

Mechanisms of acceleration and retardation of water dynamics by ions

Guillaume Stirnemann,^{†,¶} Erik Wernersson,^{‡,§} Pavel Jungwirth,^{*,‡} and Damien Laage^{*,†}

Department of Chemistry, Ecole Normale Supérieure, UMR ENS-CNRS-UPMC 8640, 24 rue Lhomond, 75005 Paris, France, and Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 16610 Prague 6, Czech Republic

E-mail: pavel.jungwirth@uochb.cas.cz; damien.laage@ens.fr

Abstract

There are fundamental and not yet fully resolved questions concerning the impact of solutes, ions in particular, on the structure and dynamics of water, which can be formulated as follows: Are the effects of ions local or long-ranged? Is the action of cations and anions on water cooperative or not? Here, we investigate how the reorientation and hydrogen-bond dynamics of water is affected by ions in dilute and concentrated aqueous salt solutions. By combining simulations and analytic modeling, we first show that ions have a short-ranged influence **on the reorientation of individual water molecules** and that depending on their interaction strength with water, they may accelerate or slow down water dynamics. A simple additive picture combining the effects of the cations and anions is found to provide a good

*To whom correspondence should be addressed

[†]Ecole Normale Supérieure

[‡]Acad. Sciences Czech Rep.

[¶]Current address: Department of Chemistry, Columbia University, New York, USA

[§]Current address: Department of Chemistry, Lund University, Sweden

description in dilute solutions. In concentrated solutions, we show that the average water re-orientation time ceases to scale linearly with salt concentration due to overlapping hydration shells and structural rearrangements which reduce the translational displacements induced by hydrogen-bond switches and increase the solution viscosity. This effect is not ion-specific and explains why all concentrated salt solutions slow down water dynamics. Our picture, which is demonstrated to be robust vis-a-vis a change in the force-field, reconciles the seemingly contradictory experimental results obtained by ultrafast infrared and NMR spectroscopies and suggests that there are no long-ranged cooperative effects in dilute solutions.

Water in our environment is never found as the pure substance but always contains dissolved salts, which affect its molecular properties and play a key role in a wide range of contexts. Examples include ions in seawater which participate in corrosion processes,¹ ions in atmospheric aerosols involved in environmentally relevant reactions,² and ions in the cellular medium affecting the stability of proteins^{3,4} and nucleic acids.³ In addition to the dramatic impact that ions can have both on the structure and dynamics of the surrounding water molecules, it was further observed that these effects are strongly ion-specific. Different ions can have radically different effects, as shown for example by their varying abilities to precipitate proteins from aqueous solutions, expressed in Hofmeister's empirical classification.^{3,4}

Despite the fact that it is crucial to understand and characterize the action of ions on water, there is still no consistent molecular picture to describe the impact of ions on water dynamics and several essential aspects are still unclear. A first fundamental but unresolved question is whether ions retard or accelerate water dynamics. All recent time-resolved experiments⁵⁻⁹ have observed that water dynamics in salt solutions is slower than in neat water but viscosity, dielectric relaxation and NMR measurements¹⁰⁻¹⁴ have suggested that some salts can increase the water lability. A related unexplained and intriguing result is the finding by these latter experiments¹² that all ions slow down water dynamics at high salt concentrations, including those which accelerate water in dilute conditions.

A second essential question pertains to the range of influence of an ion on the water molec-

ular properties. Numerous experimental and theoretical¹⁵⁻¹⁹ studies have suggested that a single ion typically perturbs only its first hydration layer, except for species with a high charge density, i.e. very small (e.g. F^- , Li^+) or multiply charged (e.g. Mg^{2+} , Ca^{2+}) ions, whose influence can extend to the second or third shells. A consequence is that, as found in several studies,^{10-12,18} in dilute solutions the influence of a given ion should be independent of its counterion. However, for salts like $MgSO_4$ and Na_2SO_4 , this standard additive picture was recently challenged by experiments⁵ which suggest instead that due to some cooperative effects the nature of the counterion can markedly change the influence of a given ion on the surrounding water molecules even in dilute salt solutions. However, these conclusions seem to contrast with those from an earlier ultrafast spectroscopy study¹⁵ on a series of salt solutions (including Na_2SO_4) which found that the addition of ions had no influence on the rotational dynamics of water molecules outside the ions' first solvation shells.

Here, we combine analytic modeling and molecular dynamics (MD) simulations to study and characterize the ion-specific effects on water dynamics. Classical MD simulations appear as an exquisite tool here because they provide a molecular picture of the reorientation dynamics while giving results that can be compared with available experimental measurements, including ultrafast infrared anisotropy decays^{5,6} and NMR orientational relaxation times.^{10,11} Due to the presence of high localized charges in ionic systems we employ polarizable force fields to account for the polarization of the surrounding waters by the ionic charges and its impact on the dynamics.²⁰ We have carefully verified that these force fields yield a description of the solution structure and of water dynamics in good agreement with the available experimental data, both at low and high salt concentration and we have also checked that our conclusions are robust vis-a-vis a change of force field. We first consider the influence of a series of single ions on water reorientational dynamics and determine why some ions accelerate the dynamics of water while others induce a slowdown with respect to the bulk situation. We then study the effect of multiple ions in concentrated aqueous salt solutions and choose two paradigm systems (Na_2SO_4 and $NaClO_4$) simulated at different concentrations. We investigate the potential presence of cooperative effects, **whereby the impact**

of a given ion on the dynamics of individual water molecules changes with the nature of the counterion. We eventually identify the reason why the same salt can have totally opposite effects on water dynamics when its concentration is changed.

Results and Discussion

Influence of a single ion

Hydration shell structure and dynamics. We start by characterizing the impact of isolated anions and cations on the surrounding water molecules. As already well established,^{16,21–23} a water molecule tends to point one of its OH bonds toward an anion while its dipole points away from a cation. However, these hydration structures are not rigid and the amplitude of the water fluctuations around these average configurations increases with decreasing ionic charge densities (Fig. 1A-B).

While a classification of ions based on their impact on water structure was shown to be ill-defined,^{22,23} considering the effect of ions on the surrounding water dynamics provides a less ambiguous alternative.^{10–12} This can be measured via the water orientation time correlation functions (tcf)

$$C_2(t) = \langle P_2[\mathbf{u}(\mathbf{0}) \cdot \mathbf{u}(\mathbf{t})] \rangle, \quad (1)$$

where P_2 is the second-order Legendre polynomial and \mathbf{u} is the orientation of a molecular body-fixed vector such as the water OH bond or dipole direction. $C_2(t)$ is accessible from time-resolved ultrafast IR spectroscopy and from MD simulations, while NMR provides the value of the time-integrated tcf for several water molecular axes or tensors, determined by the chosen isotope.²⁴

Both for water molecules in the aqueous bulk and those initially in an ion's first shell, the OH and dipole orientational tcfs exhibit a fast, sub-0.2 picosecond (ps), partial decay due to librations, followed by a ps decay leading to a full decorrelation (Figs. 1C and 1D). This slower decay is approximately exponential and its characteristic reorientation time τ_{reor} is reported in Fig. 1E. For both anions and cations, the reorientation time is observed to increase with growing ionic

charge densities, in agreement with prior NMR measurements.^{10,11} However, even with Mg^{2+} and SO_4^{2-} which induce the largest retardation factors in our study, the OH reorientation time remains short enough so that at dilute conditions water molecules in the ions' hydration layers cannot be considered as immobilized.

To rationalize how ions affect water dynamics, it might be tempting to suggest a simplified model where anions would only affect the water OH dynamics while cations would only act on the water dipoles.⁵ To assess the validity of this description, we have determined the degree of anisotropy in water reorientation dynamics, estimated through the comparison of the reorientation times associated with these two water molecular vectors. In the bulk, water reorientation was suggested to be only slightly anisotropic.²⁹ Next to ions, Fig. 1E shows that only strongly interacting ions like Mg^{2+} and SO_4^{2-} induce a significant anisotropy between the OH and dipole reorientations. This is in agreement with NMR measurements (deletion) probing the reorientation of different molecular axes,²⁴ and results from the similar interaction energies experienced by a water molecule in the hydration shell with the ion and with the other surrounding water molecules. Our simulations thus show that cations do not exclusively affect the water dipole dynamics, and similarly anions do not exclusively affect water OH bonds.

We have also examined the size of the dynamically perturbed shell of water molecules around an ion. For water molecules initially in the second shell, the reorientation dynamics is already bulk-like for all ions except those with a very high charge density, Mg^{2+} and SO_4^{2-} , for which a moderate residual slowdown is observed (deletion)(see S.I.). No effect could be detected in the third layer. This reinforces prior conclusions obtained with various techniques¹⁵⁻¹⁹ about the local and short-ranged nature of the perturbation by a single ion.(deletion)

Origin of slowdown and acceleration. (deletion)Another key point in Figs. 1C-D is that compared to the bulk, some ions accelerate the reorientation dynamics of water molecules within their shell while others slow it down, in agreement with NMR results¹² (see S.I.). We now identify the physical mechanism causing **these** opposite effects.

We analyze the reorientation time within the recently suggested extended jump model frame-

work.^{30,31} Beyond the librational decay, water molecules were shown^{30,31} to reorient both via large amplitude angular jumps when a water OH group trades hydrogen-bond (HB) acceptors and by a diffusive frame reorientation of an intact HB axis between successive jump events (see Fig. 4E). The resulting reorientation time is^{30,31}

$$\tau_{reor}^{-1} = \left(\tau_{reor}^{jump}\right)^{-1} + \left(\tau_{reor}^{frame}\right)^{-1}, \quad (2)$$

(deletion)where $\tau_{reor}^{jump,frame}$ are respectively the jump and frame contributions to the reorientation time. This model was successfully applied to water dynamics next to several anions.^{32,33} Studies of water reorientation next to a wide range of dilute solutes have revealed that the changes in the water reorientation dynamics mainly result from a change in the jump time.³¹ For a water molecule lying at the interface between a solute and the bulk, the jump time depends on two factors, the local topology and the strength of the HB to be broken,³¹ that we now discuss in the specific context of salt solutions.

The topological effect is induced by any type of ion and results from the partial hindrance of a new water HB partner's approach. Compared to the bulk situation, the volume occupied by the ion reduces the number of accessible transition state configurations for the jump exchange and leads to a slowdown $\rho_V > 1$ (where ρ_V is the excluded volume factor) in the jump rate constant.³¹ The HB strength factor arises from the free energy cost to stretch the initial HB to reach the jump transition state configuration. This ρ_{HB} factor differs from 1 only when the initial HB acceptor is an anion which either accelerates the jump rate because it accepts an initial bond weaker than a water-water HB (leading to an HB strength factor $\rho_{HB} < 1$), or slows it down if the bond is stronger ($\rho_{HB} > 1$).³¹ The jump time results from the combination of the excluded volume and HB strength factors, $\tau_{jump} = \rho_V \rho_{HB} \tau_{jump}^{bulk}$.

Anions affect water dynamics through both ρ_V and ρ_{HB} . For very weak HB acceptors, e.g. ClO_4^- , the ρ_V slowdown can be more than compensated by the ρ_{HB} acceleration, leading to an overall acceleration relative to the bulk situation ($\rho_V \rho_{HB} < 1$, as illustrated in Figure 1C by the

faster tcf decay for OHs initially bonded to the anion). All other investigated anions whose HB strength with water is comparable to or greater than that of the water–water HB induce a slowdown ($\rho_V \rho_{HB} > 1$).³³ Since the ρ_V factor changes little between anions, a good correlation is found between the water reorientation time next to an anion and the free energy cost to stretch the anion–water HB (Fig. 1F). A qualitative guideline can thus be determined: anions for which the HB elongation cost is greater than that in bulk water (approximately 0.8 kcal/mol) tend to slow down water dynamics. **While our model is not quantitative and still requires to be extended, e.g. to comprehensively describe all cations (see SI), (deletion),** we underline that the simple ρ_V and ρ_{HB} considerations can already semi-quantitatively rationalize the effects of both cations and anions on water reorientation dynamics and identify the HB strength effect as the key factor to discriminate between water-accelerating and retarding ions.

Concentrated salt solutions

We now apply the understanding gained about the influence of a single ion on water dynamics to study concentrated aqueous salt solutions including several anions and cations. In particular, we establish why some techniques like ultrafast spectroscopy experiments systematically observe a slowdown while others see an acceleration in some cases. (deletion)

Paradigm salts. To investigate the impact of an increasing ionic concentration on water reorientation dynamics, we focus on two salts, Na_2SO_4 and NaClO_4 , which exhibit qualitatively different behavior and for which femtosecond infrared and NMR spectroscopy results are available. For each salt, we have performed simulations at several concentrations (see S.I.). Figure 2 shows that for the two salts the results of our simulations are in good agreement with both the time-resolved anisotropy decays^{5,6,35,36} and with the average water reorientation time measured by NMR¹⁰ for increasing salt concentration. While water dynamics is retarded at any Na_2SO_4 concentration (Figs. 2A-B), it is accelerated at low NaClO_4 concentration and slowed down at higher concentration (Fig. 2D), as observed in NMR.¹⁰ We now establish the molecular factors which explain why a change in concentration can dramatically modify the effect of a given salt on

water dynamics.

Test of the additive picture. We first test the standard additive picture suggested by viscosity and NMR measurements.^{10,11} In dilute solutions, the average water reorientation time $\langle \tau_{\text{reor}} \rangle$ is a weighted average of the water bulk, cationic, and anionic hydration shell **reorientation times, which** are assumed to be independent of the salt concentration. As previously recognized in experimental measurements,^{10,11,37} our simulations (Fig. 2 and SI) confirm that this additive picture holds at lower concentrations (typically below 1 m). The Na_2SO_4 and NaClO_4 salts are respectively a retardant and an accelerant, and the average water dynamics changes linearly with the salt concentration. However, when the salt concentration **exceeds a** threshold value (which decreases with the ion-water interaction strength), water reorientation slows down more rapidly than predicted by the simple additive model (Fig. 2 and SI). This is observed for both salts, including NaClO_4 for which there is a dramatic qualitative change **from acceleration to retardation**. Deviations from the linear behavior imply that the reorientation times of each population change with concentration and are usually explained by the combined influences of cations and anions on some water molecules, either due to the fact that the cationic and anionic hydration shells overlap at high concentration, or because of ion pairing whose probability may be higher than expected from a simple homogeneous distribution, especially for multivalent ions.

Ion pairs. To understand how the dynamics of a water molecule is affected by the concomitant presence of several ions, we focus on water molecules between ions involved in two types of pairing:³⁸ solvent-shared ion pairs (SSIP) where the cation and anion share a fraction of their hydration layers, and solvent-separated ion pairs (2SIP) where the two ions are separated by two hydration layers (see Fig. 3A). For the OH bond and dipole dynamics of different types of water molecules engaged in those ion pairs in Na_2SO_4 solutions at several concentrations, Fig. 3B compares the slowdown directly measured in our simulations ρ_{\pm} and the slowdown predicted by combining the **perturbations induced by isolated ions** as $\rho_+\rho_-$, i.e. assuming that the changes in the reorientation free energy induced by the two ions can be simply added. In the dilute 0.5 m solution, a high correlation is found between ρ_{\pm} and $\rho_+\rho_-$, showing that the collective effect of the two ions is

simply a combination of their respective effects taken separately.

However, for growing salt concentration, the slowdown experienced by water molecules in ion pairs increasingly exceeds the simple $\rho_+\rho_-$ combination (Fig. 3), which shows that the retardation at high concentration is caused by more than the combined actions of two ions only. We now provide additional arguments suggesting that the increasing slowdown observed for the entire solution at high concentration cannot be explained by an increasing fraction of slow water molecules engaged in ion pairs. First, even though dielectric relaxation spectroscopy may underestimate the number of ion pairs since it is mostly sensitive to long-lived pairs, measurements suggested that in dilute Na_2SO_4 solutions less than 20% of the ions are engaged in ion pairs and that this fraction decreases with concentration above 0.2 m.³⁹ Second, the retardation induced by these ion pairs cannot exceed their lifetime, which was found to be usually shorter than 10 ps in our simulations.

Local electric field. Since ion pairs cannot explain the deviation from the additive behavior at high concentration, we then consider more collective effects and whether the slowdown could be due to an increase in the local electric field generated by all ions and water molecules. In our simulations we compute the electric field experienced by water hydrogen atoms (Fig. 3C). While in Na_2SO_4 solutions the field is very little affected by an increasing salt concentration, in NaClO_4 solutions the field decreases markedly with increasing concentration. Both observations are consistent with experimental infrared spectral shifts.^{6,36}

While in Na_2SO_4 solutions the average water OH reorientation time in the solution increases approximately in proportion to the average electric field, it is almost the opposite in NaClO_4 solutions where the reorientation time decreases for growing local electric field values (Fig. 3D and S.I.).(deletion)This thus clearly shows that the slowdown in water dynamics observed at high salt concentration cannot be understood by electrostatic considerations.

Extended jump analysis. We now use the framework of the extended jump model described above to identify the origin of the changes in water dynamics with salt concentration. In these ionic solutions, a water OH can be either hydrogen-bonded to another water oxygen, or bonded to an anion, or non-hydrogen-bonded. We neglect the initial fast (librational) decay since the

dangling situation is unstable and transient, and we do not explicitly consider the influence of the cation which is Na^+ in both salts and which only weakly perturbs water dynamics (Fig. 1). The average water OH reorientation time in solution $\langle \tau_{\text{reor}} \rangle$ can then be expressed as

$$\langle \tau_{\text{reor}} \rangle \simeq p_W \tau_{\text{reor}}^W + (1 - p_W) \tau_{\text{reor}}^A, \quad (3)$$

where p_W is the fraction donating an HB to a water and $\tau_{W,A}$ are the reorientation times when the HB acceptor is respectively a water oxygen or an anion oxygen. Within the extended jump model, the reorientation time in each state is given by the jump and frame contributions (Eq. 2). At a given salt concentration c , the difference between $\langle \tau_{\text{reor}} \rangle$ and the pure water reorientation time can then be decomposed into distinct contributions,

$$\langle \tau_{\text{reor}}(c) \rangle - \tau_{\text{reor}}^{\text{bulk}} = \delta \tau_p(c) + \delta \tau_f^W(c) + \delta \tau_f^A(c) + \delta \tau_j^W(c) + \delta \tau_j^A(c) \quad (4)$$

where $\delta \tau_p$, $\delta \tau_j^{W,A}$, $\delta \tau_f^{W,A}$ arise respectively from the change in the p_W fraction, and changes in the $\tau_{\text{reor}}^{\text{jump},W/A}$ and $\tau_{\text{reor}}^{\text{frame},W/A}$ reorientation times. The $\delta \tau_p$ change corresponds to the prediction of the additive picture, where the reorientation times within each population are constant.

At every concentration, each of these contributions can be estimated from our simulations **(deletion)(S.I.) in order to establish the main factors causing the slowdown in the salt solutions (Fig. 4A-B)**. For Na_2SO_4 , both the cation and the anion slow the dynamics of water when taken separately **(deletion)**. It is thus not surprising that the dominant contribution to the growing slow-down with concentration arises from the increase in the population of water OH donating a HB to a sulfate ion, which is a strong retardant¹² ($\delta \tau_p$). The next biggest contributions come from the slowdown in the frame reorientation times of waters donating a HB to another water or to an anion ($\delta \tau_f^{W,A}$).

In NaClO_4 solutions, the change in water dynamics with concentration is not monotonic. In dilute solutions the acceleration of $\langle \tau_{\text{reor}} \rangle$ with salt concentration results from the acceleration of $\tau_{\text{reor}}^{\text{jump},W}$ (Fig. 4B), due to the introduction of ClO_4^- ions which bring a high density of labile HB

acceptors in the solution, while at high concentration, the slowdown is clearly due to the increase in $\tau_{\text{reor}}^{\text{frame,W}}$. We note that in the concentrated solutions studied in the experiments of Refs.^{6,1}  water reorientation thus proceeds almost exclusively through jumps.

Figure 4 reveals how all concentrated salt solutions can retard water dynamics, independently of the ions' nature and effect on water in dilute conditions. For both NaClO_4 and Na_2SO_4 , a key contribution to the water reorientation slowdown at high concentrations arises from the frame retardation. A qualitative interpretation of the latter slowdown can be obtained by first noticing that the diffusive⁴⁰ frame reorientation time scales with the solution viscosity (see S.I.) and second by applying Eyring's description of viscosity. Although this model is certainly not quantitative, it provides an insightful description in terms of microscopic jumps⁴¹ which suggests that the frame reorientation time is proportional to τ_{jump}/L^2 , where L is the translational displacement induced by an HB jump (see S.I.). This can be used to provide a molecular interpretation of the frame slowdown in NaClO_4 solutions, where τ_{jump} decreases slightly with increasing salt concentration (Fig. 4B) while L decreases markedly, as shown in the average jump mechanism (Fig. 4C). While in dilute solutions the new HB acceptor most frequently originates from the second shell, in concentrated solutions salt-induced structural changes enhance the probability to find water HB acceptors in an interstitial position between the first and second shells, as shown by the radial distribution function Fig. 4D. These structural changes have also been observed for many salt solutions by neutron scattering⁴² (see S.I.). They lead to a decrease in the jump-induced translational displacement with increasing concentration and thus to a viscosity increase and to a frame reorientation slowdown. (deletion) This partial decoupling between angular jumps and translational displacements could provide an interpretation for the absence of correlation between the collective reorientation and translation dynamics of water respectively measured by dielectric relaxation and optical Kerr effect spectroscopy in salt solutions of increasing concentration.⁴³ Similar arguments could also explain why a solute like urea slightly accelerates water dynamics at low concentration⁴⁴ but retards it at high concentration.⁴⁵ This important and sometimes dominant viscosity contribution which arises at high concentration regardless of the nature of the ions is clearly distinct from ion-

specific contributions such as electrostatic or ion-pair effects. We underline that test calculations run with a different force field where polarization is described in an effective manner lead to the same conclusions (see SI), which strongly suggests that these results are robust.

Interpretation of experiments

We now use our description to resolve the apparent contradiction between NMR and IR/THz experimental results and test some recent suggestions about the presence of cooperative effects in ionic solutions.

First, our results **explain why NMR finds**^{10–12} that in dilute conditions some salts accelerate water reorientation dynamics while others slow it down. Our model suggests that the key factor is the anion–water HB strength. The growing slowdown due to structural rearrangements and increasing viscosity at high concentration explains why a slowdown is measured by all techniques in concentrated salt solutions. Ultrafast infrared spectroscopy requires a high salt concentration (and a clear difference in reorientation times) to distinguish the dynamics of the water molecules affected by ions from that of the bulk, which explains why all of these studies so far^{5–7} have observed a slowdown.

Our simulations, which were verified to satisfactorily reproduce the ultrafast anisotropy decays in several salt solutions (Fig. 2), clearly show that both the semi-rigid propeller-like description and the cooperative immobilization of water molecules by special combinations of anions and cations that were recently suggested⁵ to interpret those experiments are not valid, even qualitatively. **First, regarding the propeller picture, our simulations show that, in agreement with other prior experiments,^{10–12} water molecules are far from being systematically locked by ions since they are even accelerated by some ions, and their motion remains quite isotropic (Fig. 1). Second, our work provides a test of the cooperative picture which had suggested⁵ that for certain salts like MgSO₄ and Na₂SO₄, ions act cooperatively through long-ranged electrostatic interactions to lock individual water molecules and dramatically retard their reorientation dynamics. Our results on Na₂SO₄ solutions (one of the salts studied in Ref.⁵) unambiguously show that there is no such cooperative**

effect (Fig. 3). In contrast, they support a picture where ions have a short-ranged influence on water,^{15–19} and where the deviation from the additive behavior is strongly concentration-dependent and arises from the overlap of hydration shells and, more importantly from the dramatic slowdown of the frame reorientation between HB jumps due to structural rearrangements. While this latter effect is collective, it is neither electrostatic nor ion-specific. The different ultrafast anisotropy decays measured⁵ for various salts can be rationalized within our picture and are suggested to arise from two effects. First some salts combine ions with similar effects on water dynamics (e.g. Na₂SO₄ which leads to a strong slowdown) while others associate ions with opposite effects (e.g. Cs₂SO₄ which induces a moderate slowdown). Second, vibrational lifetime effects were shown³² to induce large differences between the measured anisotropy and the orientation tcf Eq. 1; for example the short OH stretch vibration lifetime next to Mg²⁺ might explain the similar anisotropy decays for MgSO₄ and Na₂SO₄ while Mg²⁺ is a much stronger retardant than Na⁺. We finally note that the THz dielectric relaxation results⁵ which had also been interpreted by cooperative effects were recently explained¹⁸ with only short-ranged additive ion effects, while the counterion influence observed⁹ in Raman spectra was attributed⁹ to the non-ideality of the studied concentrated salt solution.

Concluding Remarks

We have identified how ions in dilute and concentrated salt solutions alter the dynamics of water. Through a combination of simulations in agreement with experimental data and obtained with different force fields, together with a simple but potent extended jump model, we have shown that ions induce a strong but short-ranged static and dynamic water response. At low concentration, the impact of a salt on water dynamics is ion-specific and follows the simple additive picture. Depending on the interaction strength, dilute ions may retard or accelerate water dynamics relative to the bulk. In contrast, in concentrated solutions, the slowdown is observed for all salts and has an important contribution which is non-specific and arises from an increase in viscosity due to

a reduction in the translational displacements induced by HB jumps, also found in concentrated non-ionic solutions. For weakly hydrated ions, this contribution is dominant, while for strongly hydrated ions it reinforces the ion-specific slowdown. Seemingly contradictory experimental results have thus been rationalized. While no cooperative effect due to the locking of water by some ion pairs could be found, our study highlights the key role played by the salt concentration. Further work is underway on the implications for enzyme catalysis focusing on explaining how different salt conditions affect the protein hydration layer lability and how ions may enhance the enzymatic activity.⁴⁶

Supporting Information Available

Simulation methodology, force-field assessment and electric field calculations. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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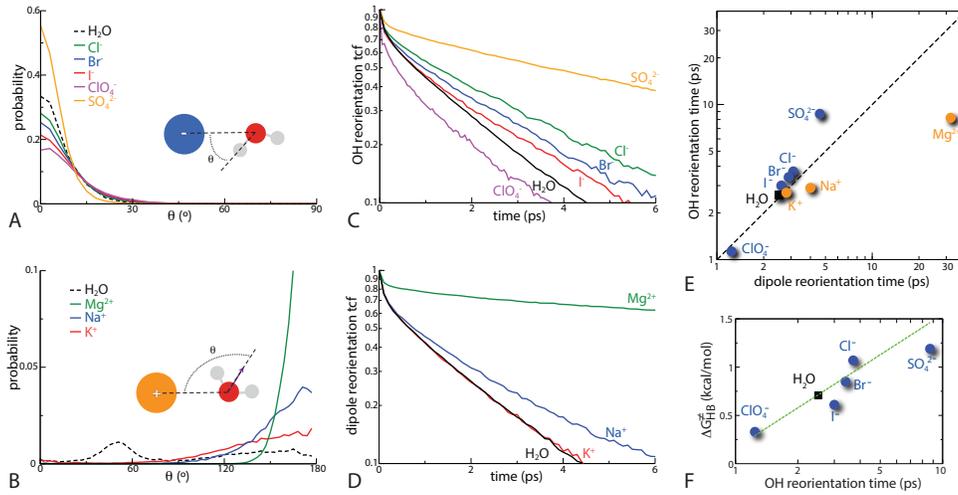


Figure 1: Effect of isolated ions on water structural and dynamical properties. A) Angular probability distribution for a water OH bond lying within an anion first shell; B) idem for the water dipole within a cation first shell; C) Orientation tcf Eq. 1 for a water OH initially bonded to an anion; D) idem for the dipole of a water initially in a cation hydration shell; E) Correlation between the OH and dipole reorientation times, where the dotted line corresponds to an isotropic reorientation; F) Correlation between the OH reorientation time and the free energy cost $\Delta G_{\text{HB}}^{\ddagger}$ to stretch the water–anion HB from its equilibrium distance to the elongation at the first maximum in the radial distribution function (dots). Within the extended jump model, $\rho_{\text{HB}} \simeq \exp \left[-\Delta \Delta G_{\text{HB}}^{\ddagger} / (k_B T) \right]$ (dashes).

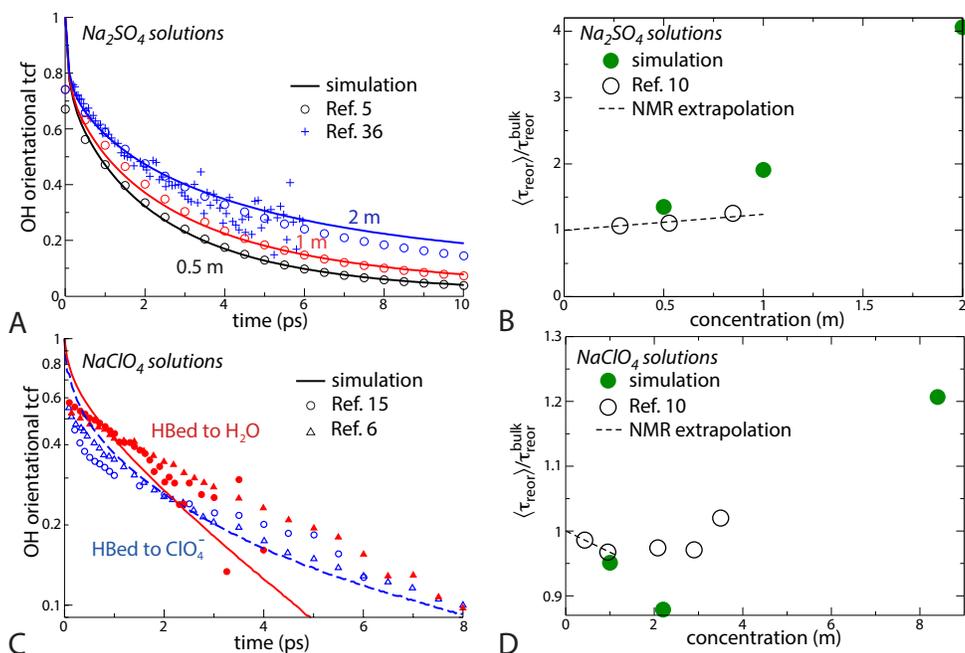


Figure 2: Experimental and simulated water reorientation dynamics in two salt solutions. A) Orientation tcf Eq. 1 in Na_2SO_4 solutions from our simulations and from ultrafast anisotropy decays^{5,36} (crosses correspond to Ref.³⁶ and circles were reconstructed from the fits given in Ref.⁵; both are shifted to compare the long-time decays). B) Ratio between the average reorientation time in the salt solution and the bulk value for increasing Na_2SO_4 concentrations from our simulations and from NMR;¹⁰ dashes represent the additive picture prediction. C) idem as A for 6 M NaClO_4 with anisotropy decays from Refs.^{6,15} the simulated tcf have been corrected for vibrational lifetime effects as explained in Ref.³² using the lifetimes from Ref.⁶ D) idem as B for NaClO_4 solutions.

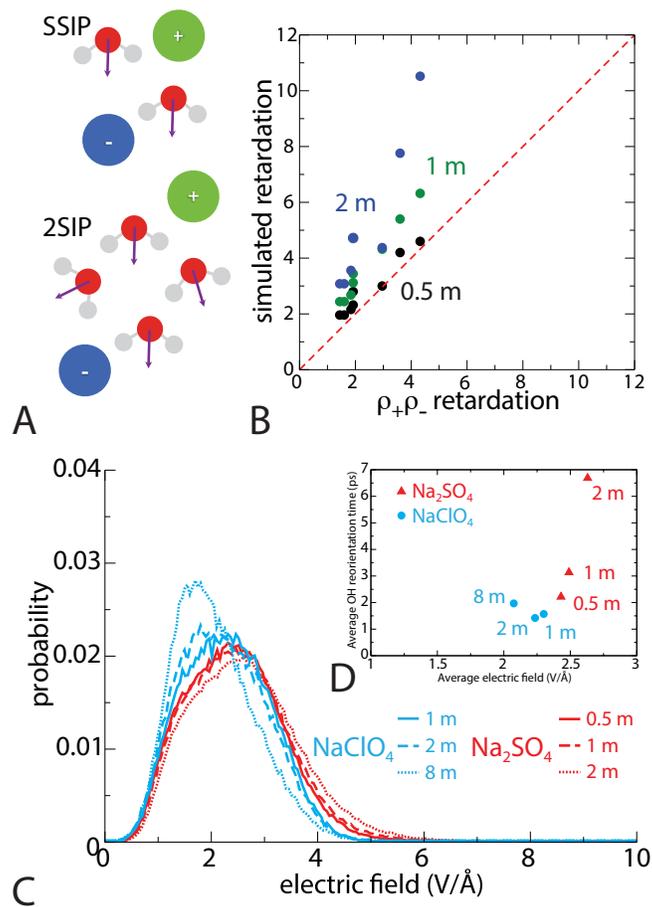


Figure 3: Cooperativity and electric fields in salt solutions. A) Schematic representations of the SSIP and 2SIP configurations; B) Correlation plot between the retardation factor for the OH and dipole orientations of the different types of water molecules depicted in panel A respectively obtained from our simulations and from the combination of the individual slowdowns $\rho_+\rho_-$ in Na₂SO₄ solutions. C) Probability distributions of the electric field modulus experienced by a water H. D) Correlation diagram between the electric field and the average water reorientation time in solution.

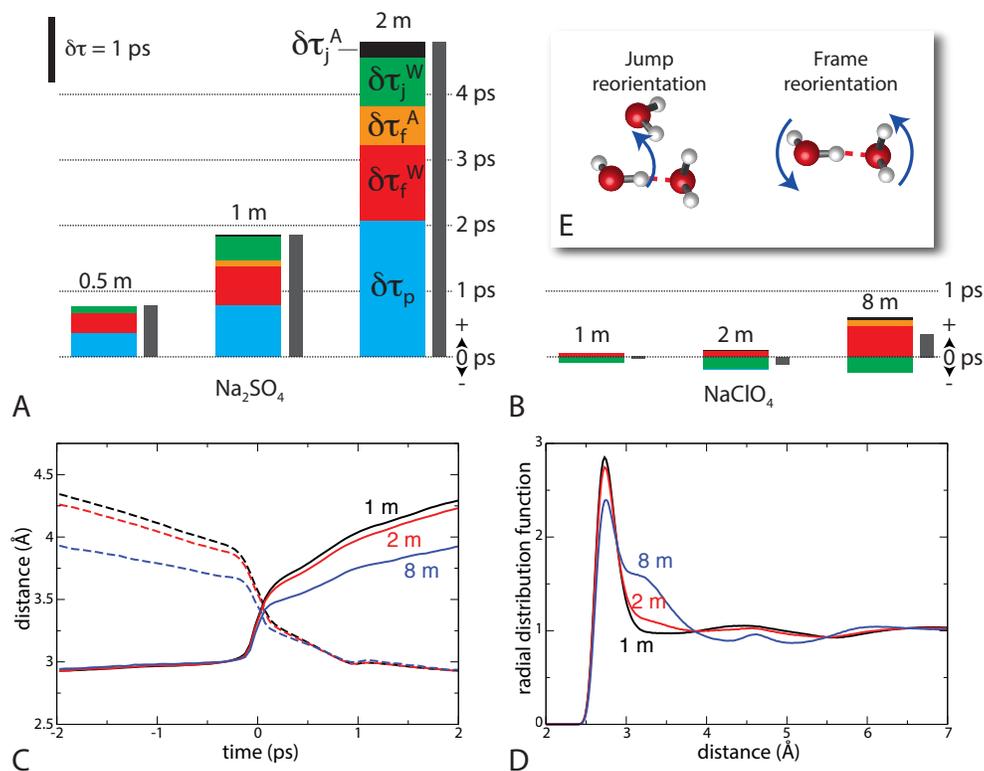


Figure 4: Contributions to the change in the average water reorientation time arising from the different terms in Eq. 4 at different concentrations for A) Na_2SO_4 and B) NaClO_4 . C) Average distances between the rotating water oxygen and the initial (solid lines) and final (dashes) water HB acceptors during a jump event and D) radial distribution functions between water oxygens in NaClO_4 solutions of increasing concentration. E) Schematic representation of the jump and frame reorientation motions.

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