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Ionic Diffusion and Proton Transfer in Aqueous Solutions under an Electric Field: State-of-The-Art

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Most of the properties and anomalies describing the behavior of water are somehow related to the hydrogen bonded (H-bonded) network [1-3]. Albeit the features of H-bonds have been investigated and depicted by an impressive amount of research, the way in which some external conditions—such as the inclusion of ionic species—affect the three-dimensional H-bonds arrangement is wrapped up in a high degree of uncertainty.

If, on one hand, the presence of solvated ions cannot be avoided even in ultra-pure water samples, on the other hand, the lack of scientific consensus about the ion-induced microscopic effects on the water structure is representative of the practical challenges faced when investigating electrolyte solutions [4,5]. However, the indisputable role played by a few atomic charged species both in biology (i.e., Na⁺, Cl⁻, Mg²⁺, Ca²⁺, etc.) [6-8] and in industry (e.g., Li⁺ batteries) [9] requires impelling and massive scientific efforts. In fact, besides the well-known Hofmeister series [10], hydrated ionic species finely rule the selectivity of cell membranes [6,7], being thus responsible of complex processes such as the nerve pulse generation. On the other hand, aqueous solutions represent the prototype of electrolytic batteries.

In all cases, a subtle balance between electrostatics, quantum mechanics (i.e., partial orbital sharing), and thermodynamics governs the delicate behaviour of the hydration process. The complexity of the problem is witnessed, inter alia, by the fact that there is no general consensus on the spatial extent of the effects induced by the inclusion of an ion in bulk water [11-13].

Recent ab initio calculations [14] have shown that the presence of a chaotrope species such as Cl^- does not have any effect on the orientation of water dipoles beyond the first hydration shell, whereas detectable perturbations—perhaps extremely small and unable to affect biological phenomena—have been observed in the polarizability of the water molecules at longer distances.

Additionally, the lack of a wide consensus on the typical coordination numbers characterizing the ionic first solvation shell is thoroughly recorded in the literature [4]. From an experimental perspective, the identification of this quantity is a very hard task for small ions such as Li^{+} and, recently, new ionic radii for this species and for Na^{+} have been proposed [4] by joining the advantages stemming from Large Angle X-ray Scattering (LAXS) and double Difference Infrared Spectroscopy (DDIR). In this respect, ab initio Molecular Dynamics (AIMD)

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[8,14] and QM/MM [15] computational techniques have proven their reliability in reproducing the ion-induced structural changes in aqueous solutions, thus becoming an invaluable tool for the characterization of electrolyte solutions at a molecular level.

In particular, it seems that at low-to-moderate concentrations the ions may replace water molecules in the aqueous H-bonded structure, by following the same "water rules". This example proves that classical molecular dynamics may fail in dealing with delicate local electrostatic balances and that first-principles approaches are necessary not only for a correct microscopic characterization of these phenomena but also in order to improve the models on which classical force fields rely.

Indeed, although sixty years ago concepts such as kosmotrope and chaotrope have been introduced to characterize the perturbation produced by a given ion on the H-bond network of water [16,17], and notwithstanding the fact that these notions were supported by classical molecular dynamics simulations [18-20], they have recently been blunted by an AIMD study [21]. Ionic conductivities are determined by applying an oriented external static electric field to electrolyte solutions. When an external electric field is applied, the situation is even tougher.

In the low field strength regime and within the Kohlrausch's law of independent migration of ions (i.e., in the limit of infinite dilution), the mobilities of the alkali metal cations are well-established and can be easily related to their respective ionic sizes [22] i.e. the bigger the cation the larger the mobility. However, at finite molarities and for stronger field intensity regimes the overall situation may dramatically change. Field intensities of the order of 1 V/Å and even stronger were detected at the atomic sites of the water molecules hydrating Na⁺ and Cl⁻ ions [23], suggesting that for moderate-to-intense field strengths more complicated phenomena may be relevant in describing the ionic diffusion. Moreover, field intensities of about 0.30 V/Å are able to induce the molecular dissociation of water and proton transfers along the H-bonded network [24-27] via the well- known proteolysis reaction:

$$2 H_{2} \rightleftharpoons 0 H^{-} + H_{3} O^{+}$$

This latter process plays a crucial role in many disparate domains, from neurobiology to electrolytic batteries and hydrogen-based technology [28,29]. Thus, it can be expected that a subtle interplay between the two deeply different mechanisms of protonic migration, on one hand, and of standard ionic diffusion, on the other, rules the complex dynamics of electrolytic solutions subjected to intense field strengths.

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