

## Effect of Cations on the Hydrated Proton

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**S** Supporting Information

**ABSTRACT:** We report on a strong nonadditive effect of protons and other cations on the structural dynamics of liquid water, which is revealed using dielectric relaxation spectroscopy in the frequency range of 1–50 GHz. For pure acid solutions, protons are known to have a strong structuring effect on water, leading to a pronounced decrease of the dielectric response. We observe that this structuring is reduced when protons are cosolvated with salts. This reduction is exclusively observed for combinations of protons with other ions; for all studied solutions of cosolvated salts, the effect on the structural dynamics of water is observed to be purely additive, even up to high concentrations. We derive an empirical model that quantitatively describes the nonadditive effect of cosolvated protons and cations. We argue that the effect can be explained from the special character of the proton in water and that Coulomb fields exerted by other cations, in particular doubly charged cations like  $\text{Mg}^{2+}_{\text{aq}}$  and  $\text{Ca}^{2+}_{\text{aq}}$  induce a localization of the  $\text{H}^+_{\text{aq}}$  hydration structures.

The hydrated excess proton behaves radically different from other ions in water. It can go in and out of existence via water's autolysis reaction,  $\text{H}_2\text{O}_{\text{aq}} \rightleftharpoons \text{H}^+_{\text{aq}} + \text{OH}^-_{\text{aq}}$ , and its structural and dynamic properties are intimately linked with the topology of the hydrogen (H) bonding network of the water solvent.<sup>1</sup> While the transport of ordinary hydrated ions proceeds via diffusion of the ion's full mass, the Grotthuss transport mechanism of the proton, on the other hand, requires relatively small nuclear rearrangements to move the protonic charge over large distances.<sup>2,3</sup> This is possible due to efficient electron-transfer reactions between the protonic hydration structure and its first solvation shell, thereby enabling a near barrier-free interconversion between the limiting Eigen ( $\text{H}_3\text{O}_4^+$ )<sub>aq</sub> and Zundel ( $\text{H}_5\text{O}_2^+$ )<sub>aq</sub> complexes.<sup>4,5</sup>

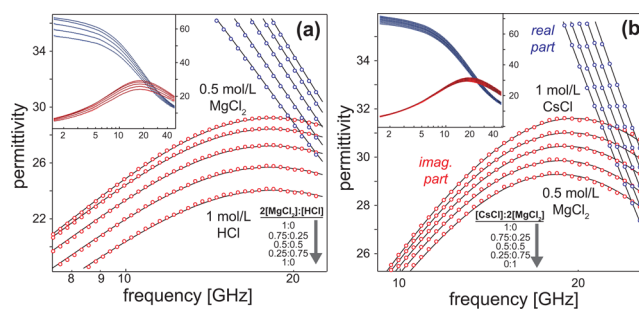
In many aqueous systems, e.g., intracellular water and proton exchange membranes, aqueous proton transfer takes place in the presence of other ionic cosolutes at high concentrations. From structure-determining experiments, such as X-ray and neutron diffraction,<sup>6</sup> extended X-ray absorption fine-structure (EXAFS), and large-angle X-ray scattering (LAXS),<sup>7</sup> it is known that the radial distributions of hydrated ions, especially those of higher valency, show substantial spatial structure extending well beyond the first solvation shell. This makes the H-bond topology of the electrolyte solution different from that of pure water. Furthermore, NMR,<sup>8</sup> dielectric relaxation,<sup>9–11</sup> ultrafast mid-infrared pump–probe studies<sup>12,13</sup> and MD simulations<sup>14</sup> have shown that the dynamics of water molecules hydrating

ionic species can be severely slowed down. Since the structural diffusion of the proton is dependent on both the water structure and its reorientation dynamics, it is expected that the conduction mechanism and mobility of the proton will be affected by other ionic cosolutes.

In this work we investigate how the hydration and transport mechanism of the proton are affected by the cosolvation of salts composed of monatomic ions using dielectric spectroscopy in the GHz frequency range. This technique is a powerful tool in studying the reorientation dynamics of liquids of small polar molecules.<sup>15,16</sup> Through measurements of the complex permittivity,  $\hat{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$ , reflecting the sample's macroscopic polarization as a function of the field frequency,  $\nu$ , information about the reorientation dynamics of the permanent electric dipoles of water molecules can be extracted. The pronounced dispersion in  $\hat{\epsilon}(\nu)$  of water in this frequency range is well described by a Debye relaxation model, with a Debye relaxation time  $\tau_D$  of  $\sim 8.7$  ps.<sup>17</sup>

Complex permittivity spectra in the range of 1–50 GHz were measured at  $22 \pm 0.5$  °C using a phase-sensitive vector network analyzer (VNA, Rhode-Schwartz model ZVA67) together with a home-built reflectometric cell for liquid samples. The setup and approach has been described elsewhere<sup>18,19</sup> and additional experimental details are given in the Supporting Information (SI).

We study ternary aqueous salt solutions with  $\text{Cl}^-$  as the common anion. In a first set of experiments, all solutions were prepared such that the cation/proton ratio was varied while keeping the  $\text{Cl}^-$  concentration constant at 1 mol/L. Figure 1 shows measured frequency dependent complex permittivity



**Figure 1.** Complex permittivity spectra of (a) aqueous mixtures of HCl/MgCl<sub>2</sub> and (b) mixtures of CsCl/MgCl<sub>2</sub> at a constant Cl<sup>−</sup> concentration of 1 mol/L. Solid lines are fits to eq 1.

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spectra (circles) of these mixtures. The main panels zoom in on the dominant water Debye relaxation mode, while the insets show overview spectra ranging from 1 to 50 GHz (Note that the conductivity contributions have been removed for visual clarity. The corresponding raw data and their decomposition into relaxation and conductivity contributions are given in the SI). In Figure 1a we show data for ternary mixtures of water,  $\text{MgCl}_2$ , and HCl, ranging from 0.5 mol/L  $\text{MgCl}_2$  to 1 mol/L HCl, over intermediate mixtures. We fitted the permittivity spectra of all investigated electrolytes with a single Cole–Cole relaxation mode<sup>16</sup> and a conductivity term (see SI for details), i.e., to the following expression:

$$\hat{\epsilon}(\nu) = \frac{S}{1 + (i2\pi\nu\tau)^{1-\alpha}} + \epsilon_\infty - \frac{i\sigma}{2\pi\nu\epsilon_0} \quad (1)$$

where  $S = \epsilon_S - \epsilon_\infty$  is the dielectric strength in which  $\epsilon_S$  and  $\epsilon_\infty$  give the static dielectric constant and the limiting permittivity at high frequencies, respectively. Furthermore, the  $\alpha$ -parameter describes the spectral broadening (in the limit  $\alpha = 0$  a Cole–Cole relaxation mode becomes a Debye mode),  $\sigma$  is the solution conductivity and  $\epsilon_0$  is the permittivity of free space. The lines in Figure 1 show the results of least-squares fits. The obtained relaxation times are slightly lower (1–2%) than for bulk water, as is commonly observed for aqueous inorganic electrolytes.<sup>9,20</sup> An interesting observation is that the amplitude of the dielectric response shows a clear nonlinear dependence on the composition for the  $\text{H}^+/\text{Mg}^{2+}$  mixtures. This nonlinearity is not observed for the  $\text{Cs}^+/\text{Mg}^{2+}$  mixtures.

As commonly observed for electrolytes, all dielectric strengths  $S$  here measured are smaller than that of pure water; this effect is commonly referred to as depolarization.<sup>10</sup> Since dilution of the water solvent by ions is a trivial (and small) contribution, we correct for this by defining the depolarization as  $\Delta S = S_n - S$ . Here  $S_n$  is the water density corrected dielectric response that would nominally be expected if the reorientational freedom of the water molecules in the solution was the same as that of pure water.<sup>21</sup>

The fact that the depolarization effect is considerable for electrolytes arises from two different effects. One of these is kinetic depolarization, originating from the coupling of the ion translation in the external electric field to the rotational motion of the solvent.<sup>10</sup> The resulting rotational polarization current is opposite to the current resulting from the rotational motion of the solvent itself.<sup>22,23</sup> The remaining part of the depolarization can be assigned to irrotational binding of the water dipoles by the ionic solutes.<sup>24</sup>

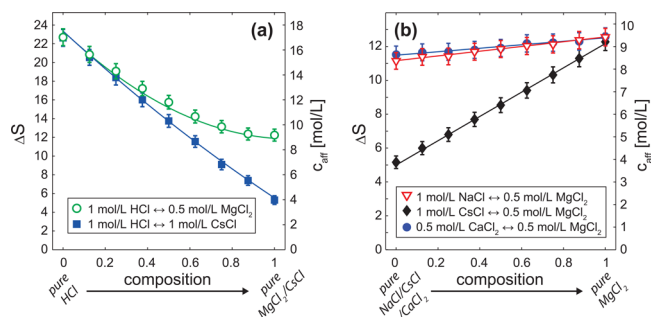
The depolarization can be related to an ‘affected’ water concentration,  $c_{\text{aff}}$  as the difference between the actual water concentration in the sample,  $c$ , and the concentration of ‘detected’ water molecules,  $c_{\text{det}}$ , i.e., which gives rise to dielectric relaxation.  $c_{\text{aff}}$  can be seen as a subset of molecules whose rotation is strongly hindered upon the dissolution of the ionic solutes, as found in several studies.<sup>25,26</sup> Using the Cavell equation,<sup>29</sup> we can determine  $c_{\text{det}}$  from the measured dielectric strength  $S$  and thus obtain  $c_{\text{aff}}$  via the following expression

$$c_{\text{aff}} = c - c_{\text{det}} = c - S \times \frac{2\epsilon_S + 1}{\epsilon_S} \frac{k_B T \epsilon_0}{N_A g \mu^2} \approx \frac{c_0}{S_0} \times \Delta S \quad (2)$$

where  $k_B$  is Boltzmann’s constant,  $T$  is the solution temperature,  $N_A$  is Avogadro’s number,  $\mu$  is the water molecule dipole moment and  $g$  is the Kirkwood correlation factor. The

approximation made in eq 2 (where  $S_0 \approx 73.5$  and  $c_0 \approx 55.4$  mol/L are the dielectric strengths and  $\text{H}_2\text{O}$  concentrations of the pure water solvent) is justified for aqueous solutions since the local field correction factor  $(2\epsilon_S + 1)/\epsilon_S$  is nearly constantly equal to 2 for these strong dielectrics. Furthermore, we assume that the effective dipole moment  $\mu_{\text{eff}} = (g)^{1/2}\mu$  of water molecules contributing to the dielectric response is the same as that of pure water, which has been shown to be a valid assumption for aqueous electrolytes at ambient conditions.<sup>11,27,28</sup> Due to the direct proportionality of  $\Delta S$  to  $c_{\text{aff}}$  as given by eq 2, we will present the data throughout the remainder of this paper using two different axes, one pertaining to each of the two quantities.

Figure 2 shows measured  $\Delta S$  values (left-hand vertical axis) together with derived  $c_{\text{aff}}$  values (right-hand vertical axis) for



**Figure 2.** Depolarization  $\Delta S$  (left-hand vertical axis) and concentration  $c_{\text{aff}}$  of water molecules missing from the dielectric response (right-hand vertical axis) for various mixed (a) salt–acid and (b) salt–salt electrolytes. For all solutions, the  $\text{Cl}^-$  concentration is constant at 1 mol/L. Solid lines are least-squares fits to the models discussed in the main text.

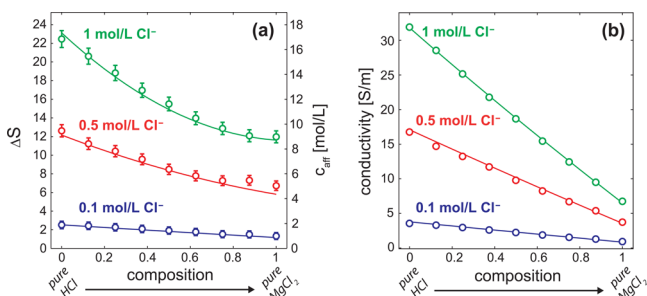
various mixed electrolytes at constant 1 mol/L  $\text{Cl}^-$  concentration. Figure 2a displays data for two acid–salt mixtures, HCl/ $\text{CsCl}$  (solid blue squares) and HCl/ $\text{MgCl}_2$  (open green circles). Remarkably, there is a notable nonlinearity in the depolarization across the composition range for the HCl/ $\text{MgCl}_2$  mixtures. While the initial decrease of  $\Delta S$  upon replacing protons with (half the amount of)  $\text{Mg}^{2+}$  is large, the decrement per  $\text{Mg}^{2+}$  is gradually becoming smaller as the mixture composition approaches pure  $\text{MgCl}_2$  (note that this is also directly visible from the nonlinear decrement in  $\epsilon''(\nu)$  in the raw data of Figure 1a). A nonlinearity is also discernible in the data of the HCl/ $\text{CsCl}$  mixtures, although much less pronounced in comparison to the HCl/ $\text{MgCl}_2$  data.

Figure 2b shows data for mixtures of  $\text{NaCl}/\text{MgCl}_2$  (open red triangles),  $\text{CsCl}/\text{MgCl}_2$  (solid black diamonds), and  $\text{CaCl}_2/\text{MgCl}_2$  (solid blue circles), all at 1 mol/L  $\text{Cl}^-$  concentration. In sharp contrast to the acid/salt mixture data in panel a, the depolarization for the  $\text{CsCl}/\text{MgCl}_2$ ,  $\text{NaCl}/\text{MgCl}_2$  and  $\text{CaCl}_2/\text{MgCl}_2$  mixtures interpolate linearly between the limiting cases of pure aqueous 1 mol/L  $\text{CsCl}$ , 1 mol/L  $\text{NaCl}$ , 0.5 mol/L  $\text{CaCl}_2$  and 0.5 mol/L  $\text{MgCl}_2$ , i.e., a global model of the form  $\Delta S = A[X\text{Cl}_n] + B[\text{MgCl}_2]$ , excellently describes the data ( $X = \text{Na}$ ,  $\text{Cs}$  or  $\text{Ca}$ ), as seen from the solid lines given together with the data in the figure. Hence, for salt–salt mixtures, the effect on the water dynamics appears to be perfectly additive.

The depolarization values of the acid–salt mixtures are consistently lower than expected from assuming additive hydration dynamics of the proton and salt cation. The fact that  $\Delta S$  deviates maximally from the linear expectation when

the composition parameter is close to 0.5, i.e., when both species are present at high concentrations, suggests the existence of a cooperative effect of the proton and the cosolvated salt cation on the dynamics of water.

We have performed further experiments for two other  $\text{MgCl}_2/\text{HCl}$  mixture series at various total  $\text{Cl}^-$  concentrations (but keeping it constant within each series). The circles in Figure 3a show depolarizations of solutions at 0.1 (blue), 0.5

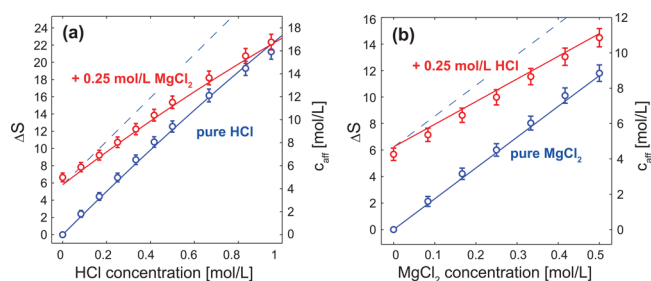


**Figure 3.** (a) Experimental values (open circles) and global fits to eq 3 (solid lines) of  $\Delta S$  and  $c_{\text{eff}}$  for mixed  $\text{HCl}/\text{MgCl}_2$  electrolytes; (b) conductivity of the same solutions (fitting procedure described in SI).

(red), and 1 mol/L  $\text{Cl}^-$  concentration (green). Interestingly, the nonlinear behavior shows a marked concentration dependence: At 0.1 mol/L  $\text{Cl}^-$  concentration,  $\Delta S$  is linearly interpolating between the limiting pure acid and pure salt cases, while deviations from this ideal behavior become pronounced upon going to 0.5 and 1 mol/L.

Within the Hubbard-Onsager model, the magnitude of the kinetic depolarization effect is proportional to the electrolyte conductivity.<sup>22,23</sup> Thus, it is of interest to establish whether the observed nonlinearity in the depolarization is associated with a corresponding nonlinearity in the electrolyte conductivities. As can be seen in Figure 3b, this is not the case, and the effects of protons and ions on the conductivity of the mixtures are close to additive. The conductivities of all the solutions plotted in Figure 3 can be fitted quite well to a simple Kohlrausch's law<sup>31,32</sup> given by the solid lines (see SI for details). We also note that the conductivity values for aqueous  $\text{MgCl}_2$  and  $\text{HCl}$  electrolytes are in good agreement with previous literature values.<sup>33,34</sup> Interestingly, this is in agreement with the MD simulation study of Xu et al.<sup>35</sup> who found that the conductivity contribution of  $\text{HCl}$  and added salt ions are close to additive.

The presence of a cooperative effect upon cosolvation of the proton and salt cations implies a reduction of the increments  $\partial\Delta S/\partial[\text{HCl}]$  upon adding a salt  $\text{XCl}_n$  to a pure  $\text{HCl}$  solution. We have performed additional experiments on solutions with and without a fixed concentration of 0.25 mol/L  $\text{MgCl}_2$  (or  $\text{HCl}$ ) and a variable concentration of  $\text{HCl}$  (or  $\text{MgCl}_2$ ); the data are given in Figure 4. The blue circles in panel a give  $\Delta S$  as a function of concentration of pure  $\text{HCl}$  solutions; the data are nearly linear with a weak tendency to level off at higher concentrations, something to which we will return shortly. If the hydration dynamics of  $\text{HCl}$  and  $\text{MgCl}_2$  would be additive, one would expect the presence of 0.25 mol/L  $\text{MgCl}_2$  to merely positively offset the curve, as illustrated by the dashed blue line. However, the experimental data (red circles) look strikingly different: The slope  $\partial\Delta S/\partial[\text{HCl}]$  is much smaller than what would be expected if the effects of  $\text{Mg}^{2+}$  and  $\text{H}^+$  on the water mobility were additive. This provides further evidence that the effect of  $\text{Mg}^{2+}$  and  $\text{H}^+$  on the orientational mobility of water



**Figure 4.** (a)  $\Delta S$  and  $c_{\text{eff}}$  for pure  $\text{HCl}$  solutions (blue circles) and for solutions in which a fixed concentration of 0.25 mol/L  $\text{MgCl}_2$  was added (red circles); (b) data for the reversed situation, i.e.,  $\text{MgCl}_2$  solutions (blue circles) and those to which 0.25 mol/L  $\text{HCl}$  was added (red circles). The dashed blue lines show the prediction from an additive model. The solid lines are the result of a global fit to eq 3.

upon cosolvation is suppressed compared to the effect of the respective ions in pure (binary) systems.

Notably, the cooperative effect does not seem to be directly related to the nature of the anion as experiments for  $\text{HClO}_4/\text{Mg}(\text{ClO}_4)_2$  mixtures give nearly identical results as for the chloride containing electrolytes (see SI). Thus, having established that the nonadditivity of the depolarization is primarily dependent on the concentrations of the salt cation  $\text{X}^{n+}$  and proton, we have found the depolarization of mixed acid-salt solutions to be well described by the expression:

$$\Delta S = A[\text{X}^{n+}] + B[\text{H}^+] - C[\text{X}^{n+}][\text{H}^+] - D[\text{H}^+]^2 \quad (3)$$

This equation yields good fits to all data over a large range of concentrations and composition ratios. Within the framework of eq 2,  $A$  and  $B$  can be interpreted as the individual effects the cations and protons have on reducing the rotational mobility of water molecules, while  $C$  gives the strength of the cooperative interaction of protons and cations on the water response. The (small)  $D$  term similarly accounts for negative deviations at high proton concentrations. The solid lines shown in Figures 3 and 4 are the result of a global fit to the data in all panels, with fit parameters  $A = 25 \text{ L/mol}$ ,  $B = 23 \text{ L/mol}$ ,  $C = 24 \text{ L}^2/\text{mol}^2$  and  $D = 3 \text{ L}^2/\text{mol}^2$ . We find a similar deviation from additivity for mixtures of  $\text{CaCl}_2/\text{HCl}$  as for mixtures of  $\text{MgCl}_2/\text{HCl}$  (see SI), while it is much less pronounced for salts of monovalent cations; a fit to eq 3 for  $\text{CsCl}/\text{HCl}$  mixtures gives  $B = 5 \text{ L/mol}$  and much weaker nonlinear term,  $C = 4 \text{ L}^2/\text{mol}^2$ , notably of similar magnitude as  $D = 3 \text{ L}^2/\text{mol}^2$  (see SI). This observation leads us to conclude that the charge of the cation cosolvated with  $\text{H}^+_{\text{aq}}$  is the most important factor in decreasing the depolarization effect of  $\text{H}^+_{\text{aq}}$ .

In identifying the origin of the observed nonadditive effect of cosolvated proton and cations on the dielectric response of water, it should be noted that the molar dielectric decrement,  $\partial\Delta S/\partial[\text{H}^+]$ , associated with the proton in binary solutions is exceptionally large ( $\sim 23\text{--}24 \text{ mol}^{-1}$ ) and corresponds to 18–19 affected water molecules per  $\text{H}^+$ . Using the model of Hubbard and Onsager,<sup>22,23</sup> the majority of the effect ( $\sim 15$  water molecules) has been thought to originate from kinetic depolarization,<sup>30</sup> arising due to the exceptionally large mobility of the proton. However, the subdivision into static and dynamic effects is less clear for the proton than for other ions as the limiting hydration structures are very short-lived and continuously undergo ultrafast structural reorganization on subpicoseconds timescales. The dynamic hydration shell of the proton is furthermore unusually extended, encompassing as



much as three hydration layers, in which a significant amount of water molecules align their dipole moments in antiparallel configurations.<sup>36</sup> The depolarization of the water response due to protons may thus largely find its origin in the stiffening of the hydrogen bonds in the (transient) hydration structures and the local reduction of the Kirkwood dipole correlation factor  $g$  due to the different arrangement of the water molecules compared to bulk liquid water, for which  $g$  is a large as  $\sim 2.7$ .<sup>17</sup>

The presence of highly charged cations will tend to reduce the delocalization of the proton charge as a result of Coulomb repulsion, thereby weakening several of the originally strong hydrogen bonds within the proton hydration structure. As a result, the cosolvated cations will induce a mobilization of the water molecules and thereby increase the overall dielectric response, i.e., reduce  $\Delta S$ . The reduction of the spatial extent of the proton hydration structure also reduces the volume over which the Kirkwood dipole correlation factor is decreased in comparison to bulk water, thus further enhancing the polarization response, i.e., decreasing  $\Delta S$ . The spatial extent of the proton hydration structure can also be reduced upon the formation of special proton–proton ion pairs as found in MD simulations of moderately concentrated HCl solutions,<sup>35,37</sup> and which will further decrease  $\Delta S$ .

The here observed nonadditive effect of small and highly charged cations on the depolarization of water induced by protons is thus likely the result of the diffuse nature of the protonic charge. This makes hydrated protons structure and their effects on the polarization response susceptible to the Coulomb field exerted by other ions. For other cations, the charge is highly localized and thus their effects are additive, as found in all experiments on salt–salt mixtures (Figure 2b).

We hope that the present observations will inspire future ab initio MD simulations that explicitly describe the structural diffusion of the hydrated proton in the presence cosolvated salts. Such simulations may provide a complete mechanistic understanding of the nonadditive effect of protons and cations on the polarization response of water unraveled here.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional experimental details and supplementary DRS and conductivity data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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