AQUEOUS ION TRANSPORT

Sticky when wet

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The aqueous hydronium cation diffuses about twice as fast as the aqueous hydroxide anion in liquid water, but the origin of this behaviour has been unclear. Now, state-of-the-art simulations provide an explanation for this long-standing conundrum.

In liquid water, H_2O molecules are in equilibrium with their dissociation fragments hydronium (H_3O^+) and hydroxide (OH^-) and the motion of these ions is at the heart of chemical reactions in aqueous solution. How they are solvated by and diffuse within water's hydrogen-bonded network has been studied since the beginning of the 19th century and our contemporary understanding is that their motion is boosted by proton jumps between the ions and water molecules; hydronium diffuses roughly twice as fast as hydroxide (see e.g. refs. 1-3). However, why diffusion of the positively charged ion is speedier than that of its negative counterpart has remained a mystery. Now, however, writing in *Nature Chemistry*, Roberto Car, Xifan Wu and colleagues provide an explanation[4]. They suggest, on the basis of state-of-the-art computer simulations, that hydronium diffusion occurs through concerted proton-transfer events, whereas hydroxide diffusion happens mainly in a slower step-wise manner.

Aqueous ion diffusion has been studied by some of the greatest minds in chemistry: Debye, Hückel, Onsager, Pauling, and Slater, to name but a few. One of the earliest concepts to emerge is the idea from von Grotthuss that proton conduction involved the hopping of protons along hydrogen-bonded water wires. Such a process involves the formation and cleavage of covalent

bonds and is generally regarded as structural diffusion, in contrast to Stokesian diffusion, in which molecules are considered as unsplit units.

Fully understanding the intimate details of the Grotthuss process is an immense challenge. From a simulation perspective, one must accurately describe the complex and dynamic hydrogen-bonding network of water, the dynamic solvation structures of the ions, and the bond-making and bond-breaking events of the proton-transfer processes. *Ab initio* molecular dynamics (AIMD) is a powerful computational approach that is capable of tackling all of these issues[5]. In AIMD the nuclei are propagated according to forces obtained from an *ab initio* electronic structure theory; generally, this is density functional theory (DFT)[6]. In DFT calculations in practice approximations are made for how the electrons in a DFT calculation interact with each other and (perversely) with themselves. Standard approximations — so-called generalised gradient approximations (GGAs) — that have generally been used to study aqueous ions have suffered from this artificial 'self-interaction' error and have also omitted long-range London dispersion forces. These are two issues that are known to have an impact of the structure of liquid water itself[7]. A key advance in the study from Car, Wu and colleagues is that it uses a DFT methodology that addresses to a large extent both of these shortcomings.

A proton can jump from a hydronium ion along a hydrogen bond to a neighbouring water molecule, converting that water into a hydronium. The net effect of this proton transfer is that the hydronium has diffused. From earlier work, we also know that multiple proton jumps can occur simultaneously along a hydrogen-bonded water chain[8], with the effect that the hydronium ion diffuses across several water molecules at once (Fig.1a). The simulations from Car, Wu and colleagues support this picture and show that double and triple jumps are preferred over single jumps. Overall, for this ion, remedying the self-interaction error and accounting for London dispersion forces does not alter the essence of the previously established mechanism.

More interesting are the insights into hydroxide ion motion. In water, hydroxide generally forms two hydration states with either three or four hydrogen bonds, with the latter state referred to as 'hyper-coordinated'. Proton transfer is facile when hydroxide is forming three hydrogen bonds, but not when it is accepting four. The calculations made by Car, Wu and colleagues using the traditional GGA methodology find a roughly 50–50 distribution of the two hydration states and rapid proton hopping involving single and multiple hopping events. However, when London dispersion forces and self-interaction errors are accounted for, the hyper-coordinated state is strongly favoured; with the more accurate calculations, the distribution of states is about 80–20 in favour of hyper-coordination. This, in turn, significantly reduces the frequency of multiple hopping events, favouring single jumps (Fig. 1b) and considerably reducing the overall hydroxide ion mobility.

The AIMD simulations reported by Car, Wu and colleagues are the most sophisticated of their type that have been performed on hydroxide and hydronium in liquid water. The diffusion rate of hydronium, estimated from their calculations using the Einstein relation, is about twice that of hydroxide, which agrees well with experimental observations. The predicted hyper-coordinated structure is also consistent with suggestions of a non-planar structure from neutron scattering measurements[9]. Overall, the methodology used has proved to be necessary and looks promising. London dispersion forces tend to compress the hydrogen-bond network, hence enhancing coherent Grotthuss processes. Ameliorating self-interaction errors improves the electronic structure of the ions and the inherent structure of the liquid water that solvates them. The calculations, however, highlight that these improvements can have quite different consequences for two seemingly similar processes; underscoring just how challenging accurate and realistic simulations of aqueous systems can be.   With this in mind it is important to recognise that the DFT methodology used is still not the exact solution, and it remains to be seen if with further DFT improvements or with accurate wave function based methods the reasonably good agreement with experiment will be retained. For the diffusion of hydronium and hydroxide, nuclear quantum effects

(tunnelling and zero-point motion) have not previously had a very significant impact on the diffusion mechanism when examined at the DFT-GGA level. However, given the sensitivity of this system to subtle changes in solvation structure it might be worth revisiting the question of nuclear quantum effects in these systems. Finally, experimentally detecting the hyper-coordination solvation structure of hydroxide as predicted by Car, Wu and colleagues would be valuable. Recent experimental progress in ultrafast infrared spectroscopy has resulted in various gaps in our understanding of hydronium solvation and diffusion being filled (see ref. 10 for example), giving hope that we might not have to wait too long. Nevertheless the calculations of Car, Wu and colleagues show how improved theoretical methodology, can provide new insights into old problems.

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