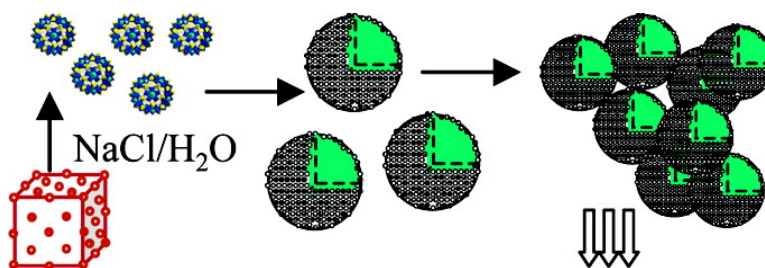


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Automatic and Subsequent Dissolution and Precipitation Process in Inorganic Macroionic Solutions

Guang Liu,^{†,‡} Yuguang Cai,[†] and Tianbo Liu^{*,†,‡}

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973, and Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

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Dissolution and precipitation are two opposite processes for solutes in solutions. It is common knowledge that for a specific solute–solvent system at a fixed external condition, only one of them (the free-energy favored one) can automatically occur. It is very rare to see both processes, driven by free energy, occur automatically and subsequently in the same system without any change of external conditions or chemical reactions. Here, we report such an interesting phenomenon in the aqueous solution of a type of inorganic macroions.

Single crystals (space group $R\bar{3}$) of 2.5 nm size, C₆₀-like hollow, spherical heteropolyoxometalate compound {Mo₇₂Fe₃₀} (Mo^{VI}₇₂Fe^{III}₃₀·O₂₅₂L₁₀₂·(~180H₂O) with L = H₂O/CH₃COO⁻/Mo₂O_{8,9}ⁿ⁻), prepared by following the established procedures,¹ were used for the current study (Figure 1b). The giant {Mo₇₂Fe₃₀} clusters are neutral in charge in crystals but exist as giant anions in solution. Each anion carries several negative charges in aqueous solution due to the partial deprotonation of the H₂O ligands chemically attached to the Fe^{III} ions.^{1,2} The macroions exist as discrete ions when first dissolved in solution but then very slowly self-assemble into a more stable single-layer, vesicle-like “blackberry” structure (Figure 1c).^{3,4} The major driving forces of this unique self-assembly are believed to be the “like-charge attraction” effects,⁵ along with van der Waals force and possible temporary Fe–O···H–O–Fe interactions between adjacent anions. The details on this issue will be discussed elsewhere.

In our current experiments, yellow {Mo₇₂Fe₃₀} crystals were added into different aqueous solutions containing 0.1–3% NaCl in order to make 0.5 mg/mL {Mo₇₂Fe₃₀} solutions. (In 3% NaCl solution, the solubility of {Mo₇₂Fe₃₀} is lower, and ~0.4 mg/mL solution was prepared.) As the mixture was stirred, the crystals were quickly dissolved to form light yellow solutions. The homogeneous solutions were dust-freed by 0.1 μm filters and then sealed and placed at room temperature without any disturbance. After some days (depending on NaCl concentration), yellow precipitates again appeared gradually at the bottom of containers where the bulk NaCl concentration was >0.3% (Figure 1d). From visual observation, the whole process looks like a cycle of solid–solution–solid without any change of external conditions. It is known that the {Mo₇₂Fe₃₀} clusters can stay stable in aqueous solution for a very long time (over years); their single crystals were originally grown from NaCl/H₂O solutions, so we do not expect that any chemical reaction has occurred and led to the precipitation. There must be some interesting physical phenomena behind it. We used laser light scattering and AFM measurements to monitor the whole process. The experimental conditions and the basis of static and dynamic light scattering (SLS and DLS) can be found in our earlier publications.⁶

SLS measurement showed very low scattered intensity when the single crystals of {Mo₇₂Fe₃₀} were freshly dissolved in NaCl/H₂O

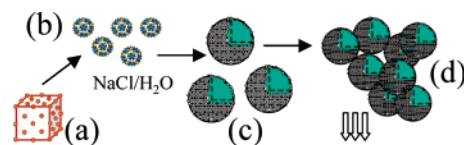


Figure 1. An automatic dissolution–precipitation process in aqueous solutions of {Mo₇₂Fe₃₀} and NaCl. (a) {Mo₇₂Fe₃₀} single crystals (solid phase); (b) {Mo₇₂Fe₃₀} anions in NaCl/H₂O solution; (c) {Mo₇₂Fe₃₀} vesicle-like “blackberry” structure formation; (d) aggregation and precipitation of {Mo₇₂Fe₃₀} blackberries (solid phase).

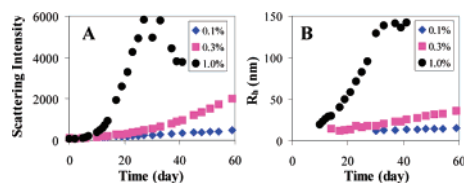


Figure 2. Increment of the scattering intensity (A) and R_h (B) at 90° scattering angle with time of 0.5 mg/mL of {Mo₇₂Fe₃₀} in 0.1, 0.3, and 1% NaCl aqueous solutions.

solutions (Figure 2a), suggesting that almost all of the {Mo₇₂Fe₃₀} clusters existed as discrete ions in solution at this moment, very similar to the situation of dissolving {Mo₇₂Fe₃₀} crystals in pure water.⁴ The scattered intensities from {Mo₇₂Fe₃₀}/NaCl/H₂O solutions continuously increased during the following days (Figure 2a), similar to those from the {Mo₇₂Fe₃₀}/H₂O solutions, suggesting the continuous formation of large species. CONTIN analysis⁷ of the DLS results indicated a new mode appeared, corresponding to a hydrodynamic radius (R_h) of ~20–25 nm (Figure 2b). It is attributed to the {Mo₇₂Fe₃₀} blackberries, as we reported before in NaCl-free solutions.³ In NaCl-free solutions, the size of blackberries does not change during the whole growing process, and the final blackberry solution is still a stable “real solution”; the solutes do not grow, aggregate, or precipitate even when heated or centrifuged, distinguishing them from colloidal suspensions. The presence of small amount of NaCl in solution (e.g., 0.1 mg/mL) does not introduce noticeable changes in solution behavior. The R_h of the blackberries does not change with time (Figure 2b). However, when the NaCl concentration is >0.3%, two obvious differences are observed. First, the blackberry formation is much faster (as indicated by the increment of scattered intensity) in the presence of NaCl once it started. (There might be a minor delay in the first several days, depending on the concentrations of NaCl and {Mo₇₂Fe₃₀}). Second, the average R_h of the aggregates continues to increase with time, with a broader size distribution. When the aggregates became larger and larger, finally they precipitated from the solution. For {Mo₇₂Fe₃₀} in 1% NaCl solutions, both scattering intensity and R_h increased continuously for the first 33 days (Figure 2). Then the R_h value kept almost constant, indicating that the blackberries stopped growing, while the scattering intensity dropped down due to precipitation. Blackberry aggregation and precipitation both become faster at higher NaCl concentrations or temperature. For

[†] Brookhaven National Laboratory.

[‡] Lehigh University.

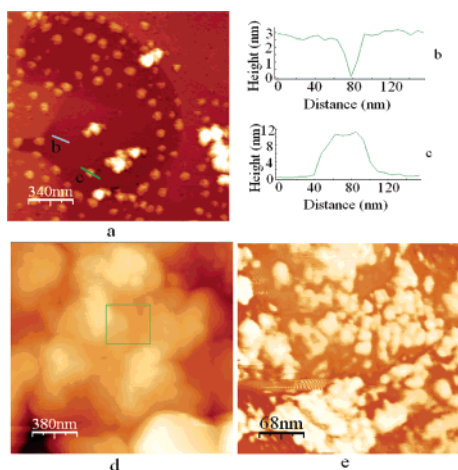


Figure 3. AFM study of the precipitates from $\{\text{Mo}_{72}\text{Fe}_{30}\}/\text{NaCl}$ aqueous solution on gold (111) substrate. (a) Image showing single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ blackberries (40–60 nm diameter) sitting on a full layer of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ single ions (2.5 nm diameter). Image size: $1.7 \times 1.7 \mu\text{m}$. (b) Line profile across a defect region in Figure 3a. (c) Line profile across a blackberry. (d) AFM topographic image of the precipitates obtained from the bottom of the containers. Image size: $1.9 \times 1.9 \mu\text{m}$. (e) A phase image offers a close look at the precipitates. They are formed by the irregular aggregation of blackberries. Image size: $0.34 \times 0.34 \mu\text{m}$.

example, the 0.3% NaCl solution showed similar behavior but took a longer time; in 3% NaCl solutions, a large amount of precipitation can be observed in only 1–2 days after the total dissolution of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ crystals.

The increase of R_h from DLS can be due to either the growth of the individual blackberries or the further aggregation of many blackberries. The latter explanation is preferred because the DLS and SLS results show that the large aggregates are highly anisotropic in shape. The R_h of the large particles in $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solution (with 1% NaCl) has broad distribution and obvious angular dependence, with a value of 336 nm at 0° degree ($R_{h,0}$). At the same time, the radius of gyration (R_g) of these large aggregates obtained from an SLS study is ~ 629 nm (i.e., $R_g/R_{h,0} \sim 1.87$), suggesting that the aggregates have nonspherical morphology.

The conclusion above is confirmed by AFM studies.⁸ Under AFM examination, the gold substrate surface is uniformly covered by layer(s) of $\{\text{Mo}_{72}\text{Fe}_{30}\}$, which yields the low surface roughness and high reflectivity (Figure 3a). The layer also shows defect, where some $\{\text{Mo}_{72}\text{Fe}_{30}\}$ are missing (Figure 3b), and the line profile indicates that the thickness of the layer is 2.5 nm, which is the diameter of single $\{\text{Mo}_{72}\text{Fe}_{30}\}$ clusters. There are also many spherical objects with diameters of ~ 25 – 50 nm adsorbed on the homogeneous layer of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ single clusters, which should be attributed to the blackberries observed by DLS. The heights of these objects are around 10 nm (Figure 3c). It is obvious that the blackberries are collapsed due to the interaction with the surface. Moreover, the heights of the blackberries continue to decrease when exposed in air on the gold surface, as a result of losing internal water. When the same blackberry is tapped with different forces, the horizontal shape (in X – Y plane) of the blackberry remains the same, while its topography changes. This is new evidence to show that the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions form soft, hollow structures, instead of solid aggregates.³

Figure 3d is an AFM topographic scan of the large, irregular domains, which are attributed to the yellow precipitates. Figure 3e is a zoom-in AFM phase scan that shows the structures within the square box in Figure 3d with a higher resolution. Figure 3e clearly shows that the amorphous structure in Figure 3d is a random packing of blackberries with sizes around 25–50 nm. From these

images, it is very clear that the precipitates do not have any crystalline structure, which distinguishes them from $\{\text{Mo}_{72}\text{Fe}_{30}\}$ single crystals, the starting material. Furthermore, the AFM results also indicate that the large aggregates (> 300 nm radius) detected by DLS and SLS are not single giant blackberries, but random aggregation of many 25–50 nm radius “regular blackberries”. In summary, the whole process has three steps. Crystals of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ dissolve in water to give discrete $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macroanions, more and more discrete $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions continuously self-assemble to blackberry structures, and blackberries aggregate to larger particles until they continuously precipitate from solution, as shown schematically in Figure 1.

Without additional salts, the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macroionic solution in the free-energy favored blackberry state is very stable. However, the blackberries have lower vulnerability than the discrete $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions in the presence of additional electrolytes due to their much larger sizes. A small amount of additional salts considerably shortens the screening length of the blackberries and leads to their aggregation when there are enough of them in solution, a typical result based on the DLVO theory.⁹ On the contrary, it is much more difficult to achieve the same “salting-out” effect on the discrete $\{\text{Mo}_{72}\text{Fe}_{30}\}$ anions, which are stable in solution until $\sim 10\%$ NaCl is added.

Finally, due to the unique slow blackberry formation,⁴ the $\{\text{Mo}_{72}\text{Fe}_{30}\}/\text{NaCl}$ solutions are able to stay as a clear solution for a considerably long time before precipitation gradually appears, making a strong impression for a cycle process. We will not be able to observe if the blackberry formation completes quickly. The first half of the whole process (dissolution) is the same as that of regular soluble inorganic salts, while the second half of the process (precipitation in the presence of electrolytes) is similar to that of lyophobic colloids. The two parts are linked by the fact that the macroions have two solution states: an entropy-favored state (homogeneous distribution) and a free-energy favored second solute state (blackberries). Understanding the unique solution behaviors of such macroionic systems will help us when exploring their biomedical applications since buffer solutions also contain salts.

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