

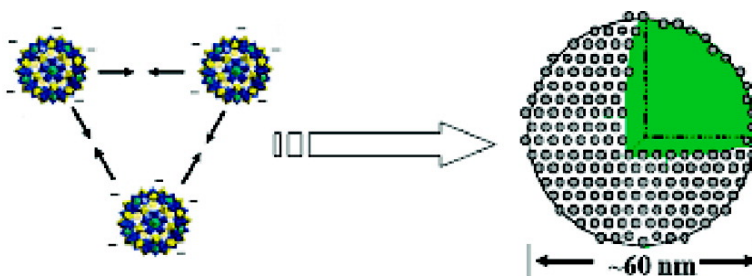
Communication

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Strong Attraction among the Fully Hydrophilic $\{\text{Mo}_{72}\text{Fe}_{30}\}$ Macroanions

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It is widely expected that soluble inorganic ions distribute homogeneously in dilute solutions, with the anions attracting cations and repelling other anions. However, recently, it was found that some giant, strong electrolyte-type polyoxomolybdate (POM) and weak electrolyte-type heteropolyoxometalate anions had totally different solution behaviors.^{1–8} Such highly soluble, fully hydrophilic macroanions exist as discrete ions in solutions when first dissolving in polar solvents, but tend to continuously (slowly for weak electrolytes)² self-associate into a more stable, hollow, spherical, single-layer vesicle-like “blackberry” structure with the size ranging from tens to hundreds of nanometers (Figure 1). For this self-assembly process, there must be driving forces to overcome the Coulomb repulsion among macroanions and attract them together. The blackberry formation is different from the formation of surfactant vesicles because such inorganic macroanions have no hydrophobic moiety (the cluster is fully covered by a layer of chemically attached water ligands), so that the contribution of hydrophobic interaction in the blackberry formation does not come into question. In this communication, we show that unique attractive forces are responsible for the blackberry formation of macroanions of a type of weak electrolyte, $\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\text{O}_{252}\text{L}_{102}\cdot\text{ca.}\cdot 180\text{H}_2\text{O}$ with $\text{L} = \text{H}_2\text{O}/\text{CH}_3\text{COO}^-/\text{Mo}_2\text{O}_8^{9-}$ ($\{\text{Mo}_{72}\text{Fe}_{30}\}$), which are 2.5 nm clusters containing C_{60} -like “Keplerate” structure.⁹

The $\{\text{Mo}_{72}\text{Fe}_{30}\}$ crystals were synthesized according to literature⁹ and then dissolved in different solvents (water, ethanol, and their mixtures) for current study. The $\{\text{Mo}_{72}\text{Fe}_{30}\}$ clusters are charged neutral in crystals, but tend to deprotonate several H^+ ions from the water ligands chemically attached to the 30 Fe^{3+} centers when dissolved in a polar solvent and become macroanions (Figure 1a),⁹ which then slowly self-associate into blackberries (Figure 1b). This self-association process can be monitored by the laser light scattering techniques (LLS), including both static and dynamic light scattering (SLS and DLS) studies, as described in our previous papers.^{2,6}

Many closed-association self-assembly processes, such as the micellization of surfactants, follows the mechanism of $nA \leftrightarrow A_n$. A major feature of such type of self-assembly is that there exists a definite critical association concentration (CAC) above which the self-assembly becomes increasingly significant.¹⁰ On the other hand, step-by-step self-assembly processes (such as the formation of open network structure by some block copolymers) or the assemblies driven by chemical interactions do not have definite CAC values. The blackberry formation, a new type of close-association process with different driving forces, also has obvious CAC values, as we determined by SLS. As shown in Figure 2, the total scattered intensity (I) obtained by SLS is very low at low $\{\text{Mo}_{72}\text{Fe}_{30}\}$ concentrations in aqueous solutions, suggesting that the macroanions stay as discrete ions and do not associate. A sudden increase in I is observed when $\{\text{Mo}_{72}\text{Fe}_{30}\}$ concentration is greater than 0.0024 mg/mL at 50 °C, indicating the formation of supramolecular structures (i.e., $\text{CAC} = 0.0024 \text{ mg/mL}$ at 50 °C). The CAC value becomes smaller at lower temperatures, suggesting a typical enthalpy-driven self-assembly process. At the same time, DLS

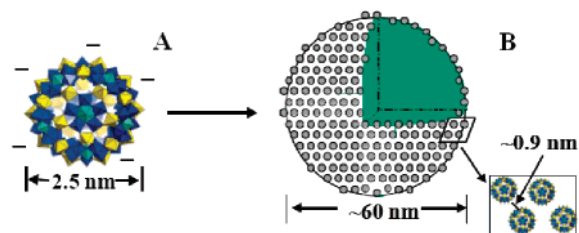


Figure 1. The self-assembly of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ into unique “blackberry” structure. (a) The Mo–Fe backbone structure of an $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macroanion; (b) the model of single-wall vesicle-like “blackberry” structure containing >1000 $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macroanions. Modified from ref 2, Figure 1.

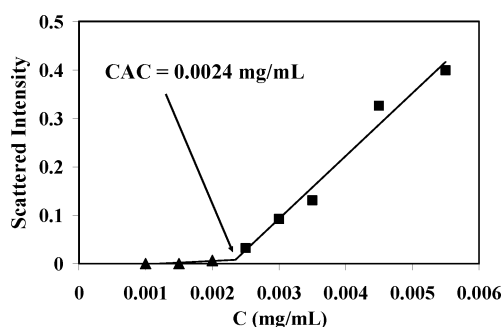


Figure 2. Determination of critical association concentration (CAC) of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ in aqueous solutions at 50 °C by SLS.

studies show the appearance of some large structures with the hydrodynamic radii (R_h) ~ 20 – 30 nm, which should be attributed to blackberries. It is interesting to notice that the radii of blackberries basically do not change with $\{\text{Mo}_{72}\text{Fe}_{30}\}$ concentration. This fact, together with the obvious temperature dependence of the CAC values, strongly suggests that the major attractive forces between macroanions leading to blackberry formation are physical interactions, not chemical bonding (some local, temporary inter- $\{\text{Mo}_{72}\text{Fe}_{30}\}$ Fe–O–Fe linking might be possible). It is expected that the aggregates would grow larger at higher solute concentrations for a typical chemical process.

The van der Waals force is a possible attractive force to balance the electrostatic repulsions among macroanions, which is the case in hydrophobic colloidal suspensions. To determine the effect of van der Waals force in current macroionic solutions, a series of 0.07 mg/mL $\{\text{Mo}_{72}\text{Fe}_{30}\}$ solutions were prepared in ethanol–water mixed solvents with different ethanol %. The solubility of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ in pure ethanol ($\sim 0.3 \text{ mg/mL}$) is less than that in water. Partial deprotonation of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ clusters also occurs in such solvents, which can be quantitatively estimated by measuring the conductance of respective solutions. The conductance of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ /ethanol/ H_2O solutions continuously decreases when the fraction of ethanol in mixed solvent increases, as the result of a lower degree of deprotonation in less polar solvents, as shown in Table 1. Because neutral $\{\text{Mo}_{72}\text{Fe}_{30}\}$ clusters are not conductive in solution, the decrease of solution conductivity indicates the decrease of concentration of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macroanions and H^+ . Considering the

Table 1. Experimental Results on {Mo₇₂Fe₃₀}/Ethanol–Water Systems

EtOH (vol %)	conductance ($\mu\text{S}\cdot\text{cm}^{-1}$)	self-association
0	9.47	yes
20	2.81	yes
30	2.39	yes
40	1.41	yes
50	1.20	yes
60	0.76	yes
70	0.56	yes
80	0.55	yes
90	0.48	yes
100	0.19	no

large size and very low charge density of {Mo₇₂Fe₃₀} macroions (compared with H⁺), their contribution to solution conductivity is much smaller than that of H⁺ and is negligible. Therefore, the change of solution conductivity reveals the change of H⁺ concentration, which is directly related to the degree of deprotonation of {Mo₇₂Fe₃₀}. It is well-known that the K_a of a weak acid becomes smaller in a solvent with lower polarity (e.g., HCl performs as a weak acid in ethanol).¹¹ For a weak acid, such as {Mo₇₂Fe₃₀}, its degree of deprotonation in ethanol solution should be lower than that in aqueous solution. The conductance of 0.07 mg/mL {Mo₇₂Fe₃₀}/ethanol solution is only 0.19 $\mu\text{S}\cdot\text{cm}^{-1}$, equivalent to only ~2% of that in pure water. It indicates that in pure ethanol, {Mo₇₂Fe₃₀} clusters can hardly deprotonate and are nearly charged neutral. Thus, the Coulomb repulsion between {Mo₇₂Fe₃₀} becomes much weaker in ethanol solution. On the other hand, the van der Waals force is related to the particle size and basically does not change with charge density of the particles. Accordingly, the attraction among the macroions in ethanol will be similar to that in water, if van der Waals force is the major attractive force between macroions. The collective result is that the attraction among macroions should be more dominant in ethanol than in water. We already know that {Mo₇₂Fe₃₀} macroions self-assemble in aqueous solutions. Therefore, we shall expect that more significant association would occur in ethanol solutions. However, LLS study on {Mo₇₂Fe₃₀}/ethanol macroion solutions recorded very low scattered intensity, and there was no increment of the scattered intensity after a long period of time, strongly indicating that there was no supramolecular structure formation in pure ethanol solutions. This result strongly suggests the existence of another attractive force other than van der Waals force, which performs as the major driving force for the blackberry formation.

The conductance of 0.07 mg/mL {Mo₇₂Fe₃₀} solution starts to increase when water content in the solvent increases (Table 1), which increases solvent polarity. The higher solution conductivity suggests higher degree of deprotonation of {Mo₇₂Fe₃₀} macroions. For solutions containing <90% of ethanol, large blackberry structure can be identified by LLS measurements, that is, SLS studies record much stronger scattered intensities (indicating the supramolecular structure formation) and DLS studies show a new mode with $R_h \sim 15\text{--}35$ nm (similar to our earlier results^{1,2}). This result is interesting because it hints that the increase of charge density on macroions leads to more significant attraction among them, that is, like-charge attraction^{12–15} does exist in hydrophilic macroionic solutions, and it determines the blackberry formation.

Another possible attraction comes from the hydrogen bonds formed between macroions in blackberries via water molecules. However, considering that no blackberry formation occurs when the charge density of macroions is low, the effect of hydrogen bonds cannot be dominant on blackberry formation. Furthermore, the deprotonation process breaks the water layer on {Mo₇₂Fe₃₀}

surface, which makes it less possible for the formation of long-range attractive hydrogen bonds between macroions (such structure is more likely to be formed in the macroions in a “strong electrolyte regime”, such as {Mo₁₅₄}³).

Our previous results suggest that the macroions are not touching with each other in blackberries.^{1,3} The interanionic distance, although hard to be determined very accurately, is ~1 nm, according to LLS and TEM measurements. Such a large distance makes it unlikely for the existence of strong short-range attractions, such as chemical bonding. But it does offer the possibility that small counterions exist among macroions and help to “connect” adjacent macroions together.

In summary, the self-assembly of {Mo₇₂Fe₃₀} macroions is indeed unique. Such macroions are fully hydrophilic and soluble in polar solvents; it is not mainly due to the charges, but due to the hydrophilic nature of the clusters (water ligands). This is a fundamental difference between hydrophilic macroions and colloids; the latter has hydrophobic nature and can only be temporarily suspended in solution with the help of charges (see the DLVO theory).^{16,17} Losing surface charges will make colloid particles unstable and precipitate quickly. The self-assembly of present hydrophilic macroions is not mainly due to van der Waals force, hydrophobic interaction, or chemical interaction, but due to the charges on their surfaces. Such negative charges have a dual effect: they contribute to both short-range repulsion and long-range like-charge attraction, possibly via small counterions in between. Besides the dominant charge effect, the van der Waals force, the hydrogen bonds formed between macroions, as well as some possible, temporary inter-{Mo₇₂Fe₃₀} Fe–O–Fe linking might also contribute to the attractive forces.

The unique self-assembly behavior of hydrophilic macroions in solution might be similar to the unclear association behavior of many long-chain polyelectrolytes,^{18,19} particularly the self-assembly of capsid proteins into single-layer vesicles which act as the shells of many types of viruses.^{20,21}

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