

Hydrophilic Inorganic Macro-Ions in Solution: Unprecedented Self-Assembly Emerging from Historical “Blue Waters”

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Our story starts when *phlogiston* (derived from the Greek “to burn”) was thought to be involved in any kind of combustion, that is, redox processes. The underlying theory was originated by Johann Joachim Becher (1635–1682) in the late 17th century and extended by Georg Ernst Stahl (1660–1734). It states that flammable materials contain *phlogiston*, a substance without color, taste, or weight that is liberated on burning. Once burned, the dephlogisticated substance was then in its “true” form, the *calx* (chalk). This way of thinking influenced the early chemists for almost a century. The discoverers of oxygen, Carl Wilhelm Scheele (Sweden) and

Joseph J. Priestley (England) were phlogistonists while Antoine de Lavoisier (France) was the first leading anti-phlogistonist.

In fact, it was Scheele (1a) who described the first reproducible experiment related to the “molybdenum blue solutions” that were obtained by a redox process. It should be noted that Scheele discussed this with another Swedish chemist, Torbern Bergmann (1735–1784; ref 1b). Interestingly, such blue solutions also exist naturally: centuries ago the Native Americans observed the “blue waters”—the solution of natural *soluble molybdenum blue* formed by partial oxidation of molybdenite, MoS_2 (forming the mineral ilsemannite, approximate formula $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$) near today's Idaho Springs and the Valley of the Ten Thousand Smokes (2). In *Chemische Untersuchung über das Molybdänum oder Wasserbley* (Chemical Studies on Molybdenum or Water Lead), which refers to work done between 1778 and 1783, Scheele was already aware that molybdenum blue was a reduced molybdenum oxide (i.e., in his terms, containing *phlogiston*). However, it took almost forty years before Jöns Jakob Berzelius reported the first formula for the blue powder isolated from such solutions (3). Over time, this analysis has been repeated by several groups with slightly varying results ($\text{MoO}_x \cdot n\text{H}_2\text{O}$, $x = 2.5\text{--}2.96$, $n = 3\text{--}5$) (2), owing to, as we now know, the formation of species with varying degrees of reduction and, therefore, differing compositions. Although Wilhelm Biltz in 1903–1905 found negatively charged species of colloidal size in these solutions, the question of the respective cations was never raised. Even Duclaux and Titeica (1929), who found that the solutions of molybdenum blue flocculated when positive colloids such as $\text{Al}(\text{OH})_3$ or electrolytes such as NaCl were added, did not refer to this point. A possible reason might be that the molecular mass of the solutes from the molybdenum blue solutions obtained from freezing point depression experiments by Marchetti (1899) and Dumanski (1910) was 440–481 g/mol, similar to that of a single Mo_3O_8 entity (416 g/mol). Thus most of the early researchers regarded those solutes as small single molecular entities of this composition (neglecting the contribution from the cations). This interpretation remained state-of-the-art until almost the end of the 20th century when chemists succeeded for the first time to get crystals from these solutions. However, it took more than two years from the first preliminary published data (4) to determine the exact formula of the first crystalline compound, that is, $(\text{NH}_4)_{28}[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{448}\text{H}_{14}(\text{H}_2\text{O})_{70}] \cdot n\text{H}_2\text{O}$ containing the $\{\text{Mo}_{154}\}$ giant wheel cluster anions (Figure 1), (5). One reason was due to the problem in determining the number of protons. This compound was obtained from the blue solutions when hydroxylamine was used as the reducing agent (4).

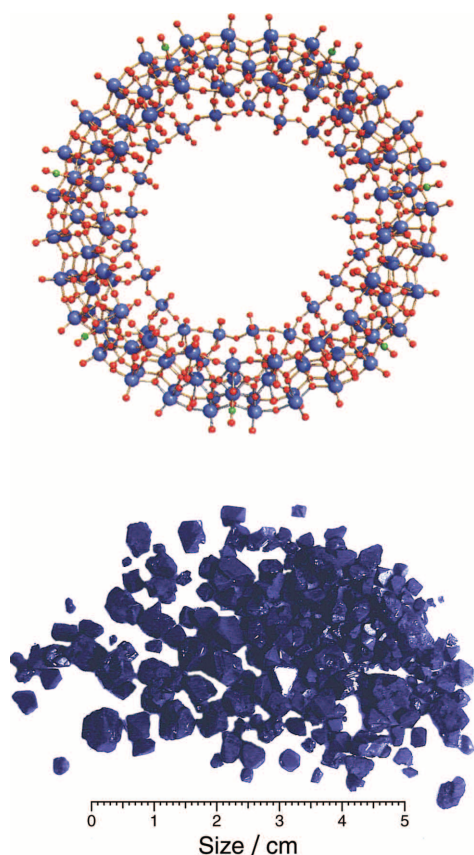


Figure 1. (top) Ball-and-stick presentation of the $[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{448}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{28-}$ cluster anion (view parallel to the approx. C_7 axis; Mo-large dark gray, N-small dark gray, O-small light gray. (bottom) Crystals of “molybdenum blue” that today normally are synthesized by using reducing agents like hydrazine or dithionite. In that case the 14 MoNO^{3+} are replaced by 14 MoO^{4+} groups (for the corresponding formula see refs 5, 6).

From the first crystal structure, it became evident why earlier trials failed to result in a crystalline material, namely, because the anion has a high solubility in water owing to the presence of a hydrophilic surface of the $\{\text{Mo}_{154}\}$ -type cluster anion caused by a large number of coordinated H_2O ligands (5, 6*b–e*, 7*a*, 8). This information resulted in the development of a facile synthetic method: by destroying the hydration shell and thus decreasing the solubility crystals formed. Since this breakthrough pure crystalline materials, not only containing giant, wheel-shaped species (7*b*, 8), but also of hollow, spherical- (6, 7*b*) and “hedgehog”-shaped (7*c*) clusters, with radii in the several nanometers range, were synthesized and structurally characterized. Such giant polyoxomolybdates (POMs) are formally formed by connecting MoO_6 or MoO_7 polyhedral units via corners or edges (for structural details, see refs 5, 6). Here we describe our recent progress on the characterization of supramolecular structures formed by these highly soluble inorganic species in dilute solution, which has led to the discovery of a new solute state of inorganic ions. The amazing solution behavior of the molybdenum blues links those of simple inorganic ions and of many complex systems, including polyelectrolytes, colloids, and biological macromolecules.

Remaining Puzzle—Soluble But Still Aggregate

The discovery and structural characterization of the wheel-shaped giant polyoxomolybdates offered an answer to the historical “blue waters” puzzle. However, it still did not answer the next puzzle: the Tyndall effect observed from those solutions, as shown in Figure 2. As we know, the Tyndall effect is the result of scattered light from suspended particles of colloidal size and is not expected to appear in classical inorganic salt solutions containing homogeneously distributed soluble inorganic ions. These giant wheel-shaped anions are highly soluble in water or other polar solvents such as alcohols and acetone, in spite of their size. However, we found that they do not persist as discrete ions, obviously contradicting our common knowledge; instead, they tend to further aggregate into large spherical assemblies (9). The “aggregates” do not look like regular aggregates formed by less soluble species, which usually have broad size distributions and tend to continue to grow until precipitating from the solution. Our supramolecular structures formed by the wheel-shaped macroions have different properties: they might even be fairly stable in solution and are hollow. An energy dispersive X-ray spectroscopy analysis (EDX) showed considerable quantities of solvent existing inside the aggregates, while the aggregates could suddenly burst when switching the scanning electron microscope (SEM) from environmental mode to the high-vacuum mode (9). In addition, a surprisingly narrow size distribution of the aggregates formed by the blue wheels was also observed employing dynamic light scattering (DLS). These findings attracted us to further pursue this problem.

By realizing that the radii of the giant anions (2–6 nm) and the aggregates (50–500 nm) are in the range of colloidal particles, we realized that laser light scattering techniques (LLS) (10), that is, both static and dynamic light scattering (SLS and DLS) measurements, would be useful for obtaining information about those macro-ionic solutions. LLS is particularly suitable for studying solutes in solution and par-

ticle suspensions with sizes between 1–1000 nm. These methods are widely used for the characterization of polymer solutions and colloidal suspensions. On the contrary, regular inorganic molecules or ions are too small to be detected by LLS.

In general, by detecting the interactions between the solute particles in solution and the probing radiation (visible laser light), LLS measurements can give information on some physical properties of solute particles, such as particle molar mass, size, shape, and internal structure. Figure 3 shows a commercial spectrophotometer capable of performing high quality SLS and DLS experiments.

SLS measures the scattered intensity from sample solutions at different scattering angles and concentrations. This results in information about the particles in solution, such as weight-average mass (M_w) and radius of gyration (R_g), as well as the nature of interparticle interactions. SLS data are usually treated by the Zimm plot. On the other hand, DLS measurements are used to determine the hydrodynamic radius (R_h) and the size distribution of particles (e.g., polymers, colloids, or biomacromolecules) in solution, by using special software such as CONTIN (11). Detailed descriptions of the

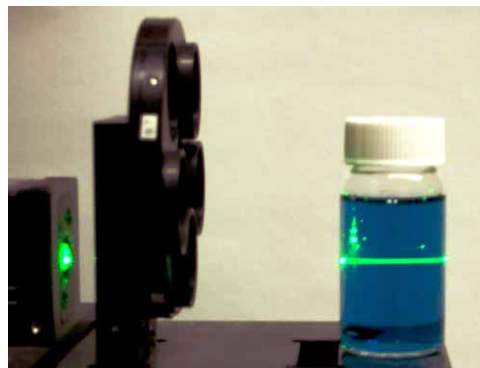


Figure 2. The Tyndall effect is observed in various “molybdenum blue solutions”. The example refers to an aqueous solution of $\{\text{Mo}_{154}\}$ -type wheel-shaped clusters, where a green laser beam traversing the blue solution becomes visible owing to scattering.



Figure 3. A commercial laser light scattering spectrophotometer. Picture courtesy of Brookhaven Instruments Inc.

SLS and DLS techniques can be found in monographs (10) or book chapters (12).

Characterization of POM Supramolecular Structures—Strong Electrolyte Regime

Detailed SLS and DLS measurements of the aggregates formed by highly soluble $\{\text{Mo}_{154}\}$ -type macro-ions are described in ref 13. The parent solution was prepared using

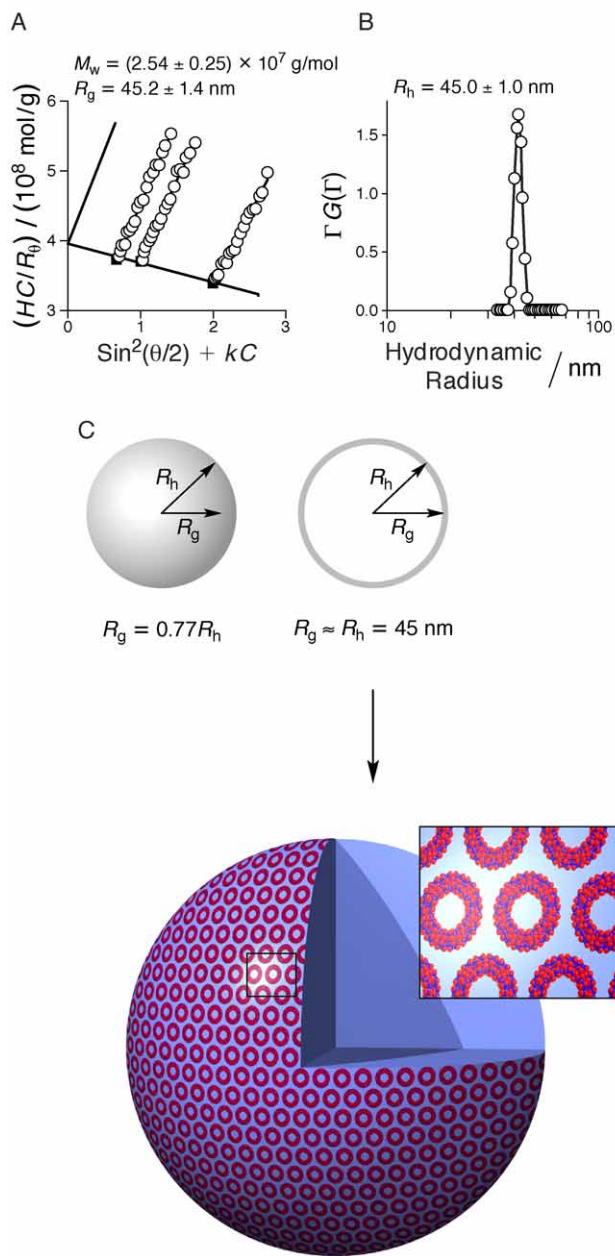


Figure 4. (A) Zimm plot based on SLS measurements on $\{\text{Mo}_{154}\}$ aqueous solutions (three different concentrations are measured), showing an average R_g of $\sim 45 \text{ nm}$. (B) CONTIN analysis of DLS data (scattering angle = 60°) on the same solution, showing an average R_h value of $\sim 45 \text{ nm}$ [cited from ref 13, Figures 2 and 3, respectively]. (C) For spherical particles, $R_h = R_g$ suggests that all the mass is distributed on the surface of the sphere, that is, a vesicle structure.

the pure crystalline product $\text{Na}_{15}[\text{Mo}^{\text{VI}}_{126}\text{Mo}^{\text{V}}_{28}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]_{0.5}[\text{Mo}^{\text{VI}}_{124}\text{Mo}^{\text{V}}_{28}\text{O}_{457}\text{H}_{14}(\text{H}_2\text{O})_{68}]_{0.5} \cdot [\sim 400\text{H}_2\text{O}]$ (7a, 8). This mixed crystal compound contains two anions: the first corresponds to that given in the caption of Figure 1 (but with 14 MoO^{4+} instead of 14 MoNO^{3+} groups) and the second to the same anion but with a minor defect (for details see ref 5). A CONTIN analysis of the DLS measurement shows that the $\{\text{Mo}_{154}\}$ macro-ions aggregate in solution into larger, almost monodisperse structures with an average R_h of $\sim 45 \pm 1 \text{ nm}$ (Figure 4B). SLS data show that the average R_g of the aggregates is $45.2 \pm 1.4 \text{ nm}$ (Figure 4A), which means $R_g = R_h$. While it is known that for a solid spherical particle $R_g = 0.77R_h$ (Figure 4C), the ratio R_g/R_h increases if more mass in a sphere is distributed closer to the surface. We also know that the aggregates are spherical from the TEM pictures shown in Figure 5. If a spherical object has all its mass on its surface, R_g/R_h approaches 1, which corresponds to a typical model for a hollow sphere (Figure 4C). Consequently, our results indicate that the aggregates in solution are not solid clusters, but vesicle-like hollow spheres.

More interestingly, the mass of the aggregates (M_w) as determined by SLS is $(2.54 \pm 0.25) \times 10^7 \text{ g/mol}$ corresponds to ~ 1165 single $\{\text{Mo}_{154}\}$ wheels. This M_w value also suggests a hollow interior of the aggregates because a solid $\{\text{Mo}_{154}\}$ -type nanocrystal of 45-nm radius would contain the much larger number of individual $\{\text{Mo}_{154}\}$ macro-anions, greater than 14,000, and would be, therefore, much heavier. In our structural model, as shown schematically in Figure 4C, all the molecular giant wheels are homogeneously distributed to form a *single* layer on the surface of the “vesicles”, with their molecular isotropic xy plane parallel to the surface. This model can reasonably explain how such giant wheels can form uniform, spherical, higher-level aggregates. Based on this M_w value, it is estimated that the average closest center-to-center distance between two adjacent $\{\text{Mo}_{154}\}$ anions is $\sim 4.9 \pm 0.4 \text{ nm}$. Considering that the diameter of the $\{\text{Mo}_{154}\}$ anion is $\sim 3.6 \text{ nm}$ (6, 7a, 8), it follows that the cluster anions are not touching each other in the “vesicles”. The term vesicle is widely used for bilayer hollow spherical assemblies by the close packing of surfactants or biolipids. However, our current supramolecular structure is fundamentally different and we give it the nickname of “blackberry” as it shares a similar shape and dark-blue color of the well-known fruit. The water components inside the blackberries do not contribute to the scattered intensity so that the measured M_w does not include them, otherwise their actual M_w would be >10 times greater.

High-resolution transmission electron microscope (TEM) studies can directly confirm the above results (13). Figure 5A shows a typical TEM image of the $\{\text{Mo}_{154}\}$ -type blackberries as obtained in aqueous solution. Figure 5B displays a broken blackberry, which clearly shows that the vesicle wall is thin and is hollow inside. Figure 6A is a magnification from a patch of a broken blackberry wall flattened on the support carbon film. No long-range ordered packing of $\{\text{Mo}_{154}\}$ wheels on the burst blackberry surface was observed, but some ordered packing was observed in small local areas (Figures 6D and 6E). The lattice spacings are in the range of $3.6\text{--}4.2 \text{ nm}$, similar to the size of $\{\text{Mo}_{154}\}$, suggesting that the wheels form the blackberry surface.

Blackberry structures have been observed for “strong electrolyte”-type blue POM macro-ions in water and additionally in polar solvents (the term “strong electrolyte” corresponds to the presence of H^+ and other cations). For example, $\{Mo_{154}\}$ anions were found to form even larger blackberries in acetone. The $\{Mo_{176}\}$ cluster, the corresponding larger wheel-shaped anion (14), also forms uniform, 70-nm radius spherical blackberries in aqueous solution at pH = 2.3 (15). Recently, we observed the blackberries formed by the largest structurally characterized POM $\{Mo_{368}\}$ (7c) in water/acetone mixed solvent (15). Zhu et al. reported that the Keplerate-type (C_{60} -like) POM anion $\{Mo_{132}\}$ (7b) also forms spherical supramolecular structures of a hollow nature (~40-nm diameter), which could be identified by TEM measurements (16, 17).

Moreover, many polyoxometalate giant clusters with totally different electronic and surface structures, such as the giant molybdenum–iron–oxide cluster $\{Mo_7Fe_{30}\}$ (18) and the tungsten–oxide cluster $\{W_{48}Cu_{20}\}$ (19), can also self-assemble (15, 20). Such processes, however, show thermodynamic and kinetic features and driving forces (21, 22) quite different from those of the macro-ions in the “blue waters”.

What Is the Driving Force Behind the Self-Assembly?

The term self-assembly suggests that such processes can occur spontaneously, that is, are favored by negative free energy changes. However, assembling species together from a homogeneous distribution is usually an entropy-loss process. Therefore, some driving forces must exist in the self-assembly process to compensate for the loss of entropy. For example, hydrophobic interactions are important in assembling amphiphilic surfactant-micelle and bilayer-vesicle structures (23). The hydrophobic interaction is a short-range force; therefore, in regular lipid vesicles we can always observe closely packed hydrophobic regions stabilized by outside hydrophilic parts. But here, each molybdenum blue ion is covered with a “layer” of H_2O ligands that make them strongly hydrophilic. Therefore the mechanism of this self-assembly must be substantially different from those of amphiphilic surfactants.

It is obvious that a delicate balance between attractive and repulsive forces makes the blackberries stable. The repulsive force is due to the electrostatic interaction between the giant anions while the attractive forces are more complicated. Besides the unlikely hydrophobic interaction, the contribution from attractive van der Waals forces can also not account for the attraction as we have shown (24). We believe that the counterion effect (so-called like-charge attraction) could be an important factor, because the strong attraction among giant anions leading to the blackberry formation occurs only when the macro-ions carry enough (although not too many) charges. The counterion effect has been described before by scientists dealing with polyelectrolyte solutions (25–28) and colloids such as latex particles (29–32) as well as many biological macromolecules such as DNAs and proteins (33). It suggests that the macro-ions are surrounded in solution by many small counter ions, here H^+ , Na^+ , or NH_4^+ . The POMs are naturally repulsive towards each other. However, when two macro-ions approach close enough the counter ions will share two macro-ions and as the result, act

as “connectors” to help keep the two macro-ions a short distance from each other. Such interactions eventually help to maintain the large hollow, spherical blackberry structure. It should be noted that conductivity measurements indicate that a large fraction of small counterions (e.g., H^+ , Na^+ , or NH_4^+) cannot move freely, even in very diluted solutions. They are closely associated with POM macro-ions, leading to a lower solution conductance value than expected (34). Recently, we found that the blackberry structure does not form if the giant, discrete clusters do not carry net charges; in other words, blackberry formation only occurs when the clusters are charged (24).

In the blackberries, the wheel-shaped anions are not directly touching each other. There must be other entities to fill this space: most likely the solvent (preferably water) (13). In Figure 5, the burst blackberry exhibited a wrinkle feature and a high contrast around the edge (typical for an empty

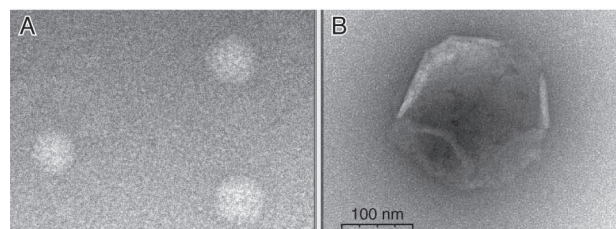


Figure 5. (A) Transmission electron micrograph of some blackberries. (B) A larger, broken vesicle showing the thin-walled hollow nature.

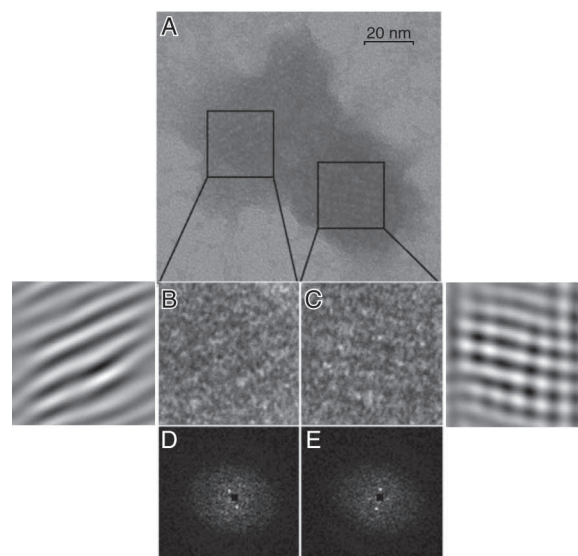


Figure 6. (A) TEM from a broken blackberry flattened surface; (B) and (C) show two magnified areas from this flake displaying some structure in the noise. The left-most and right-most pictures were obtained by Fourier filtering, (D) and (E) are the corresponding power spectra indicating some degree of order.

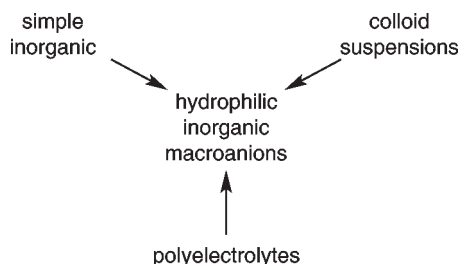


Figure 7. The hydrophilic inorganic macro-anions described in this article represent a new research field, which seems to connect traditional fields, such as that of simple ions, colloids, and polyelectrolytes.

sphere, e.g., lipid vesicles) that indicates the biomembrane-like soft nature of the blackberry surface. Considering that the present POM-type wheels are rather “hard” inorganic species, the soft nature of the blackberry surface clearly suggests the effect of additional linking materials between adjacent macro-ions. It may be assumed that the existence of highly structured water nanoassemblies is responsible for this feature, because “free” water molecules will not hold the isolated POMs to form the fairly stable supramolecular structure. The viscosity of water could increase several orders of magnitude in a nanoscale confinement, that is, water molecules linked with hydrogen bonds act as “viscous glue” to assemble the whole supramolecular structure (35, 36).

Small ions like Na^+ or Cl^- are never seen to exhibit such an association behavior in water. Our previous understanding of soluble inorganic ions in diluted solutions was straightforward: they should homogeneously distribute in a solvent and exist as single ions, reaching the minimum free energy (ΔG) and the maximum entropy (ΔS) simultaneously. However, this general solute state for inorganic ions is not valid for the hydrophilic macro-ions described here. These macro-ions have two different states: an entropy favored first (general) state, in which the solutes distribute homogeneously, and a thermodynamically favored second state, in which the solutes self-associate into supramolecular structures owing to strong inter-solute interactions.

The discrete macro-ions have to overcome a high energy barrier to form more stable blackberries. But the formation and dissociation of blackberries can be achieved by changing solvent quality or solution pH. The blackberry structure will not form if the macro-ions carry no charge or too many charges (24). One way is to add a large quantity of cationic surfactants (e.g., dimethyldioctadecylammonium bromide, or DODA-Br) in an immiscible organic solvent (e.g., chloroform). The cationic surfactants break the blackberry structure and form surfactant–single macro-ion complexes that can be stabilized in the organic phase (37).

Macro-ions in Solution: An Important Link between Simple Ions, Polymers, Colloids, and Biosystems

Macro-ionic solutions are different from regular ionic solutions containing small inorganic ions, and we need new methods and techniques to understand this new area. It is important to compare hydrophilic macro-ionic solutions with other types of solutions or suspensions. A century ago, spe-

cies in the range of 1–1,000 nm dispersed in solutions were all called “colloids”, with some common features, such as the Tyndall effect. Later it was found that there were two groups of different colloids called “lyophobic” and “lyophilic”, respectively. Examples of lyophobic colloids include emulsions, aerosols, and gold and AgO nanoparticles dispersed in suspending media. Such dispersed systems are thermodynamically unstable. The species can be temporarily dispersed in a medium because of their small sizes and charges, with the help of Brownian movement. But they have the tendency to aggregate and precipitate from the media (phase separation). Nowadays, these lyophobic colloids are called colloids. On the other hand, lyophilic colloids form real solutions in which the solutes are homogeneously distributed at the molecular level, and the systems are thermodynamically stable. They show some colloidal properties because the solutes are large (in the 1–1,000 nm range), such as polymer solutions including biopolymers (e.g., proteins and DNAs). Nowadays the lyophilic colloids are called macromolecules. Colloidal suspensions and macromolecular solutions represent two types of different species in fluids: for colloidal suspensions, the attractive force is stronger than the repulsive force, while for polymer solutions it is exactly the opposite. Some special molecules containing both lyophilic and lyophobic parts, for example, surfactants and block copolymers, tend to self-assemble into micellar or vesicular structures in solution via solvent-philic and solvent-phobic interactions. These special molecules are called “associated colloids”.

By carefully examining the categories described above, it seems that the giant POMs do not belong to any of them, and they cannot be treated as simple ions either. POMs form thermodynamically stable “real solutions” based on the cluster species abundant in the crystalline phase, which is different from colloidal suspensions, that is, we cannot make a colloidal solution of gold by dissolving a piece of gold metal in water. The giant POMs are also quite different from regular polymers in that many polymer molecules exist as single chains and distribute homogeneously in solution. The hydrophilic nature of the present POMs and the driving force of the self-assembly clearly distinguish them from conventional amphiphilic materials. Therefore, we expect that the “second solute state” of inorganic ions, in the form of blackberry type structures, represents an important transitional state among single ions, colloids, and polymers (Figure 7).

The present macro-anions show some similarities with a special type of polymers, that is, long-chain polyelectrolytes, including proteins and DNAs. Macromolecular polyelectrolytes show a much more complex solution behavior that is not yet totally understood. It is known that the polyelectrolyte chains tend to interact strongly with each other to form a long-range order in solutions without extra electrolytes. For most of the polyelectrolytes, the solution behavior is complicated owing to variable chain conformations. In contrast, the present inorganic macro-ions have huge advantages as model systems: fixed sizes and shapes as well as number of charges on each ion and furthermore, well-defined functionalities with options for further modifications. A number of hydrophilic POMs with different sizes are available for detailed studies. Interestingly, the self-organization of these macro-ions suggests similarities to the formation of virus

shells—formed by the ordered assembly of capsid proteins. Related to the similar sizes and topologies, in a general sense the comparison between inorganic macro-ionic assemblies and biosystems should be intriguing (38, 39).

Connecting Our Research to Future Teaching Activities

Well-developed traditional areas such as small ions, polymers, surfactant micelles, or colloids have been systematically covered in the current college chemistry curricula at different levels, from some introductory materials in general chemistry to specialized courses for graduate students. The fact that the present macro-ions show a new type of self-assembly in solution that is different from those well-known systems indicates that the progress in the study of macro-ionic solutions could also make an impact on our chemistry curricula. For example, some of our widely accepted concepts, such as *soluble inorganic ions distribute homogeneously in solutions* and *soluble ions reach equilibrium states quickly in dilute solutions* may not always be correct, but we should be aware of their more limited applications to only regular small ions. It is suggested that instructors remind our students that soluble inorganic ions can behave differently when they are large. When the whole area of macro-ionic solutions has been systematically studied, we may incorporate it as a separate part of the chemistry curriculum.

Conclusions

In summary, after more than 200 years of continuous explorations, scientists have formed a better understanding of the longtime puzzle of “molybdenum blue solutions”. With the discovery of various structurally well-defined, giant, hydrophilic species, inorganic chemists have successfully pushed the size limit of inorganic ions into the nanometer scale. Consequently, this progress provides new opportunities in different fields, for example, the physical chemistry of solutions. The giant anions show totally different solution behavior when compared to regular inorganic ions, owing to their size, surface properties, and charges. However, significant differences among these giant anions occur. This leads to the discovery of a second solute state for inorganic ions, which is free energy favored by macro-ions containing a moderate number of charges. The inorganic macro-ionic solutions behave differently from other systems currently covered in our chemistry curricula. We suggest that instructors should mention the difference between macro-ions and regular ions during teaching, and the area of macro-ions might be developed into a separated direction in the future, following a thorough understanding of this new field.

Acknowledgments

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