

CHEMISTRY

Electric buzz in a glass of pure water

Hydrogen bond charge transfer in water may have far-reaching chemical implications

By Dor Ben-Amotz

Water is far more than a collection of neutral H_2O molecules, linked by hydrogen bonds, with a trace of hydrogen (H^+) and hydroxide (OH^-) ions. Indeed, recent work has revealed that pure water has an additional shimmering buzz arising from electron transfer between neighboring water molecules, in which the hydrogen atom on one water molecule forms a hydrogen bond with a neighbor's oxygen atom (1–4). This charge transfer, and the resulting attraction between the pair of oppositely charged water molecules, contributes to the strength of the hydrogen bonds among water molecules (4). Hydrogen-bonding defects in liquid water lead to the accumulation of negative or positive charge on water molecules with an odd number of hydrogen bonds (2–4). These charged waters may play an overlooked role in chemical reactions at the air–water and oil–water interfaces that are ubiquitous in biological, geological, and environmental chemistry.

The importance of hydrogen bonds in dictating the structure of water, as well as the presence of H^+ and OH^- , has been well understood since the early half of the 20th century. This understanding includes the propensity for each water molecule to donate two and accept two hydrogen bonds, and it is precisely these four hydrogen bonds that give ice its tetrahedral geometry. However, a partial breakdown of this geometry is what makes ice float on water, whose slightly denser structure includes water molecules that form an odd number of hydrogen bonds.

It has recently become clear that there is something big missing in this long-standing view of the structure of water. Specifically, recent work implies that water must also be teeming with additional, previously un-

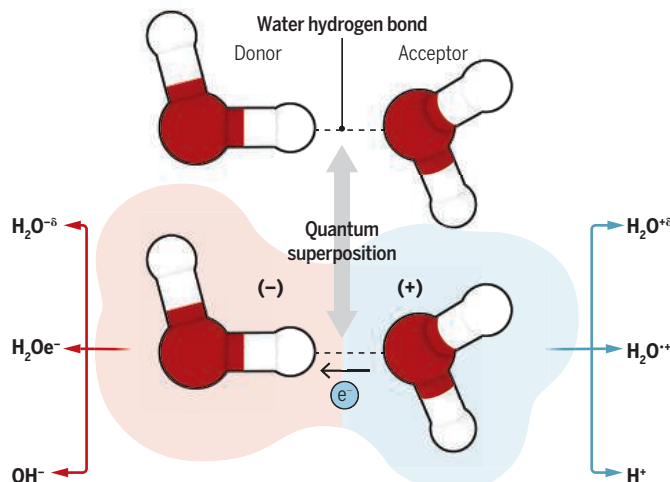
recognized, charged water molecules (1–4). The formation of these charged waters is a consequence of the quantum mechanical delocalization of electrons, which allows an electron on one water molecule to stray onto its neighbor. The resulting transfer of charge between hydrogen-bonded water molecules is supported by both theoretical predictions (2–4) and experimental evidence of charge buildup at an oil–water interface resulting from water charge transfer (1). This transfer of electrons between H_2O molecules is akin to the phenomenon known as quantum superposition (see the figure). Like Schrödinger's cat, which is both dead and alive, a pair of hydrogen-bonded water molecules can be either charged (i.e., as $\text{H}_2\text{O}^+\cdots\text{H}_2\text{O}^-$) or uncharged (i.e., as $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$). The charged waters are formed when the hydrogen bond acceptor transfers an electron to the hydrogen bond donor. This charge transfer has a predicted probability of at least 2% (2, 3), which corresponds to an average charge exchange of $\pm 0.02 e$ for every hydrogen bond in liquid water. The resulting attraction between the positively and negatively charged waters increases the strength of all the hydrogen bonds in liquid water (4).

These charge transfers can also influence the average charge of individual water molecules. For most water molecules, which have an equal number of hydrogen bond donors and acceptors, the average charge is zero. However, 30% of the molecules in liquid water have an odd number of hydrogen bonds, with either two donors and one acceptor, or two acceptors and one donor. This hydrogen bond imbalance leads to a persistent average charge of $\pm 0.02 e$ on the water molecules with an odd number of hydrogen bonds (4). Because water has a concentration of 55.5 moles per liter (M), this implies that these partially charged water molecules have a tremendously high concentration of ~ 17 M (from $55.5 \text{ M} \times 30\%$) (4). As electron charges are indivisible, a partial charge of $\pm 0.02 e$ on a water molecule, in reality, means that this water molecule has a 2% chance of carrying a full charge of $\pm e$. Thus, the 17 M concentration of partially charged water molecules implies that, at any instant, pure water contains 0.3 M of fully charged water molecules (from $17 \text{ M} \times 2\%$).

This instantaneous concentration of H_2O^+ and H_2O^- is about a million times higher than the 10^{-7} M equilibrium concentration of H^+ and OH^- in pure water. This implies that the trace amount of H^+ and OH^- is in equilibrium with a million times higher concentration of charged water molecules. This further suggests that there is a probability of roughly one in a million (0.0001%) of converting these charged waters to H^+ and OH^- . Converting $\text{H}_2\text{O}^+\cdots\text{H}_2\text{O}^-$ to $\text{H}_3\text{O}^+\cdots\text{OH}^-$ requires only a slight displacement of a hydrogen atom from the hydrogen bond donor toward the acceptor (note that the hydronium ion, H_3O^+ , is formed by attaching a H^+ ion to a neutral H_2O molecule). Thus, hydrogen atom transfer provides a possible mechanism that converts charged water molecules to the trace amount of H^+ and OH^- in pure water (5). Moreover, the experimentally observed increase in the concentrations of H^+ and OH^- in water with in-

Fleeting charge transfer and longer-lived ions in water

Hydrogen bond charge transfer generates a fleeting positive (+) or negative (–) charge on water molecules. This may give rise to longer-lived partially charged water molecules ($\text{H}_2\text{O}^{+\delta}$ and $\text{H}_2\text{O}^{-\delta}$ with $\delta \approx 0.02$) in equilibrium with hydrogen (H^+) and hydroxide (OH^-) ions, and perhaps also hydrated electrons (H_2Oe^-) and water radical cations ($\text{H}_2\text{O}^{+\bullet}$).



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creasing pressure and temperature implies that the hydrogen atom transfer probability increases with increasing water density and thermal energy. In other words, although the presence of H^+ and OH^- in pure water has long been known, the possibility that these ions may be generated by the much higher concentration of charged water molecules has not been considered.

The quantum superposition of $H_2O \cdots H_2O$ and $H_2O^+ \cdots H_2O^-$ also implies a rapid charge fluctuation with an on-off blinking rate on the order of a thousand terahertz—estimated by assuming the round-trip time of an electron bouncing between two neighboring water molecules. Although these fleetingly charged waters are very short-lived, they bear a striking resemblance to much longer-lived H_2O^+ and H_2O^- ions. Long-lived H_2O^+ has recently been discovered in charged water droplets and found to be chemically reactive (6). Long-lived H_2O^- is closely related to a “hydrated electron,” whose structure has long been debated, with the current consensus being that it can best be described as an extra electron partially bound to a water molecule. However, the fleetingly charged waters, which constantly blink in and out of existence, must be structurally and chemically distinct from their longer-lived relatives. This is because long-lived ions contribute to electrical conductivity and hydrated electrons have a blue color. Thus, the experimental conductivity and optical transparency of water imply that these long-lived H_2O^+ ions and hydrated electrons have lower concentrations than H^+ and OH^- .

Water charge transfer has additional implications for interfacial water chemistry, including that occurring at macroscopic air–water or oil–water interfaces and at the surfaces of molecules such as alcohols and some amino acids dissolved in water. At all of these interfaces, there is an increase in the number of water molecules with an odd number of hydrogen bonds, and thus a buildup of charged layers near the water surface, as well as charge transfer from water to oil (1, 2). The resulting layer of excess negative charge near the surface is consistent with the observed negative charge of air bubbles and oil droplets (1, 2). Although the interpretation of such experimental evidence remains a subject of debate, there is no escaping the intimate link between hydrogen bonding, charge transfer, and the building up of charge layers at air–water and oil–water interfaces (2, 4), as well as the following broader chemical implications.

Chemical reactivity at the surface of water is a subject of intense current interest,

fueled by the discovery of up to a million-fold increase in the rates of some reactions at the surface of water compared with the rates in water (7). The buildup of charges near the surface, resulting from the greater number of charged water molecules with an odd number of hydrogen bonds, has been proposed as a mechanism for the observed reactivity changes (8).

The buildup of charge near the surface of water may also affect chemical equilibria involving H^+ , OH^- , and other ions, and influence the solubilities of oily molecules in water. Although the affinities of H^+ and OH^- for air–water and oil–water interfaces remain controversial (5), surface tension and solubility experiments imply that such interfaces tend to expel OH^- and attract H^+ . Specifically, adding OH^- ions to water increases its surface tension and decreases the solubility of oily molecules, such as benzene, whereas adding H^+ ions has the opposite effect. These observations indicate that the interfacial concentration of OH^- is lower than that in bulk water, while the opposite is true for H^+ , which implies that H^+ has a slightly higher concentration near air–water and oil–water surfaces. The affinity of H^+ for such surfaces is apparently consistent with the attraction between H^+ and the negative surface charge layer induced by charge transfer. However, there may be other contributing factors, as simulations that did not consider charge transfer have also predicted that an oily methane molecule repels small positive ions less than small negative ions (9).

All interfacial reactivity changes, including changes in reaction rates and product yields, are linked to the propensity of the reactants, intermediates, and products to adsorb onto the surface. Such adsorption differences may depend on various chemically specific mechanisms (10), including stabilization of reaction intermediates resulting from the same interfacial imbalance of hydrogen bond donors and acceptors that is responsible for interfacial charge layering (11). More general arguments indicate that adsorption should be more favorable for neutral than charged molecules, and for larger molecules or ions than smaller ones (12). The resulting high interfacial concentrations of neutral molecules or large molecular ions may greatly increase reaction rates, even if the associated activation energies required for the reaction to occur are unchanged. Additionally, the activation energy may decrease, and thus rate constants increase, at surfaces—particularly for reactions involving intermediates that are physically larger than the corresponding reactant species. This expectation is consistent with recent

observations of the interfacial acceleration of bimolecular, but not unimolecular, reactions (13), as bimolecular reactions necessarily have intermediates that are larger than the corresponding reactants.

A detailed understanding of the chemical implications of water’s electrical buzz is only now beginning to emerge. There is no doubt that this buzz strengthens hydrogen bonds and produces a high concentration of partially charged water molecules. However, the precise concentrations of charged waters and the resulting interfacial charge layering have yet to be determined. The influence of water’s electric buzz on interfacial chemistry is an even newer subject whose details and implications remain to be explored. This is particularly true of the similarities between chemical reactivity at both macroscopic interfaces and the molecular surfaces of solutes dissolved in water. Such similarities imply that the recently discovered acceleration of the rates of some reactions at macroscopic air–water interfaces (7) may also occur inside of water that contains oily molecules, as is the case in biological systems. Additionally, observations of the effect of oil chain-length on ion–oil interactions (14) and the effect of the concentration of oily molecules on water structure (15) raise questions regarding the influence of interfacial curvature and crowding on water charge transfer and chemical reactivity. Although the answers to many of these questions, as well as their practical implications, remain to be discovered, the ubiquity of water and aqueous interfaces leaves little doubt that there is much to be gained from such pursuits. ■

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