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Caught in the Act of Dissolution

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In 1887, the young Svante Arrhenius got an icy reception when he proposed that neutral compounds like HBr could almost completely dissociate in water, releasing independent, oppositely charged ions (*1*). Three decades later, Born showed ionic dissociation to be driven by the substantial energy released when an ion is immersed in a dielectric medium (*2*).

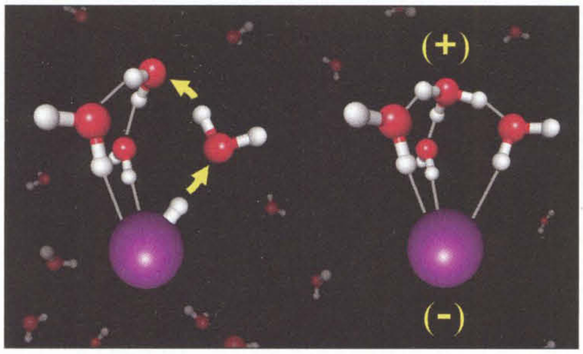
Born's dielectric energy falls off as the inverse radius of a spherical droplet, suggesting that the droplet size can be used to control and study the ionization process. But only about a third of the bulk solvation energy is lost in a 10 Å–radius droplet, which contains ~125 water molecules. The "droplets" must therefore be pretty small before the solvation energy becomes too small to sustain charge separation. On page 202 of this issue, Hurley *et al.* (*3*) explore just how many water molecules it takes to crack open $HBr \cdot (H_2O)$ into the separated H_3O^+ and Br^- ions.

Acid dissolution involves the collective action of an extended water network. The figure depicts a web of water molecules participating in the charge separation process (*4*). Clusters consisting of 10 or so water molecules and 1 acid molecule can be treated as a single "supermolecule" in an electronic structure calculation. This approach naturally accommodates the large anticipated distortions of both the acid and the network of water molecules.

Recent calculations (*5–7*) suggest that the initial charge separation in simple acids like HBr and HCl occurs upon contact with as few as four water molecules. The charge-separated arrangement (see right panel in the figure) is calculated to be the most stable form of the $HBr \cdot (H_2O)_4$ cluster. This structure features three water molecules prying apart the Br^- and H_3O^+ ions in a high-symmetry configuration.

Testing this picture of solvent-assisted acid ionization experimentally is a challenging task. Examination of the theoretical "supermolecule" directly requires working with an ensemble of clusters in which each member contains a precisely determined number of acid and water molecules.

Several cluster experiments have already determined the shapes displayed by the smallest ice nanocrystals of pure water (*8*, *9*) and of water bound independently to the hydronium (*10*) and bromide (*11*) ions. Hurley *et al.* now report an ingenious approach designed to monitor the extent of charge separation in size-selected $HBr \cdot (H_2O)_n$ clusters.



Dissociation of hydrogen bromide in a cluster of four water molecules. The water network is an integral part of the charge separation process, leading to the solvent-separated ion-pair shown on the right. The reaction path shown here is highly schematic; HCl dissociation appears to involve a sequence of several discrete steps (*4*).

The authors exploit the different optical properties of intact and dissociated HBr. When HBr is intact in an overall electrically neutral cluster, it can act as a chromophore for resonant multiphoton ionization, a process that creates easily detectable cationic clusters. When HBr dissociates into H_3O^+ and Br^-, the chromophore disappears, eliminating the pathway for photoionization and hence the cation signal. Hurley *et al.* show that the signal disappears upon addition of the fifth water molecule, consistent with ion-pair formation and the beginning of spontaneous ionic dissociation.

This report of acid dissolution comes amid a flurry of papers tracking down the molecular-level aspects of everyday chemical processes involving ions in water. Of particular interest are those species and processes that, like acid dissociation, owe their existence to the symbiotic relation between solute and solvent. Another classic case is presented by the sulfate anion. Because it is doubly charged, SO_4^{2-} is intrinsically dependent on its hydration shell to avoid spontaneous dissociation into singly charged fragments, and the species appears in the gas phase only when accompanied by at least four water molecules (*12*).

The colors displayed by anions in water are another example of solvent/solute interdependency. The lowest optical absorptions of simple anions (usually in the ultraviolet) result from charge transfer to the solvent. The upper state of such an electronic transition is created by the order imposed on the surrounding water by the presence of the ion. Cluster studies have shown that this diffuse excited state is already developed in the $I^- \cdot (H_2O)_4$ cluster (*13*). Time-resolved studies of reaction kinetics and energy transfer have explored how the first shell of solvent molecules affects the dynamics of simple reactions such as photodissociation (*14*, *15*).

Motivated by theory and the results of Hurley *et al.* on HBr dissolution in small water clusters, spectroscopists should next obtain the vibrational spectrum of isolated $HBr \cdot (H_2O)_4$. These data will be essential to establish the intramolecular and intermolecular bonding arrangements at play.

Further experiments may involve freezing an acid/water cluster of controlled composition and then injecting it with a precisely determined amount of energy. One could then follow time-resolved structural changes, including phase transitions and chemical rearrangements (like acid dissolution). Rare-gas nanomatrices could be used as the growth media (*16*). As the next steps of this endeavor unfold, we witness the beginning of an era where we can watch how the solvent participates and modifies the fundamental events of chemical change.

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