Interactions between Keggin Anions in Water: The Higher Their Charge, the Higher Their Condensation? A Simulation Study

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Invited for the front cover of the Cluster Issue on Polyoxometalates is the group of Georges Wipff at the University of Strasbourg. The cover image shows the interaction of POMs with various components of the solution and their adsorption at the interface.

In a few words, how would you describe your research?

We use molecular dynamics to simulate ions and molecules in solution (aqueous or nonaqueous solvents, interfaces, ionic liquids) to obtain nanoscopic views of their distributions and micro-environments. Particularly helpful guidelines stem from supramolecular chemistry: molecular recognition, transport, assembly, organization.

What is the most significant result of this study?

Common sense requires that like-charged species repel each other, according to Coulomb’s law. We show, however, that in water, “big ions” (POM\(\text{\textsuperscript{3-}}\) anions of ca. 1 nm size) approach each other closely to form dimers, oligomers, and aggregates. Moreover, comparison of POM\(\text{\textsuperscript{3-}}\) ions with charges of 3 to 5 reveals a quite counterintuitive feature: the highest POM···POM condensation is observed with POMs that have the highest charges! These results provide clues for understanding the formation of highly complex systems with supramolecular organization.

How can you explain these counterintuitive observations?

We introduced the concept of “ionic sociology”, which stipulates that interactions depend on the medium (here, water), on the other species (counterions), and the concentrations of the components. Two main sources of POM···POM “attraction” are highlighted: (1) hydrophobic forces are dominant for POMs with low charges; (2) counterions condense more onto the most highly charged POMs, especially in the bridging region, thereby acting as “glue” (see, for example, H\(3\)O\(^+\) protons connecting a POM\(\text{\textsuperscript{5-}}\)···POM\(\text{\textsuperscript{5-}}\) dimer).

How did you enter the POMs field?

We initiated the simulation of liquid···liquid ion extraction in supramolecular chemistry (e.g. cryptates, crown ether or calixarene complexes), ions in solutions, and at interfaces. We also reported early studies on small like-ion pairs in solution. Then we were curious to extend these to the chemistry of POMs. Furthermore, beyond their individual properties, POMs constitute fundamental building components of organized systems. Our studies thus contribute to a better understanding of the underlying driving forces, that is, where the “glue” comes from.

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