ACCOUNTS
of chemical research

GUEST EDITORIAL
Water

Water, as the most abundant molecule on the earth's surface and in our own bodies, is ubiquitous in terrestrial chemical processes. These processes range from conventional solution reactions, to critical atmospheric reactions enabled by the presence of water clusters, to the myriad of biological chemical transformations. The role of water in biology includes most fundamentally its essential participation in dictating structure, including protein secondary and tertiary structure, the spontaneous formation of membranes, and the recognition of polynucleotide sequences in transcription. These same molecular driving forces are important in the development of strategies for synthetic self-assembly and for drug development and delivery. As a result of the prevalence for water to be involved in natural chemistry, there have been a great many studies of water, as a molecule, as a liquid, solid, or vapor, as a medium for reactions, and as a reactant. Nevertheless, water and its many important roles in chemistry remain vibrant areas for research, a tribute both to the importance of water to our lives and to the difficulty of mastering its chemical behavior.

The qualities of water that lead to its complexity lie in the relatively strong intermolecular interactions between molecules and the directional character of these interactions. The water molecule possesses a highly polar covalent bond, involving a hydrogen atom and a relatively electronegative oxygen atom. Thus, it can interact, by a predominantly electrostatic mechanism involving the proton donor O–H directions, with the electronegative centers of other molecules, for example, the oxygen of another water or a carbonyl group, or through its own electronegative oxygen center when a proton donor group is nearby. Such a molecular interaction, which we all typically term a "hydrogen bond", entails quite a large interaction energy, as large as roughly 10 times the typical thermal energy that is available at room temperature (k_BT, where k_B is Boltzmann's constant and T is the absolute temperature). Further, since these donor and acceptor interactions are directed tetrahedrally from the center of each water molecule, there exists in liquid water a space-filling three-dimensional network of these interactions with which all of aqueous chemical processes must reach some compromise. We all learned in our first chemistry course that water plays an active chemical role in all of acid–base chemistry, including that in the biological arena, but the development of a full understanding implies a quantitative description of the subtle balance of large intermolecular and intramolecular forces that evidently cause this chemistry to be accessible under ambient conditions. While chemical equilibrium can at least be framed in a very precise thermodynamic context, the elucidation of the dynamics of structural and chemical changes in an aqueous system presents an even greater challenge. It is no wonder, then, that fully understanding these thermodynamic and time-dependent processes in the aqueous environment has been a grand challenge with many remaining open avenues of pursuit today.

In this Special Issue, a collection of 14 Accounts of current research on aqueous systems is presented with the intent of providing a close-up look at a representative sampling of the wide range of research topics and techniques within the area. These include studies of molecular clusters, which serve as model systems allowing a more detailed probe of hydration structure and dynamics than is accessible in bulk solution. Applications of state-of-the-art spectroscopic techniques are discussed which probe with remarkable detail the dynamics of water in alternative environments, chemical reaction dynamics, and the hydration structures determining the behavior of the elementary species appearing in acid–base chemistry. Interfacial water plays a major role in chemistry and in this collection, including studies aimed at a detailed characterization of the hydration of membranes, reactions occurring on the surface of ice, the chemical composition of the aqueous solution–vapor interface, the structure of catalysts, and the interfaces hosting many atmospheric reactions. Cutting-edge molecular-level theory not only appears in the contexts of spectroscopy, cluster dynamics, and interfacial characterization already mentioned, but also in the context of the mechanisms that allow rapid dynamics in these strongly hydrogen bonded networks, including the specific role of water in biomolecular aggregation.

As will be clear from the Accounts in this collection, there is a great deal of progress being made in elucidating the

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molecular details of aqueous processes, both via the development of truly innovative experimental, theoretical, and computational methods and the innovative implementation of our ever expanding arsenal of methods. Nevertheless, we hope that these Accounts will provide the eager new researcher with as many ideas for outstanding unresolved problems as it provides answers to the many challenges of aqueous chemistry.

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