatively charged; therefore, the strong repulsive electrostatic interactions prevent the blackberry formation. Furthermore, the blackberry formation is not observed in dilute {Mo_{132}} solutions because the blackberry formation is known to have a critical

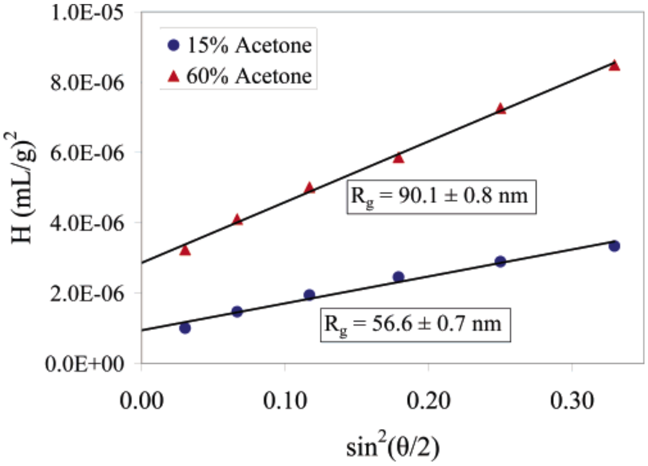

Figure 6. SLS studies at low scattering angles yield the radius of gyration (R_g) of $\{Mo_{132}\}$ blackberries.

association concentration (CAC). The CAC value could be fairly small, as with poorly charged "weak electrolyte" $\{Mo_{72}Fe_{30}\}$ solutions.[15] However, the CAC value for $\{Mo_{132}\}$ in aqueous solution could be very high and beyond the concentration of 1.0 wt % used in the current study. This explanation becomes more plausible when the fact that more cations associate with $\{Mo_{132}\}$ macroanions and decrease the charge density of the macroanions at higher $\{Mo_{132}\}$ concentrations is considered.

For the 1.0 wt % $\{Mo_{132}\}$ solutions containing 3−70 vol % acetone, blackberry structures with different average R_h but relatively narrow size distribution are observed by DLS. The blackberries formed in each different $\{Mo_{132}\}$ sample reflected narrow, parabolic ranges of R_h, Figure 5A. However, in solvents containing more than 70 vol % acetone, no $\{Mo_{132}\}$ supramolecular formation is observed over a long period of time and with heating. $\{Mo_{132}\}$ clusters become almost charged neutral and less soluble (1.0 wt % $\{Mo_{132}\}$ can be soluble in solvents containing <90% acetone) in such solvents, but the clusters remain as discrete clusters in solution. The nearly neutral charged $\{Mo_{132}\}$ clusters are unable to form the supramolecular structures and thus confirm that the existence of charges on macroions is critical for the blackberry formation. This process clearly proves that the van der Waals forces are not the major attractive forces responsible for the self-assembly of $\{Mo_{132}\}$ macroions. If van der Waals forces were the major attractive forces, more serious aggregation should occur in solutions with higher acetone content, as the loss of charge decreases the repulsive interaction between macroanions and does not greatly affect the van der Waals attractive forces. We have reached similar conclusions in studies of the "weak electrolyte" $\{Mo_{72}Fe_{30}\}$ macroions in water/methanol mixed solvents.[15]

Change of Blackberry Size with Solvent Quality. The average R_h of the blackberries clearly depends on the solvent quality. Increasing acetone content in solution results in the formation of larger blackberries. Average blackberry size changes from ∼30 nm in 5 vol % acetone solution to ∼100 nm in 70 vol % acetone solution, as shown in Figure 5B. The size distributions of the blackberry structures formed in different solvents are very similar (Figure 5A). The relationship between the R_h of the blackberries and the solvent quality (given as the inverse dielectric constant) is obvious. In a separate paper we present, with our collaborators, a general formula to describe the relationship between the R_h of blackberries and the solvent dielectric constant.[36]

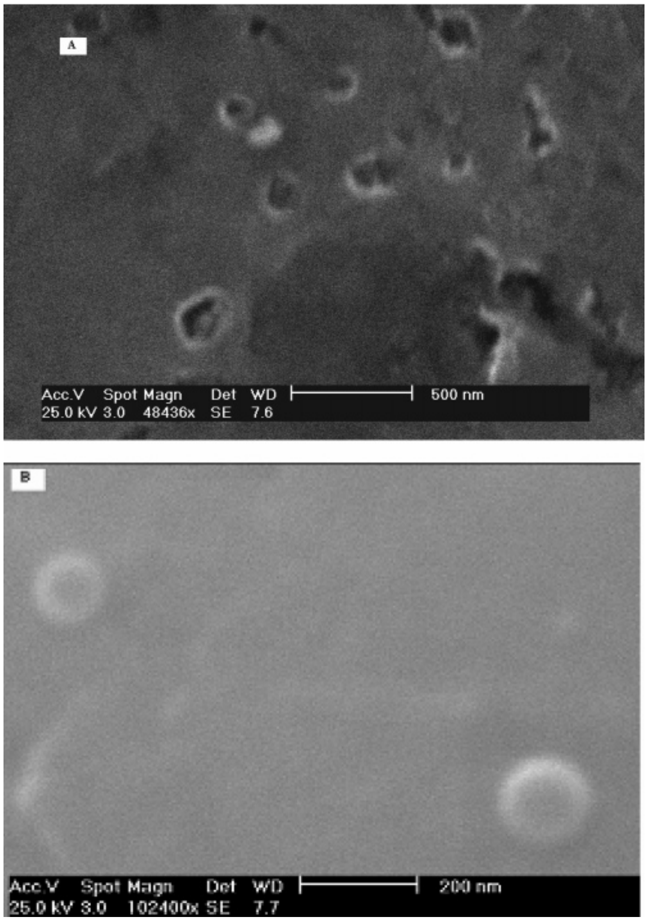

Figure 7. SEM images showing the hollow, spherical $\{Mo_{132}\}$ clusters in (A) 30 vol % acetone with radii between 35−110 nm and (B) 45 vol % acetone with a diameter of ∼150 nm.

SLS measurements at low scattering angles are used to obtain the radius of gyration (R_g) based on the Rayleigh−Gans−Debye equation,[44] as shown in Figure 6. The R_g of $\{Mo_{132}\}$ blackberries was determined as 56.6 ± 0.7 and 90.1 ± 0.8 nm for those in 15 and 60 vol % acetone, respectively. As mentioned earlier, the R_g of the blackberries only shows very weak concentration dependence; thus, extrapolation to zero concentration becomes less important. Since the values obtained for R_g and R_h are almost equal for all the supramolecular assemblies with different solvent quality, and the blackberries are spherical, as shown from SEM studies described below, the $\{Mo_{132}\}$ blackberry structures are confirmed as hollow, vesicle-like structures.

Information about the shape and size of the $\{Mo_{132}\}$ clusters was directly obtained through SEM examination. Figure 7 shows SEM micrographs of blackberries formed in 30 and 45 vol % acetone. The observed spherical particles have radii of 35−110 nm. The size of the $\{Mo_{132}\}$ clusters found by SEM is in agreement with the results of LLS studies.

Transitions of $\{Mo_{132}\}$ Supramolecular Structures in Solutions of Varied Solvent Quality. Blackberry structures are not easy to form due to the high-energy barrier between the two states: single macroanions and supramolecular structures. Furthermore, it is even more difficult to break the blackberry structure.[16−18] To our knowledge, the breaking or reassembly of blackberry structures by simply changing solvent composition

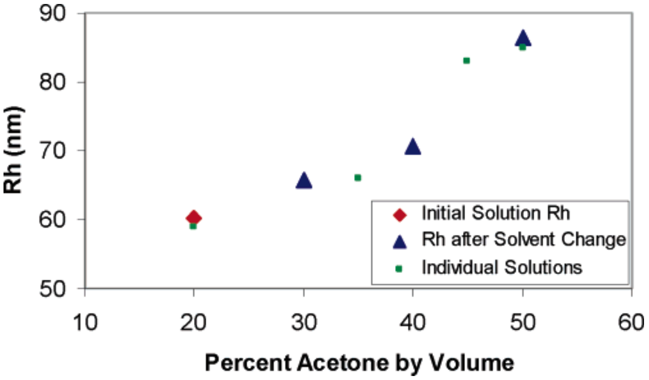

Figure 8. Average hydrodynamic radii of $\{Mo_{132}\}$ vs percent acetone by volume during solvent quality changes from 20 to 50 vol % acetone. The results of Figure 5B, in which blackberry sizes measured from individual solutions without the process of changing solvent quality, are also included for comparison.

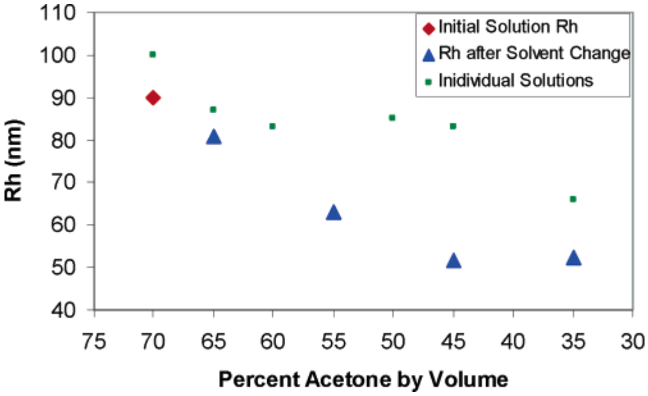

Figure 9. Average hydrodynamic radii of $\{Mo_{132}\}$ vs percent acetone by volume during solvent quality change from 70 to 35 vol % acetone. The results of Figure 5B are also included for comparison.

has not yet been reported, nor has change of the blackberry size by tuning the solvent quality been reported. We now describe a series of experiments which successfully achieve the formation and dissociation of the blackberry structures in water/acetone mixed solvents.

The 1.0 wt % $\{Mo_{132}\}$ solutions were prepared in water/acetone mixed solvents containing 20 and 70 vol % acetone, respectively. Upon the formation of blackberries in solutions, the solvent quality was changed by the addition of either acetone or water. For the 70 vol % acetone solution, water was added to change the solvent quality step by step to 65, 55, 45, and finally 35 vol % acetone. For the 20 vol % acetone solution, acetone was added stepwise to make solutions containing 30, 40, and finally 50 vol % acetone.

A $\{Mo_{132}\}$ solution initially prepared in 20 vol % acetone contained blackberries with an average R_h of ~60 nm and was in agreement with the R_h values in Figure 5B. With the addition of acetone to the solution, the R_h value increased after 3−4 days at 30 °C, as shown in Figure 8. It is clear that changing the solvent quality can change the $\{Mo_{132}\}$ blackberry size correspondingly. In addition, the new $\{Mo_{132}\}$ blackberry sizes are also in very good agreement with those from the original sample solutions having the same solvent quality. The reproducible formation of the $\{Mo_{132}\}$ blackberry clearly indicates that the blackberry formation is a thermodynamically favored process. Furthermore, the sizes of blackberries reported in Figure 5 are clearly in the thermodynamically stable states.

$\{Mo_{132}\}$ solutions initially prepared in 70 vol % acetone solution showed an average R_h of 90.1 nm. As the percentage of acetone in solution was decreased by the addition of water, the R_h value decreased accordingly (Figure 9). The R_h values of blackberries in solutions with solvent quality tuning are within the range of expected values for R_h (Figure 5B). The transition of $\{Mo_{132}\}$ in solvents changing from 70 to 35 vol % acetone again shows the size of the blackberry decreases with decreasing acetone concentration, as a result of increasing solvent dielectric constant.

During the study, the change in scattered intensity of the solutions was monitored by SLS. As the percent acetone by volume was increased, the intensity of the $\{Mo_{132}\}$ solution also increased. The increment of the scattered intensity may arise from two sources. First, the blackberries grow into larger sizes in response to the change of solvent quality. Second, there are more blackberries in solution with higher acetone content. To identify which factor is dominant, we can use the simplified Rayleigh−Gans−Debye equation[13,44] to

$$I \propto C{\cdot}M_w = C{\cdot}R_h^{\,2} \tag{2}$$

where I, C, and M_w are the scattered intensity from blackberry solution, the blackberry concentration, and mass, respectively. The scattered intensity was 5 times greater when the volume percent of acetone increased from 20 to 50 vol %, while the R_h of blackberries increases from 60 to 86 nm. From eq 2 the conclusion is that more blackberries were formed at higher acetone content, suggesting that the higher acetone content (or lower dielectric constant) is favored by the blackberry structure, in the current experimental regime.

More interesting phenomena were observed by SLS during the above experiments. On average 6 days are required for the initial blackberries to form; however only 3 days are required for the blackberry transition to occur. The time required for blackberry formation indicates that the addition of acetone to the solution does not completely destroy the blackberries present in the initial solution and that the blackberries are allowed to re-form during the transition from one solvent quality to the next.

State of Counterions in Blackberry Solutions. The mean ζ potentials of the blackberry structures in water/acetone solutions were determined by ζ potential analysis. For a 0.5 mg/mL $\{Mo_{132}\}$ solution, the ζ potential values range from −9.13 to −49.48 mV depending on the acetone content in solvent. It is expected that the ζ potentials of the blackberry structures also depend on the solvent dielectric constant, but only logarithmically.[36] To determine the charge on the surface of the $\{Mo_{132}\}$ blackberries, ζ potential studies were performed. The ion mobility is related to the charge on particles via the Hückel equation

$$\mu_0 = q/6\pi\eta r \tag{3}$$

where μ_0, η, q, and r are the absolute mobility of particles at zero buffer ionic strength, the solvent viscosity, the charge on particles, and the particle radius, respectively.[45,46] In our current case, the solution contains no buffer ions; thus, the measured mobility is μ_0. The average total charge on each $\{Mo_{132}\}$

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(46) Roy, K. L.; Lucy, C. A. *Anal. Chem.* **2001**, *73*, 3854.

blackberry-type structure, dependent upon the solvent quality of each solution, is estimated as −61 to −200, where the negative sign denotes negative charges. The absolute charge decreases as more acetone is added. Since the total number of $\{Mo_{132}\}$ clusters on each blackberry can be estimated from SLS (over 1000 macroions), the number of charges per cluster can be calculated, which ranges from 0.1 charges for solution containing 10 vol % acetone to 0.02 charges for solutions containing 60 vol % acetone. Considering that each $\{Mo_{132}\}$ macroanion carries at least 42 negative charges in crystals, it is clear that most cations are strongly associated with large blackberries in dilute solutions.

Conclusion

We report the discovery of the first discrete macroion−blackberry−discrete macroion transition by using $\{Mo_{132}\}$/water/acetone as a model system. The continuous, highly reproducible transitions achieved by simply adjusting the solvent quality reveal important properties of the blackberry formation, a new type of self-assembly process with intriguing driving forces. The behavior of the $\{Mo_{132}\}$ in water/acetone solutions exemplifies that the presence of the counterions in solution is critical to the solution behavior of macroions. The blackberry formation and dissociation of $\{Mo_{132}\}$ macroions are closely related to the charge density on the macroions. No blackberry formation occurs when the POM clusters are chargeless or carry too many charges. The states of small counterions in solutions containing discrete $\{Mo_{132}\}$ macroions and large blackberry structures were also studied.

Furthermore, the size of $\{Mo_{132}\}$ blackberries is found to be directly related to the solvent dielectric constant, with R_h being 25 nm in 3 vol % acetone solution and 100 nm in 70 vol % solution. After the blackberries are formed in a given solution, their sizes can be accurately tuned by adjusting solvent quality, suggesting that the blackberry structure is truly the thermodynamically stable state.

Our work strongly shows that the blackberry formation is a new type of free-energy-favored self-assembly behavior for various types of macroions in polar solvents. The simple, rational control of the formation and dissociation of the blackberry structures, as well as the accurate size control of their nanoscaled self-assembled structures, may find applications in different fields.

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