Polyoxometalates

DOI: 10.1002/anie.200902050

Counterion Distribution around Hydrophilic Molecular Macroanions: The Source of the Attractive Force in Self-Assembly**

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The interaction between large macroions and small counterions has always been an important topic as it is directly related to many fundamental problems in physical, biological, and materials sciences, such as the solution behavior of proteins, DNA, and various polyelectrolyte and colloidal systems.[1] In this vein, nanoscaled polyoxometalate (POM) molecular clusters serve as valuable systems for studying counterion associations and counterion-mediated attraction among macroions. POMs, which are high-nuclearity inorganic oxoanions formed by transition-metal polyhedra, are highly soluble in water and other polar solvents because multiple (and often adjustable) negative charges and water layers localize on POM surfaces.[2–4] In polar solvents, large POMs carrying a moderate charge tend to further self-assemble into hollow, single-layered, spherical "blackberry" structures.[5] This behavior is basically analogous to the self-assembly of virus capsid shells.[6]

We have demonstrated before that blackberry formation is not a result of van der Waals forces, hydrophobic interactions, or chemical reactions alone or in combination.[5] This distinguishes POMs from colloids and surfactants as well as solvent extraction systems wherein the micellization of polar solutes in nonpolar diluents is driven by dipole–dipole attraction.[7,8] Rather, we speculate that counterion-mediated attraction and hydrogen bonding are most likely responsible for this unique associative behavior,[5c–e] but direct experimental evidence regarding the role of counterions is still unavailable.

Precedent in this regard comes from a significant body of research demonstrating that counterions play an important role in many biological molecules and polyelectrolyte solutions.[9–13] In various macroionic solutions, because of the size disparity between the cations and anions, the attraction between small counter cations and large macroanions may overcome entropic behaviors, which results in the well-known phenomenon called counterion association. For medium-size POM clusters, such as the eponymous Keggin (size ca. 1 nm) heteropolyoxoanion, close ion pairing has been suggested by electrochemical experiments.[14] Separately, Leroy et al. used molecular dynamics simulations to reveal direct, contact ion pairing with monovalent cations in aqueous solution.[15] In this study, an aqueous environment was simulated with 1000 water molecules and three to five cations per Keggin anion (54 mM total Keggin concentration) to maintain electrostatic neutrality. The probability of finding a monovalent cation at a specific distance from the Keggin anion was used to evaluate the type of ion pairing. Counterion association might be even more significant in solutions containing larger POMs. Moreover, instead of only forming close ion pairs, the spatial distribution of counterions around POMs through loose, solvent-shared and -separated associations might also be possible.

To accurately describe this phenomenon and to clarify its relation to the self-assembly of hydrophilic macroions, we use small-angle X-ray scattering (SAXS) to monitor the counterion distribution around a 2.5 nm, hollow, spherical POM (see Figure 1) in water and mixed solvents (acetone/water). We have previously reported on counterion associations with giant POMs,[5c] but herein we focus on the application of direct measurements to determine the distribution of monovalent cations around the $\{Mo_{72}V_{30}\}$ cluster, which is built up of 12 pentagonal $\{(Mo^{VI})Mo^{VI}_5\}$ units connected by 30 V^{IV} linkers, and how this distribution is related to blackberry self-assembly. All of the metal atoms in $\{Mo_{72}V_{30}\}$ are distributed on the surface of this POM, which is just one example of a remarkable series of so-called Keplerate structures.[3b]

At dilute concentrations in aqueous solution, $\{Mo_{72}V_{30}\}$ is stable in the form of discrete, unassociated macroanions (theoretically each cluster carries approximately 31 negative charges, balanced by eight Na^+, 14 K^+, two VO^{2+}, and five H^+ counter cations).[5g] Upon introduction of some acetone into the solution, these macroanions can strongly attract each other to form blackberry-type structures as depicted in Figure 1. Not only do these POMs remain discrete macroions in solution, but also the self-assembly is quite slow at room temperature (several weeks to months). Both factors enable us to use SAXS to monitor any change of these macroions in mixed solvents.

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[**] T.L. acknowledges support by the NSF (CHE0723312), the Alfred P. Sloan Foundation and the ACS-PRF. C.-Y.S. is grateful for discussions with Prof. K. Yoshikawa (Kyoto University) and the support from the CUNY PSC awards. This work is also supported by the U.S. DOE-BES, under contract No. DE-AC02-06CH11357. We thank Dr. S. Seifert for generous assistance at the APS 12-ID facility.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200902050.

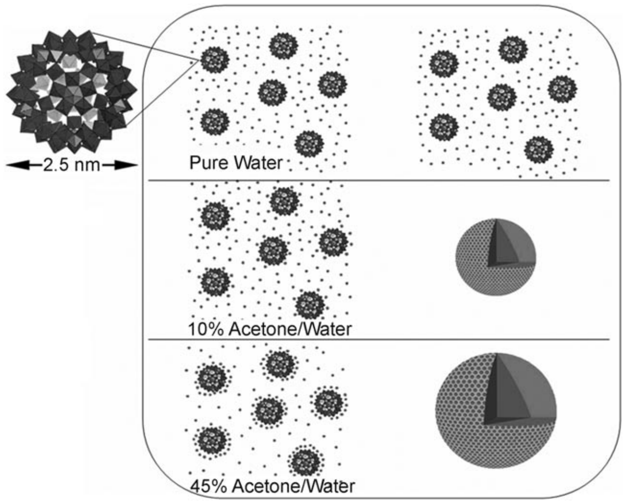

Figure 1. Hollow, spherical, single-layer blackberry structure formed by {Mo$_{72}$V$_{30}$} macroanions (full crystallographic formula $\mathrm{Na_8K_{14}(VO)_2[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_3\}_{10}\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_3(SO_4)\}_2\{V^{IV}O(H_2O)\}_{20}\{V^{IV}\}_{10}(\{KSO_4\}_5)_2]\cdot ca.\ 150\,H_2O}$; in solution the bare macroion does not contain Na$^+$, K$^+$, and VO^{2+} cations and ca. 150 water molecules).[4a] The macroanions are surrounded by small counterions. The transition between discrete macroanions and blackberries depends on the effective charge density of the {Mo$_{72}$V$_{30}$} macroanions, which can be controlled by decreasing the solvent polarity.

The experimental SAXS data for {Mo$_{72}$V$_{30}$} in pure water at a concentration of 0.26 mM (Figure 2) and the calculated atomic scattering for discrete {Mo$_{72}$V$_{30}$} macroanions (Figure S1, Supporting Information) are in close agreement. Both curves show two distinct maxima at $Q = 0.45$ and $0.75\ \text{Å}^{-1}$ where Q is the scattering vector. The experimental data were best fitted by using a form factor for a 2.5 nm diameter spherical shell, which provided direct evidence that the {Mo$_{72}$V$_{30}$} macroanions exist as discrete ions in dilute aqueous solution, and also that there is no major decomposition of the materials.

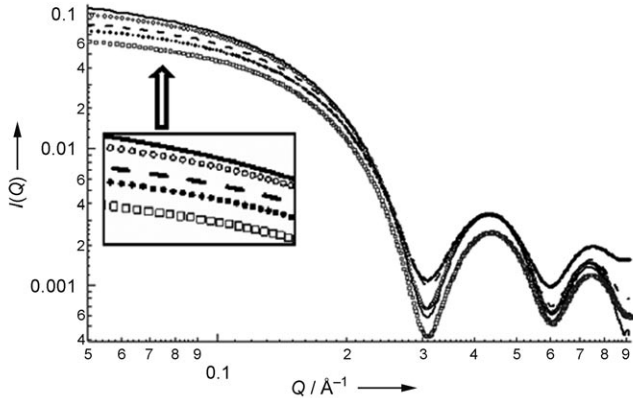

Figure 2. Log–log plot of the SAXS data for 0.26 mM {Mo$_{72}$V$_{30}$} in acetone/water mixed solvents containing various amounts of acetone (an effect which would increase the R_g value). (——): 75% acetone/water, (○): 65% acetone/water, (-----): 45% acetone/water, (•••••): 10% acetone/water, (□): in pure water. Inset: Expansion of data.

A quantitative measure of the macroanion size in aqueous solution is provided by its radius of gyration, R_g, which is the root-mean square of mass-weighted distances of all subvolumes in a particle from the particles' center of mass. The R_g remains constant within the level of experimental uncertainty (±5%) at 10.8(5) Å for different {Mo$_{72}$V$_{30}$} concentrations, which suggests that the {Mo$_{72}$V$_{30}$} macroanions do indeed exist as discrete ions in solution. This is consistent with observations for other monodisperse Keplerate POMs,[16] and is sound evidence that there is no significant counterion association around the macroions at low {Mo$_{72}$V$_{30}$} concentrations, an effect which would increase the R_g value.

The distance pair distribution, $p(r)$, provides a more physically meaningful description of the particle morphology than R_g, where $p(r)$ is the probability of finding the vector length r in the molecule that will become zero at the maximum vector length. For {Mo$_{72}$V$_{30}$} in dilute aqueous solutions (0.013–0.052 mM), the $p(r)$ curves shown in Figure 3 (top) exhibit an asymmetric rise on the low-r side of the peak maxima at 17 Å, after which the intensity decreases smoothly to zero at about 26 Å. The $p(r)$ plot obtained from the experimental data is very similar to the one calculated from the atomic coordinates of the molecular structure of the discrete {Mo$_{72}$V$_{30}$} macroanion. Both responses agree with a core–shell spherical particle with a maximum linear dimen-

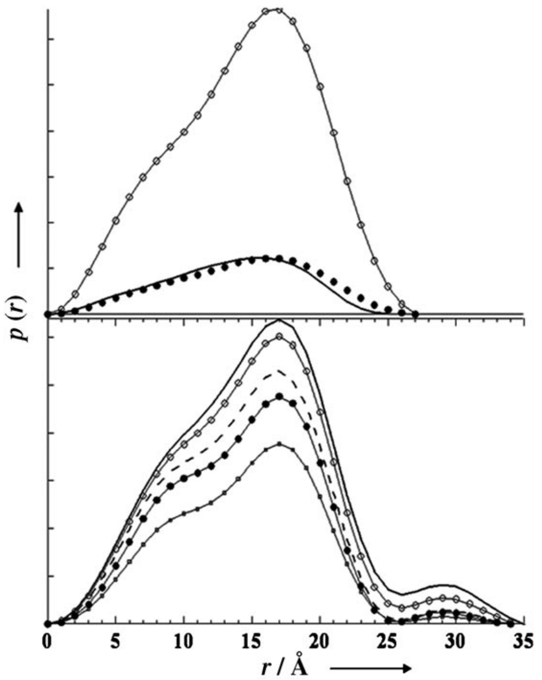

Figure 3. Top: Distance distribution functions based on calculated and experimental scattering data for {Mo$_{72}$V$_{30}$} obtained by using an indirect Fourier transform of the primary SAXS data. (○): 0.052 mM {Mo$_{72}$V$_{30}$}, (●): 0.013 mM {Mo$_{72}$V$_{30}$}, (——): {Mo$_{72}$V$_{30}$} calculated. Bottom: Experimental distance distributions for 0.26 mM {Mo$_{72}$V$_{30}$} in water and acetone/water mixed solvents with various acetone content (in vol%). (——): 75% acetone/water, (○): 65% acetone/water, (-----): 45% acetone/water, (•••••): 10% acetone/water, (□): in pure water.

sion of approximately 26 Å, which is consistent with the crystallographic dimension of the $\{Mo_{72}V_{30}\}$ cluster.

From Figure 3 (top), it is clear that counterion association is not present in dilute aqueous $\{Mo_{72}V_{30}\}$ solutions up to the concentration of 0.052 mM, as only one effective distribution in $p(r)$ extending to approximtely 26 Å is observed. At higher macroionic concentrations, such as 0.26 mM $\{Mo_{72}V_{30}\}$, there is an obvious change in the $p(r)$ plot, as shown in Figure 3 (bottom). A weak, distant peak centered at about 30 Å appears, which extends the effective distribution to about 34 Å. The original distribution, attributed to the nude $\{Mo_{72}V_{30}\}$ clusters, remains unchanged, thus indicating that the $\{Mo_{72}V_{30}\}$ macroanions still exist as discrete ions in solution. However, the appearance of the second peak suggests that some additional electron density exists around the $\{Mo_{72}V_{30}\}$ macroanions. That is, additional species distribute closely and organize around the macroions in solution. In $\{Mo_{72}V_{30}\}$ solutions, the only solutes besides $\{Mo_{72}V_{30}\}$ anions are the small counter cations. In so far as the SAXS response is dominated by the metals in the system, any contrast for what would be an organized solvation shell is expected to be weakly scattering by comparison. Therefore, we conclude that the high-r distribution is a result of the close association of counterions around the macroions, particularly for the cations capable of producing effective X-ray scattering contrast—which means heavy atoms—here mainly K^+ because of its relative abundance in solution, and minor effects from the more dilute Na^+ and VO^{2+} ions. Based upon simple electrostatic arguments, the divalent VO^{2+} ion is expected to interact more strongly with the macroions than Na^+, which is also expected to produce weaker X-ray scattering contrast because of the lower atomic number of Na.

The above observations are confirmed by conductivity measurements. For a 0.013 mM $\{Mo_{72}V_{30}\}$ aqueous solution, the measured conductivity is very close to the theoretical value (by assuming that all the cations are free in solution). When the macroionic concentration is 0.26 mM, the measured solution conductivity is significantly (39%) lower than the theoretical value, which suggests that a fraction of the cations do not contribute to the solution conductivity. They must be closely associated with the $\{Mo_{72}V_{30}\}$ macroions and are not free to contribute to the bulk response.

SAXS data for 0.26 mM $\{Mo_{72}V_{30}\}$ macroions in water/acetone mixed solvents with different acetone content (10–75 vol% acetone, Figure 2) show patterns similar to those observed in pure water, with maxima at 0.45 and 0.75 $Å^{-1}$. These curves are consistent with the response for a 2.5 nm hollow sphere. With increasing acetone content, the $I(Q)$ response becomes steeper in the low-Q region, which indicates that the R_g of the $\{Mo_{72}V_{30}\}$ clusters increases, as determined by the Guinier plots (Figure S2, Supporting Information). The average R_g is 11.0(5) Å for $\{Mo_{72}V_{30}\}$ macroanions in a solution containing 10 vol% acetone, and R_g increases to 11.1(6), 11.6(6), and 12.0(6) Å when the acetone content increases to 45, 65, and 75 vol%, respectively. The small yet incremental expansion of the R_g value indicates that the effective size of $\{Mo_{72}V_{30}\}$ macroanions becomes larger with higher acetone content, even as the molecular skeleton of $\{Mo_{72}V_{30}\}$ is retained (proven by the $p(r)$ distribution, see below). These results show that counterion association is present and the degree of the association increases with increasing acetone content.

The $p(r)$ plots for $\{Mo_{72}V_{30}\}$ in acetone/water mixtures shown in Figure 3 (bottom) resemble the $p(r)$ plot for $\{Mo_{72}V_{30}\}$ in pure water at 0.26 mM—all of which have a second peak at 29–30 Å. This feature is a direct indicator of counterion association around discrete $\{Mo_{72}V_{30}\}$ macroanions, starting from the solvent with lowest acetone content (10 vol%). Moreover, a comparison of the relative peak areas for the two peaks in each $p(r)$ curve shows that the distant one centered at approximately 29 Å becomes more significant with increasing acetone content (or decreasing dielectric constant of the solvent) in relation to the major one at 17 Å. The systematic variation reflects the fact that the number of associated counterions increases during the dissolution process. This result is entirely consistent with the incremental change of R_g described above. Consideration was given to the possibility of interparticle interferences, which can lower the $p(r)$ function at higher r values.[17] These issues are clearly absent in our $\{Mo_{72}V_{30}\}$ solutions.

The $p(r)$ data indicate that the highest probability of finding a K^+ ion near the surface of a $\{Mo_{72}V_{30}\}$ macroanion is at r within the range of approximately 28–29 Å, that is, 2–3 Å from the surface of the $\{Mo_{72}V_{30}\}$ macroanions, consistent with a typical K–O bond length of approximately 2.6 Å[18] as well as distances found for contact ion associations, such as those observed between alkali-metal cations and the small Lindqvist hexaniobate isopolyoxoanion.[19] The counterions associated with macroanions are distributed over a range of approximately 2–9 Å from the surface of the $\{Mo_{72}V_{30}\}$ macroanions. Likewise, Leroy et al. described simulations showing that monovalent counterions are distributed around the α-Keggin anion at approximately 3–4 Å from its surface, which indicates the formation of ion pairs in aqueous solution.[15]

The SAXS-measured counterion distance distribution is consistent with our original model wherein we estimated that the inter-POM distance was below 1.0 nm (but difficult to be accurately measured).[5b] The current result indicates that with such an inter-macroionic distance, the counterions can stay in between macroions, thereby decreasing the free energy of the blackberry structures. The overall picture that emerges, therefore, is that the POM macroanions are not in direct contact on the blackberry surface (because of electrostatic, anion–anion repulsion), but are separated by counterions. Our SAXS results demonstrate that the degree of counterion association at 2–9 Å around $\{Mo_{72}V_{30}\}$ macroanions increases with increasing acetone content. In a solvent with low polarity, the counterion association around discrete macroanions becomes significant and, thus, decreases the effective charge density of the macroanions. In turn, the decreased charge density allows for an increased attraction interaction amongst the $\{Mo_{72}V_{30}\}$ that leads to an increase in preferred curvature for the blackberries. Correspondingly, the blackberries are found to grow larger in size during this structural ripening process.

To complement our experiments, a mean-field model was developed to qualitatively understand the interaction between two like-charge macroions in salt-free solutions with medium dielectric constant D. The aim is to address the fundamental nature of the attraction in terms not adequately explained with traditional theories.[20] The starting point is to divide counterions into free and bound cations, as suggested in the literature.[21,22] The formation of a bound cation is assumed because of strong electrostatic attraction with macroions, dictated by a free-energy gain $\Delta\mu^{\circ}_{\mathrm{bm}}$ (D-dependent) relevant to the equilibrium ratio of bound and free cations. The bound cations on a macroion further induce electrostatic attraction with the second macroion. These attractions are balanced with the repulsions among the bound counterions in a macroion and between two like-charge macroions. The reduced interaction potential $V(H)$ between two macroions is defined as the energy difference when their separation is decreased from infinity to the distance H, the shortest distance between the surfaces of the two spherical macroions with bound counterions. Figure 4 contains a schematic of the model for which details are given in the Supporting Information.

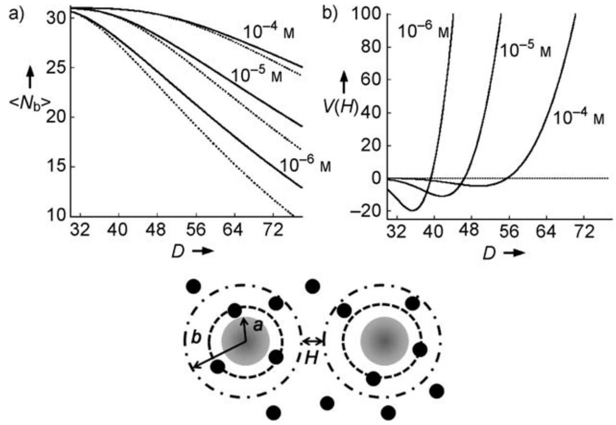

Figure 4. a) Variation of the mean number of bound counterions $\langle N_b \rangle$ with dielectric constant D when $H=6$ (——) and 80 Å (•••••) and b) interaction potential $V(H)$ against D when $H=6$ Å for different macroion concentrations from 10^{-6} to 10^{-4} M. The drawing below denotes two macroions (solid circles) of radius a separated by a distance H and surrounded by cations (open circles) with bound cations confined between radii a and b.

In our calculations, $\Delta\mu^{\circ}_{\mathrm{bm}}/k_BT = -9 \times (78/D)$ is chosen, equivalent to the counterion–macroion attraction of approximately $9\,k_BT$ in pure water and $33\,k_BT$ in pure acetone. Figure 4a shows the variation of the mean number of bound counterions $\langle N_b \rangle$ with D for various macroion concentrations, as marked, when $H=6$ and 80 Å. $\langle N_b \rangle$ increases as D decreases from 78 to 30 with the diminishing net charge at lower D. Unlike higher macroion concentrations, $\langle N_b \rangle$ becomes low at lower macroion concentrations. This result qualitatively agrees with the findings of Figure 3, which shows that counterions are bound at high macroion concentrations. Also, $\langle N_b \rangle$ decreases for larger H values.

Figure 4b shows $V(H)$ against D for different macroion concentrations, as marked, when $H=6$ Å. For all concentrations, $V(H)$ first decreases as D decreases and then gradually exhibits attraction at low enough D. Such an attraction may explain the macroion association enhanced by low-dielectric-constant media in the experiment. After passing through its minimum, $V(H)$ increases again and gradually approaches zero for smaller D values, which means that self-association is weakened by further increasing the acetone concentration, consistent with previous observations.[17h] For higher macroion concentrations, the minimum shifts to larger D, which indicates that a higher macroion concentration facilitates their self-association. Our results are comparable to the self-association behaviors of giant (micrometer size) DNA molecules[23] that, after mixing with high-valent cations, reorganize into highly ordered toroidal structures whose formation is enhanced by reducing the dielectric constant of the solvent.[23] The high-valent cations act as our monovalent counterions do, namely inducing attraction among like-charge DNA monomer units.

In summary, we have used SAXS to study the distribution of monovalent counterions (mainly K^+) around the hydrophilic $\{Mo_{72}V_{30}\}$ Keplerate macroanion in aqueous solution. The results indicate that almost all the counterions are free at very low $\{Mo_{72}V_{30}\}$ concentrations, but tend to partially associate with the macroions at higher $\{Mo_{72}V_{30}\}$ concentrations. The same effect (even stronger) is observed when the dielectric constant of the solvent becomes lower by adding aliquots of acetone to the aqueous solution.[5g] More counterions are associated with the macroions with increasing acetone content. The monovalent counterions distribute 2–9 Å away from the surface of macroions, with the highest probability appearing at 2–3 Å within the surface of the macroions. A simple mean-field model is developed to qualitatively elucidate the role of bound counterions in the attraction between two like-charge macroanions, as well as the effect of the dielectric constant of the medium on the interplay between counterion binding and the self-assembly of the like-charge macroions. The results from experiment and calculation confirm that macroion–counterion association is the pivotal contributing source of the attractive forces between the macroanions and, in turn, of their self-assembly into blackberry structures in solution.

Experimental Section

$\{Mo_{72}V_{30}\}$ single crystals were synthesized according to the procedure reported in the literature.[4a] The crystals were then directly dissolved in deionized water or water/acetone mixed solvents. A series of 0.013–0.26 mM $\{Mo_{72}V_{30}\}$ aqueous solutions were prepared, as well as a series of 0.26 mM solutions in acetone/water mixed solvents with different acetone content ranging from 0 to 75 vol%. The samples used for SAXS background subtraction were prepared from the same stock solutions to closely match the background in the sample.

The SAXS experiments were performed at the 12-ID-C beamline, Advanced Photon Source (APS), Argonne National Laboratory.[24] The incident photon energy was 15 keV. The solutions were placed in 2-mm-diameter, thin-walled quartz capillaries. Five camera shots were taken for each sample with an exposure time of 5 s. Only the data with less than 2% difference between each of the five camera shots were averaged and analyzed. Details of the analyses can be found in the Supporting Information and elsewhere.[25–28]

Received: April 16, 2009
Revised: June 1, 2009

Keywords: cluster compounds · counterion association · polyoxometalates · self-assembly · solvent effects

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