



Mechanisms of the viscosity decrease and increase of aqueous CsCl

Max Moncada Cohen^a , Laura Kacenauskaite^{a,b}, Tristan R. Heck^a, Junkun Pan^a, and Michael D. Fayer^{a,1}

Affiliations are included on p. 10.

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Aqueous salt solutions occur in many aspects of chemistry, biology, and geology. Increasing the concentration of most aqueous salt solutions increases the viscosities. In contrast, adding CsCl to water initially decreases the viscosity, but at moderate concentration further addition increases it. While this phenomenon is well known, the molecular mechanisms for the reduction and increase have not been elucidated. We used ultrafast optical heterodyne-detected optical Kerr effect (OHD-OKE) and IR pump-probe experiments, as well as density functional theory to investigate the impact of Cs⁺ ions on water dynamics, interactions, and structure. OHD-OKE experiments demonstrated that the dynamics of the water hydrogen bond (H-bond) network underpin the viscosity of CsCl solutions. Transient IR spectra of HOD in H₂O interacting with Cs⁺ showed a significant blue shift, a hallmark of hydrogen bonds weaker than those of pure water. Due to its low charge density, Cs⁺ is distinct from high charge density cations, e.g., Na⁺ and Li⁺, which have been observed to strengthen water hydrogen bonds and drive a large, monotonic increase in viscosity with concentration. The results showed that water hydrogen bonds in the Cs⁺ second solvation shell are weaker than typical water–water hydrogen bonds, and these weak hydrogen bonds give rise to faster collective structural dynamics, leading to reduced viscosity. However, at sufficiently high salt concentrations, the low number of water molecules per ion pair leads to water clusters. Water confined in small clusters slows H-bond rearrangement, leading to an increase in viscosity.

cesium chloride | salt solutions | ultrafast dynamics | hydrogen bonding | viscosity

Aqueous salt solutions are the venues for many essential processes, from biochemical reactions in the cell to the development of water-based technologies. Ions alter the nanoscale structure of water and play an essential role in determining the conformation and stability of biomolecules (1). The transport properties of aqueous solutions are altered by ion–water interactions (2–4) and have been leveraged extensively in technological applications such as water purification and recycling (5, 6) as well as in the development of batteries (7). The nature of these alterations is strongly dependent on the specific cations and anions (8). Ion-specific effects are often manifested as distinct changes in the concentration trend of the viscosity (9, 10). Most salts cause the viscosity to increase monotonically with concentration. However, there are some exceptional salts that do not follow the typical trend. CsCl, and, to a lesser extent, RbCl, and KCl, decrease the aqueous solution viscosity as the salt concentration increases from zero. In CsCl solutions, the focus of this paper, the viscosity decreases until it reaches 0.1 ion mole fraction (IMF) or 2.9 m (*SI Appendix, Table S1* provides useful concentration conversions), then increases rapidly.

This nonmonotonic viscosity trend is currently unexplained qualitatively or by analytical theory, even at dilute concentrations, and experiments have failed to provide consistent explanations (11, 12). The anomaly is most pronounced in CsCl; however, the mechanism of this effect should also apply to other charge-diffuse alkali cations, e.g., Rb⁺ and K⁺. As an active participant in many biological processes and the most abundant cation in the cell, K⁺ is integral to homeostasis and a multitude of cell signaling pathways (13, 14). Cs⁺ and Rb⁺ are being studied as additives to Li⁺ water-in-salt batteries to broaden the electrochemical window (15, 16). Given the ubiquity of aqueous ions and their many applications, a detailed understanding of how charge diffuse cations modify nanoscale and macroscale solution properties is important for both fundamental and practical reasons.

The unique properties of highly concentrated aqueous salt solutions arise from the ability of ions to influence the structure, strength, and dynamics of the water hydrogen bond (H-bond) network; however, the field is divided on specific mechanisms (17–20). Due to the complex nature of H-bond network dynamics, ion solvation, and ion pairing, it is difficult to relate specific microscopic parameters to the macroscopic observables. However, it is generally accepted that the effect of a specific cation on the viscosity depends

Significance

CsCl solutions initially decrease in viscosity as the salt concentration increases from zero. This anomalous viscosity trend has intrigued researchers but has not been explained. We apply two ultrafast spectroscopic techniques; one reports on collective ion/water structural dynamics, and the other the strength of H-bonding in the Cs⁺ second solvation shell. Together with DFT calculations, these experiments establish a cogent mechanism for the reduction in CsCl viscosity. The low charge density of Cs⁺ weakens water–water hydrogen bonds between the first and second solvation shells, resulting in faster than bulk water hydrogen bond rearrangement and a concomitant decrease in viscosity. At high salt concentrations, small water clusters cause the viscosity increase. Clustering occurs because water–water interactions are stronger than water–ion interactions.

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¹To whom correspondence may be addressed. Email: fayer@stanford.edu.

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strongly on the ionic radius and charge density. Fig. 1 demonstrates that smaller, charge dense cations, like Na^+ and Li^+ , drive a strong, monotonic increase in the viscosity while the charge diffuse ions, Cs^+ and Rb^+ , cause a different trend.

The alteration of solution properties by different ions has been the subject of intense theoretical and experimental study. The Jones–Dole (21) and Vogel–Fulcher–Tammann (22) equations were introduced to explain changes in viscosity as a function of concentration and temperature. These empirical relations vary in their success. More sophisticated theories, such as the “Mayonnaise effect,” have been used to treat high concentration regimes (12, 23). Consistent and quantitative descriptions of the effects of ions on the water H-bond network are still incomplete, and, to date, *ab initio* molecular dynamics (MD) studies are of limited use in the highly concentrated water-in-salt regime (24–26).

Methods such as X-ray and neutron scattering experiments (27, 28) NMR (29) nonlinear infrared (IR) spectroscopies (30) and optical Kerr effect experiments (31) have provided valuable insights into the structural dynamics of small, charge-dense ions and solvating waters. These experiments have addressed the extent of ion pairing and clustering, hydration and coordination numbers, and timescales of H-bond network relaxation (27–30, 32). Similar techniques applied to investigate charge diffuse ions such as Cs^+ have provided contradictory results. X-ray-based experiments show extensive ion pairing and a relatively large hydration

shell of Cs^+ accommodating up to 8 water molecules (33–35). Dielectric spectroscopy experiments show faster water relaxation times as concentration of CsCl increases up to ~ 2 M (36). Cs^+ physically accommodates more water molecules in its near vicinity with its large ionic radius than small high charge density cations; however, the low charge density of the ion may not be able to maintain an ordered, relatively stable hydration shell typical for small ions like Li^+ or Na^+ . These differences suggest that the dynamics of water in the ion solvation shells may be central to explaining ion-specific effects on viscosity (26, 28, 37, 38), challenging a popular theory that rationalizes viscosity changes as alterations of the extended H-bond network (39, 40).

In the studies presented here, we employed optical heterodyne-detected optical Kerr effect (OHD-OKE) and IR polarization selective pump–probe (PSPP) experiments, as well as density functional theoretical (DFT) calculations to quantify the effect of CsCl on the structural dynamics of the water H-bond network and ion/water interactions. While both experiments are ultrafast pump–probe spectroscopies, their different observables yield complementary information. The OHD-OKE experiment provides the polarizability–polarizability correlation function (PPCF), which contains detailed information on the collective dynamics of the H-bond network and water/ion clusters (31). The IR PSPP experiment, with the IR tuned to the frequency of the OD stretch of dilute HOD in CsCl /water solutions, provides lifetime amplitude spectra (LAS). The LAS uses the distinct vibrational lifetimes of water hydroxyls (ODs) in different H-bonding environments to measure spectra of different species even though the linear FT-IR spectrum contains a single broad featureless band (37). The spectra of different species can elucidate the nature of ion–water interactions.

The OHD-OKE, IR PSPP, and DFT results show that the dynamics of water in the Cs^+ first and second solvation shells give rise to the anomalous viscosity reduction. Previously, studies of several salt and acid solutions containing charge-dense cations found that ion/water clustering largely determined viscosity (31, 38). For Cs^+ , the viscosity is instead shown to be correlated with the H-bond network relaxation times, which are measured with OHD-OKE. We propose a molecular explanation for this effect in which Cs^+ weakens H-bonds between the waters in the first and second solvation shells, leading to accelerated structural relaxation of the water H-bond network. The faster H-bond rearrangement reduces the viscosity. The hypothesis of Cs^+ weakening H-bonding is confirmed by IR PSPP experiments and DFT calculations that measure and analyze the spectrum of hydroxyls interacting with Cs^+ . The measurements and calculations show that water–oxygen association with Cs^+ is very weak, producing H-bonds between the first and second Cs^+ solvation shells that are weaker than water–water H-bonds and much weaker than those involving hydroxyls influenced by smaller cations like Li^+ . In the high salt concentration regime, the viscosity increase with concentration is caused by the slowing of H-bond rearrangements due to water confinement effects.

Results

Hydrogen Bond Network Relaxation and the Bulk Viscosity. In pure water, structural dynamics are determined by H-bonding. Water is both an H-bond donor and acceptor, forming 4 H-bonds on average in an approximately tetrahedral arrangement. Each water molecule shares H-bonds with other water molecules, forming an extended network that randomizes on a 2 ps time scale (see below) (41). Ions can dramatically alter the structural dynamics of water, but the magnitude and nature of this effect

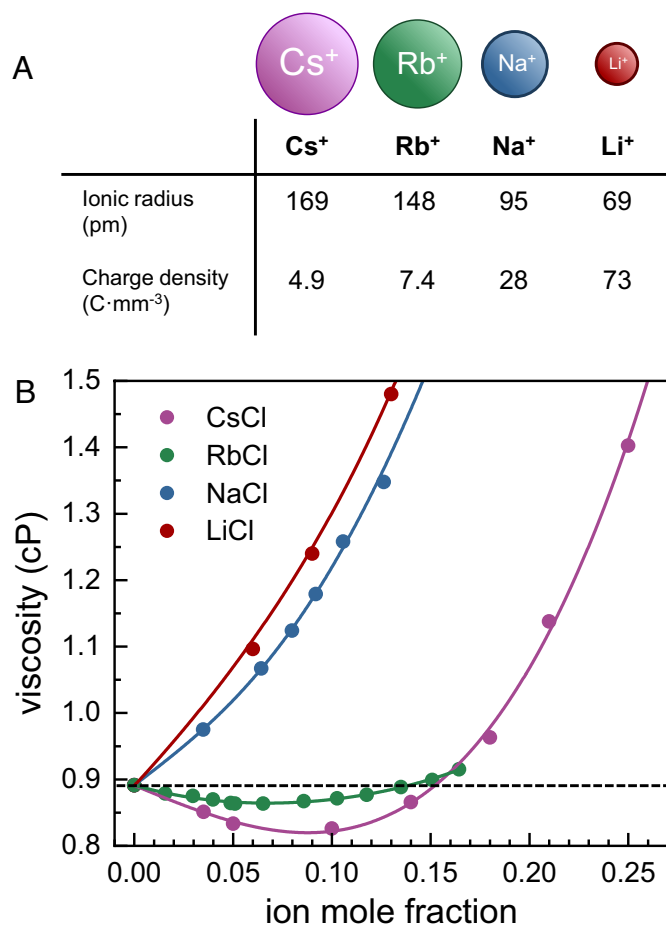


Fig. 1. Properties of selected alkali chloride solutions. (A) Ionic radii and charge densities of Cs^+ , Rb^+ , Na^+ , and Li^+ . Accurately scaled representations of the ions are given to demonstrate size differences. (B) Dynamic viscosities of CsCl , RbCl , NaCl , and LiCl with solid lines provided as guides to the eye. Note the nonmonotonic viscosity trend for CsCl and RbCl . Data were compiled from the literature (9–11).

depend strongly on the charge density of the ion. Concentration-dependent studies of aqueous LiCl have built a cogent molecular-level picture of how high charge density cations affect solution structural dynamics. These studies are valuable for understanding the CsCl results (37, 42, 43). With its high charge density, Li^+ has a strong cation–water oxygen interaction, which gives rise to stronger H-bonds between the first and second solvation shells than typical water–water H-bonds. The Li^+ withdraws electron density from the solvating water oxygens, which in turn withdraws electron density from the hydroxyl Hs. Therefore, the hydroxyl Hs are more δ^+ than the corresponding moieties of pure water, forming stronger H-bonds to the second solvation shell than pure water–water H-bonds. These strong cation-associated water H-bonds were identified by ultrafast IR PSPP experiments on the OD stretch of dilute HOD in LiCl solutions. The LAS of the cation-perturbed hydroxyls (ODs) was shifted to lower frequency (red shifted) relative to HOD in pure water (37). The red shift indicates a shorter O–D...O distance (shorter oxygen–oxygen distance) and a stronger H-bond. H-bonds influenced by cations are referred to as cation-perturbed H-bonds.

Because of its very low charge density, Cs^+ has weaker interactions with solvating water oxygens than water hydroxyls donating H-bonds to water oxygens. The Cs^+ perturbed hydroxyls form weaker H-bonds to water molecules in the second solvation shell. The weaker H-bonds of the cation-perturbed hydroxyls to waters in the cations' second solvation shell speed up H-bond network rearrangement dynamics and, in turn, decrease the viscosity. As the Cs^+ concentration is increased, there is a concomitant increase in the fraction of weak H-bonds, which causes faster H-bond rearrangement and the viscosity to decrease. Weaker H-bonds result in blue-shifted OD stretching frequencies for the cation-perturbed hydroxyls compared to those in pure water, contrasting with the red shift induced by Li^+ . The following sections present experiments and DFT calculations that confirm and expand on the altered structural dynamics and their effect on the viscosity.

OHD-OKE signal decays, $S_{\text{OKE}}(t)$, of aqueous CsCl solutions are shown in Fig. 2A. The decays, which are the derivatives of the PPCF, are triexponential and after integration give the following PPCF.

$$R(t) = C_1 e^{-t/t_1} + C_2 e^{-t/t_2} + C_3 e^{-t/t_3}. \quad [1]$$

The t_i are the decay time constants, and C_i are the normalized correlation coefficients; i.e., the sum of the C_i is 1. The decays span four decades of amplitude. Datasets were collected from the dilute regime to near the solubility limit. For comparison, the dashed line in Fig. 2A shows the OHD-OKE decay of LiCl at the same concentration as the highest CsCl concentration (purple curve). In contrast to LiCl, the OHD-OKE signals of the CsCl solutions decay faster at a given concentration, and the decays slow only mildly with increasing concentration. The triexponential decay constants and PPCF coefficients associated with each component of the PPCF are given in Fig. 2B and C. Two fast-decaying components, t_1 and t_2 , dominated the signal, though a third low-amplitude component (t_3) was also observed and accounts for <3% of the total signal at all concentrations.

The t_1 and t_2 components of the CsCl decays are present in the OHD-OKE decay of pure water. In pure water and studies of other salt and acid solutions, e.g., LiCl (42) LiBr (31) and NaCl (38), and acids H_2SO_4 (44) and HCl (38) t_1 and t_2 have been identified by comparison to two-dimensional infrared (2D IR) experiments on isotopically dilute HOD in pure water (41). 2D

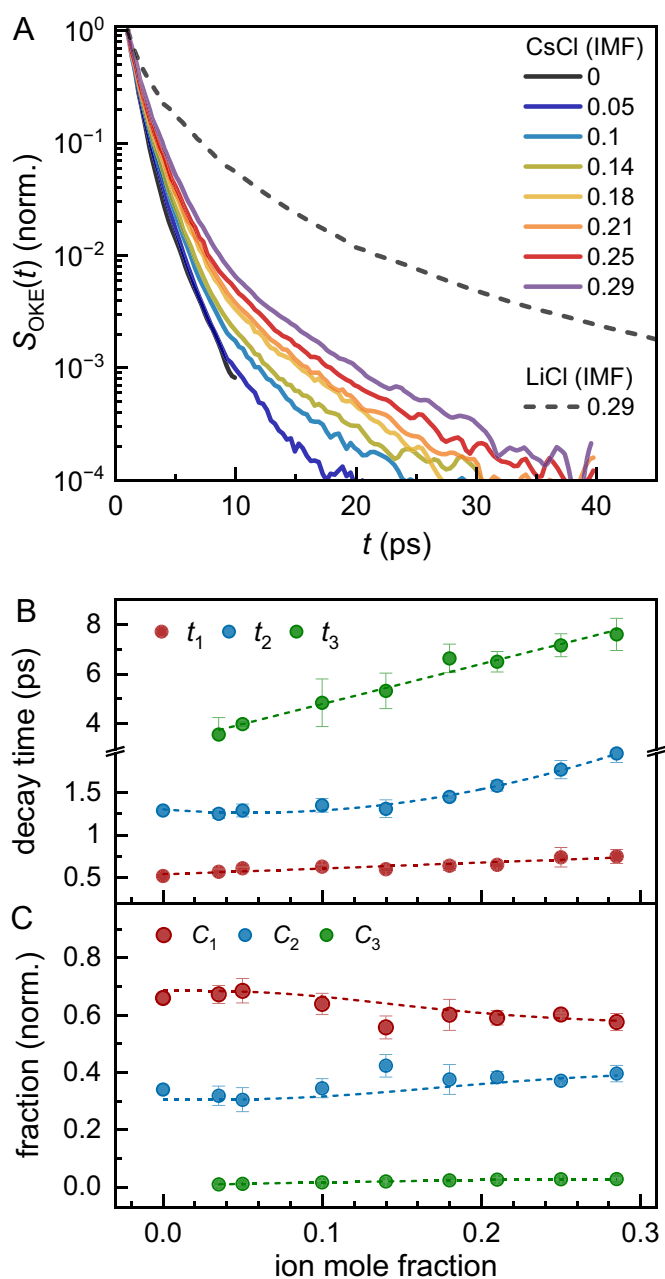


Fig. 2. (A) OHD-OKE decays of CsCl solutions showing only mild slowing compared to pure water (black curve). A LiCl solution decay (dashed line) at 0.29 IMF has a much slower decay than the same concentration of CsCl (purple curve). (B) Decay constants obtained from fitting the OHD-OKE transients to Eq. 3. The decays are triexponential. (C) Correlation function coefficients (fractions) for each decay component.

IR is a third-order nonlinear experiment that measures the decay of the frequency–frequency correlation function (FFCF), which is determined by structural dynamics of water. The pure water FFCF has two time components, 0.4 ± 0.1 ps and 1.7 ± 0.2 ps (41). Simulations have identified these dynamics as local fluctuations of intact H-bonds, O–H...O, mainly the O–O distance fluctuations (t_1) and the randomization of the extended H-bond network (t_2) (45). The randomization occurs through a concerted process in which multiple water H-bonds “jump” to new partners. This same mechanism gives rise to jump reorientation, which is responsible for orientational relaxation in pure water (46).

The OHD-OKE experiment is a third-order nonlinear experiment that measures the PPCF. In both experiments on pure water,

the slowest decay component requires randomization of the water H-bond network connectivity. In the 2D IR experiment, structural randomization is required to randomize the frequencies across the inhomogeneous absorption, that is, the decay of the FFCF. In the OHD-OKE experiment, structural randomization is required to completely relax the polarizability anisotropy (decay of the PPCF) induced by the pump pulse. As the two experiments measure different correlation functions, the measured time constants are not expected to be identical. Based on the similarity of the time constants for pure water in the two types of measurements [2D IR: 0.4 ps and 1.7 ps (45) OHD-OKE: 0.5 ps and 1.3 ps (42)] and the fact that the two dynamical processes identified by the simulations of the 2D IR experiments are the main dynamical processes in water, it was hypothesized that OHD-OKE measured time constants are also the local H-bond fluctuations (t_1) and H-bond rearrangements (t_2). In CsCl and other salt solutions studied, t_1 and t_2 do not change a great deal with increasing concentration, and in all the salt solutions, the t_1 and t_2 values go to their pure water values as the salt concentration approaches zero. Therefore, t_1 and t_2 in the salt solutions are taken to be the same type of process as those that occur in pure water; the time constant changes with increasing salt concentration due to the effects of cations and anions in solution.

Concentrated aqueous solutions of LiCl, LiBr, and NaCl have been examined in detail previously (31, 38, 42). Linear relationships between the viscosity and correlation times obtained from OHD-OKE experiments were observed. These experiments showed that the ion/water dynamics that cause the PPCF to decay slowed significantly as the concentration increased, particularly at very high salt concentrations where the number of water molecules is insufficient to fully solvate the ions. At high concentrations, the dynamics slow because of the formation of large ion–water clusters and extended ion/water networks (31).

As shown in Fig. 1B, CsCl and, to a lesser extent, RbCl exhibit viscosity trends that differ markedly from those of NaCl and LiCl. The CsCl viscosity initially decreases to a minimum at 0.1 IMF, then increases at higher concentrations. Fig. 3 shows that the viscosity and t_2 from the OHD-OKE experiments exhibit the same concentration dependence within experimental error. As discussed above, at the lower concentrations, adding Cs^+ to water causes the H-bonds among water molecules in the cation second solvation shells to become weaker. OHD-OKE data for t_2 support this

model. The weaker H-bonds lead to faster H-bond network rearrangement, and, therefore, a faster t_2 decay. The fact that the viscosity tracks the H-bond network randomization time, t_2 , indicates that H-bond randomization dynamics underlie viscosity.

Weak Hydrogen Bonds. OHD-OKE experiments described above report on the collective dynamics of the water H-bond/ion network. To gain further insight into the relationship between water structure and dynamics, IR PSPP experiments were performed on aqueous CsCl solutions, and the population lifetimes and lifetime amplitude spectra (LAS) were obtained from the data. LAS provides information not available from FT-IR spectra (shown in SI Appendix, Fig. S4) by separating different populations of H-bonded ODs into distinct spectra by their vibrational lifetimes and spectral shifts.

The IR PSPP experiments revealed three principal species of water in the solutions: pure water, water bound to anions, and cation-perturbed water H-bonded to other waters. By pure water, it is meant that at dilute to moderate salt concentrations, there is enough water for some HOD molecules to be H-bonded in water clusters, essentially as they would be in pure water. The appearance of a distinct LAS peak depends on the OD stretch in a particular H-bonding configuration (water H-bonded to water, water H-bonded to anion, cation-perturbed water), having a different vibrational lifetime and/or frequency distribution (spectrum) compared to the other species. The different lifetimes give rise to multiexponential population decays, $P(t)$. Because there are potentially three species, the decay is taken to be triexponential.

$$P(t; \omega) = \alpha_1(\omega)e^{-t/\tau_1} + \alpha_2(\omega)e^{-t/\tau_2} + \alpha_3(\omega)e^{-t/\tau_3}. \quad [2]$$

The time constants in the multiexponential decays are independent of the frequency. However, the amplitudes change with frequency, ω . Plotting the amplitude, $\alpha_i(\omega)$, of a particular component of the multiexponential lifetime decay is the LAS of the OD stretch H-bonded to the particular species that gives rise to that decay time and spectrum. For conciseness, we will refer to the water–water LAS peak as W–W and the LAS peak associated with a Cs^+ perturbed water H-bonded to water in the second solvation shell as W– Cs^+ . The assignment of these peaks in the LAS data is not trivial as discussed in the following section.

To help understand the CsCl LAS data, it is useful to discuss the well-studied spectra of LiCl solutions. In LAS measurements on LiCl solutions at very high concentrations, there is so little water that only two species of HOD probe molecules exist: ODs H-bonded to Cl^- and Li^+ perturbed ODs bound to water in the second solvation shell (37). Therefore, the population decay is biexponential. Water H-bonds to the Cl^- anions are weaker than pure water H-bonds because of the lower charge density of Cl^- compared to a water oxygen. ODs H-bonded to Cl^- have a spectrum that is blue shifted from the pure water spectrum, and have a lifetime that depends on the concentration but is >4 ps at all concentrations (47). Li^+ perturbed ODs H-bonded to second solvation shell water molecules make stronger H-bonds compared to those of pure water. The stronger H-bonds are caused by the high Li^+ charge density, which withdraws substantial charge from the solvating oxygens. The solvating oxygens, in turn, withdraw charge from their hydroxyl hydrogens, making them more δ^+ than those of pure water. Thus, they form stronger H-bonds to the second solvation shell water molecules than water–water H-bonds. The stronger H-bond (OD) produces a red shift compared to the pure water spectrum. The LAS of these ODs is observable at the very high concentration solutions in which there is no pure water, however, they have a lifetime that is almost identical to that of the OD

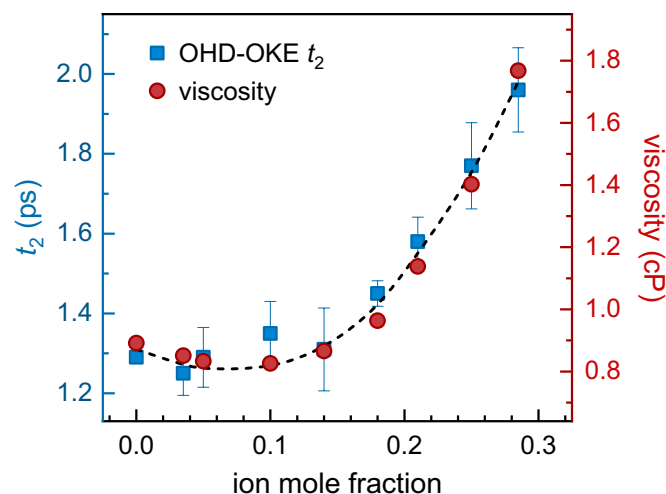


Fig. 3. The concentration dependencies of the CsCl viscosity (Right axis) and t_2 (Left axis). t_2 was scaled for comparison. Like the viscosity, t_2 does not slow monotonically with increasing CsCl concentration. t_2 and the viscosity have the same concentration dependence, within error.

stretch in pure water (1.8 ps). In lower concentration LiCl solutions where there is a large pure water LAS band, the 1.7 ps Li^+ perturbed OD lifetime is indistinguishable from that of pure water. In addition, the pure water vibrational $1 \rightarrow 2$ transition, which occurs in nonlinear IR spectra, obscures the red portion of the LAS where the Li^+ perturbed hydroxyl spectrum would appear. Therefore, at lower concentrations with a significant pure water peak, the LAS of the Li^+ perturbed water OD bound to water cannot be obtained.

The lifetime of the W-Cs^+ species is indistinguishable from the W-W lifetime, rendering the population decay effectively biexponential. However, we can obtain the W-Cs^+ LAS peak because the vibrational frequency of a Cs^+ perturbed HOD is sufficiently shifted from the pure water spectrum to be manifested as a shoulder on the blue side of the 1.8 ps pure water LAS, and the spectrum of hydroxyls H-bonded to chlorides is eliminated from the 1.8 ps LAS. Therefore, the vibrational population relaxation of the CsCl solutions were fit with biexponential decays. The fast time constant (τ_1) is 1.8 ps, the same as in pure water and is independent of CsCl concentration. The slow component (τ_2) is constant at ~ 4 ps < 0.06 IMF and slows at higher concentrations. These trends in the CsCl τ_1 and τ_2 are essentially the same as those seen in LiCl solutions (SI Appendix, Fig. S5) (37). Fig. 4 shows LAS of pure water (decay component $\tau_1 = 1.8$ ps) and the slow component ($\tau_2 \geq 4$ ps), OD- Cl^- , for several concentrations. The OD- Cl^- spectra are independent of concentration within experimental error. The spectra are truncated below $2,450 \text{ cm}^{-1}$ due to overlap of the positive-going $0 \rightarrow 1$ transition with the negative-going $1 \rightarrow 2$ transition. The τ_2 LAS peak arises from ODs bound to chloride anions. As discussed above in connection with LiCl solutions, this interaction leads to a blue-shifted OD stretching frequency due to the low charge density of Cl^- . OD- Br^- has a larger blue shift and OD- I^- an even larger blue shift than OD- Cl^- because these halides have even lower charge densities than Cl^- (48, 49). For the halides, only OD- F^- is red-shifted from the pure water spectrum because of F^- 's very high charge density. The unnormalized LAS of the decay components of the biexponential population decays, $P(t; \omega)$, i.e.,

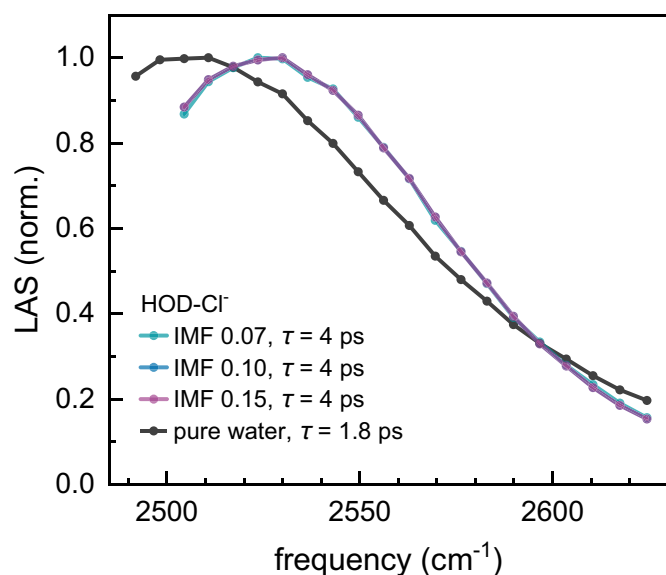


Fig. 4. LAS of the OD stretch of HOD in pure water with lifetime $\tau_1 = 1.8$ ps, and spectra at several concentrations of OD hydroxyls bound to chloride, with lifetime of $\tau_2 \geq 4$ ps. The OD bound to chloride is blue shifted relative to the pure water spectrum because the OD H-bond to Cl^- is weaker than a water–water H-bond.

the water–water-associated lifetime component, $\tau_1 = 1.8$ ps, and the water–chloride associated lifetime component, $\tau_2 \geq 4$ ps are given in SI Appendix, Fig. S3.

The addition of CsCl to water leads to a significant broadening of the $\tau_1 = 1.8$ ps LAS on the blue side of the line compared to the pure water LAS. The broadening is shown in Fig. 5A, which displays the $\tau_1 = 1.8$ ps LAS of a 0.10 IMF solution and that of pure water. The shoulder on the blue side of the spectrum is not present in LiCl solutions, where the Li^+ perturbed ODs bound to water are stronger than water–water H-bonds, and the Li^+ perturbed hydroxyl spectrum is red-shifted (37). A distinct blue-shifted peak was obtained by subtracting the pure water LAS from the LAS of various concentrations of CsCl. The resulting difference spectra are shown in Fig. 5B. The blue-shifted bands are spectra of the OD stretch of Cs^+ perturbed hydroxyls as shown by the results of the DFT calculations given in Table 1. Fig. 5C provides another method of obtaining the W-Cs^+ peak: The $\tau_1 = 1.8$ ps LAS were fit with two Gaussians. One has its parameters fixed to the W-W peak except for its amplitude; the W-Cs^+ peak parameters were allowed to float to give the best overall fit. In Fig. 5C, the points are the LAS data as a function of frequency for a range of CsCl concentrations. The gray curves through the points are the results of the two Gaussian fits. The red solid curves are the pure water Gaussians, and the blue solid curves are the concentration-dependent spectra of the W-Cs^+ structure. The red and blue bands at each concentration sum to give the corresponding gray curve. Fig. 5A–C show that the LAS for Cs^+ perturbed hydroxyls (OD) bound to water oxygens in the second solvation shell are blue shifted. The blue shift demonstrates that the H-bonds to the second solvation shell are weaker than water–water H-bonds. As the CsCl concentration increases, the number of weakened H-bonds increases. The weak H-bonding is consistent with the OHD-OKE results at low concentration (Fig. 3) where t_2 becomes faster as the concentration of CsCl is increased from zero, tracking the viscosity at all concentrations.

In water–water H-bonding, the lone pairs of a water molecule form H-bonds with the hydroxyls of two other water molecules. The δ^+ charges on the hydroxyl hydrogens withdraw electron density from the oxygen lone pairs. The electron density withdrawal from the oxygen causes the oxygen's hydroxyls to have larger δ^+ charges than they would have if the oxygen lone pairs were not H-bonded. The result is that hydroxyls H-bonding to an oxygen's lone pairs are, in part, responsible for the strength of water–water H-bonds.

Although it is positively charged, the charge density of Cs^+ is very low. In addition, Cs^+ is so large that it blocks water hydroxyls from H-bonding to the solvating oxygens. The result is that the water molecules in the Cs^+ first solvation shell have hydroxyls that are less δ^+ than hydroxyls in pure water. Therefore, these first solvation shell water molecules make weaker H-bonds to the second solvation shell than occur in pure water.

The results shown in Fig. 5 indicate that the blue-shifted band in the $\tau_1 = 1.8$ ps LAS arises from water hydroxyls solvating Cs^+ forming weaker H-bonds to the second solvation shell than H-bonds in pure water. To confirm this assignment and further examine the weak second solvation shell H-bonding induced by Cs^+ , we performed DFT calculations on a pure water cluster and three water–ion clusters that have a sufficient number of water molecules in appropriate geometries to provide reasonable approximations of OD stretch frequencies that occur in aqueous solutions. These calculations are not intended to be simulations, but are sufficiently detailed to confirm the experimental observations.

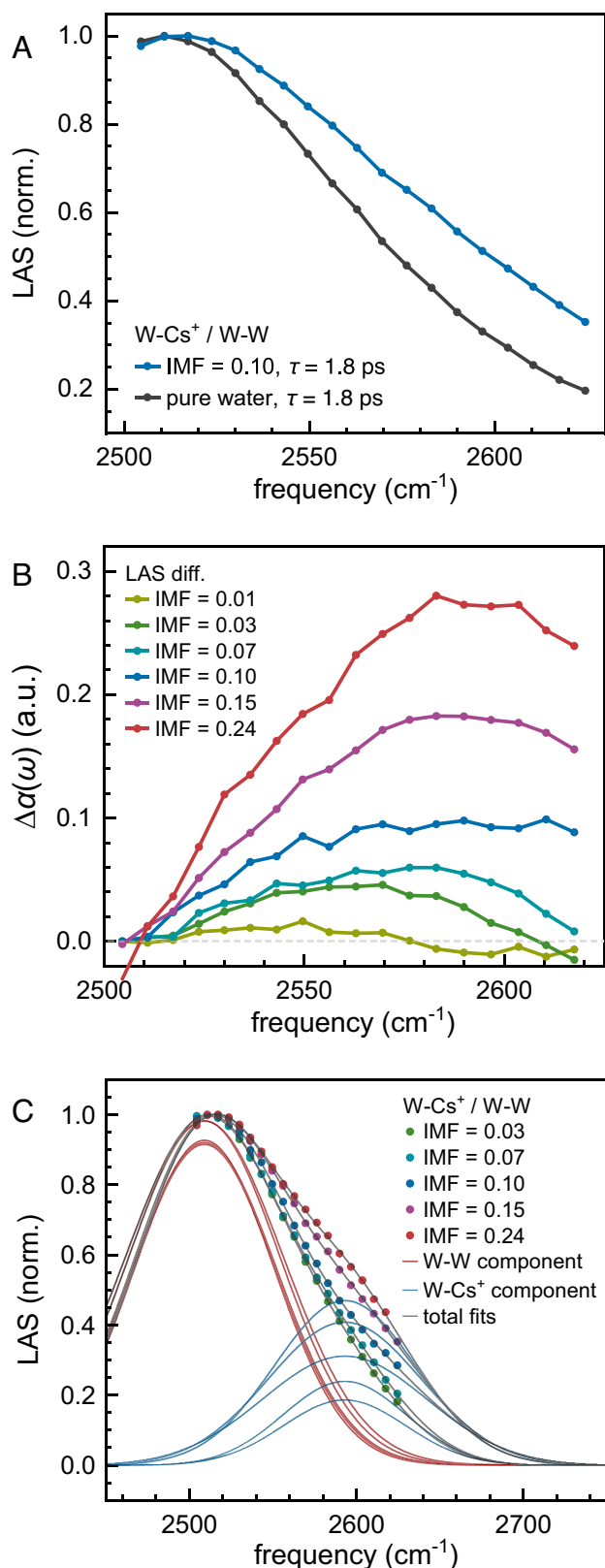


Fig. 5. (A) LAS of pure water and a solution with CsCl IMF = 0.10 (OD of HOD in H₂O). The CsCl spectrum is broadened on to the blue relative to the pure water spectrum. (B) The difference between the $\tau_1 = 1.8$ ps LAS component of CsCl solutions and the pure water LAS. The resulting difference spectra are blue shifted from the pure water spectrum. These are spectra of Cs⁺ perturbed hydroxyls bound to water (W-Cs⁺). The blue shift indicates weaker H-bonds. (C) Bi-Gaussian decomposition of the CsCl $\tau_1 = 1.8$ ps LAS component shows that two peaks, the W-W and W-Cs⁺ associated peaks, are needed to reconstruct the spectrum.

Fig. 6 displays the clusters used in the DFT calculations, and Table 1 presents the calculated results, i.e., vibrational frequencies and H-bond lengths. The clusters were chosen to give reasonable values of the OD stretch vibrational frequencies. The hydroxyls with the stars are the OD stretches for which the frequency was calculated for each structure. The exact values of the stretch frequencies are less important than the directions of the shifts relative to pure water. The calculated OD stretch frequencies are within ~1% or better of the experimental frequencies (Table 1). For Cs⁺ and Li⁺, the ODs are making H-bonds to water oxygens in the second solvation shell of the cations. The pure water OD stretch frequencies are experimental, 2,509 cm^{-1} ; DFT, 2,527 cm^{-1} . In agreement with experiments, the OD frequency in the W-Li⁺ cluster (W for water) is red shifted compared to the water only cluster: experimental—2,490 cm^{-1} , DFT—2,491 cm^{-1} . The H-bonds of hydroxyls with their oxygens associated with Li⁺ make stronger H-bonds to the second solvation shell than H-bonds in pure water. In Fig. 6, $r_{\text{D-O}}$ is the distance from the starred D to the O that it is H-bonded to, and $r_{\text{O-O}}$ is the corresponding O to O distance. A stronger H-bond corresponds to shorter $r_{\text{D-O}}$ and $r_{\text{O-O}}$ distances compared to those of pure water. Table 1 shows this effect.

In agreement with experiments, the OD frequency in the W-Cs⁺ cluster is blue shifted compared to the water only cluster: experimental—2,590 cm^{-1} , DFT—2,595 cm^{-1} , demonstrating that the H-bonds to the second solvation shell of Cs⁺ solvating waters are weaker than those in pure water. Weaker H-bonds are also longer. In the W-Cs⁺ cluster, the $r_{\text{D-O}}$ and $r_{\text{O-O}}$ distances are longer than in the W-W cluster (Table 1). The experimental and calculated frequency shifts show that a water-Cl⁻ H-bond is also weaker than H-bonds in pure water. These results demonstrate the central feature of Cs⁺ interactions with water: Although Cs⁺ is a cation, its charge density is so low that it interacts very weakly with solvating water molecules; it withdraws less electron density from solvating oxygens than is withdrawn by two hydroxyls H-bonding to the lone pairs of water oxygens in pure water.

Together, the OHD-OKE experiments (Fig. 3), the LAS (Fig. 5), and the DFT calculations (Fig. 6) delineate the reason for the decrease in viscosity relative to pure water as the CsCl concentration increases. The viscosity tracks the OHD-OKE time constant, t_2 , the time constant for H-bond rearrangements. At dilute CsCl concentrations, t_2 becomes faster because an increasing fraction of the water–water H-bonds are weaker. The faster H-bond rearrangement in CsCl solution contrasts with LiCl and NaCl solutions, in which H-bonds between waters in the first and second solvation shells are stronger than pure water–water H-bonds. The LAS data in Fig. 5 show that OD stretch spectra of HODs solvating Cs⁺ that are H-bonding to the second solvation shell. The spectra are blue-shifted relative to the OD stretch of HOD H-bonding in pure water. The blue shift demonstrates that the H-bonds are weaker than those in pure water. The weaker H-bonding of the first to second solvation shells of Cs⁺ is further supported by the results of DFT calculations on the clusters shown in Fig. 6 and given in Table 1.

Discussion

Adding CsCl to water causes H-bonds in the Cs⁺ second solvation shell to be weaker than those in pure water, resulting in faster H-bond network rearrangement and a reduced viscosity. As the CsCl concentration increases, there is an increasing fraction of weak H-bonds, further reducing the viscosity. However, as the concentration of CsCl continues to increase, the rate of the viscosity decrease lessens. A minimum in viscosity is reached at

Table 1. Comparison of DFT calculated and experimental OD stretch frequencies

	W-W Cluster		W-Cs ⁺ Cluster		W-Li ⁺ Cluster		W-Cl ⁻ Cluster	
DFT	ν_{OD} (cm ⁻¹)	2,527	ν_{OD} (cm ⁻¹)	2,595	ν_{OD} (cm ⁻¹)	2,491	ν_{OD} (cm ⁻¹)	2,568
Exp.	ν_{OD} (cm ⁻¹)	2,509	ν_{OD} (cm ⁻¹)	2,590	ν_{OD} (cm ⁻¹)	2,490	ν_{OD} (cm ⁻¹)	2,530
	r_{D-O} (Å)	1.78	r_{D-O} (Å)	1.83	r_{D-O} (Å)	1.75	r_{D-Cl} (Å)	1.79
	r_{O-O} (Å)	2.76	r_{O-O} (Å)	2.80	r_{O-O} (Å)	2.73		

The row labeled DFT are the calculated OD stretch (labeled with a * in Fig. 6) frequencies that are H-bonded to a water oxygen except for the W-Cl⁻ cluster for which the OD is H-bonded to Cl⁻. The experimental frequencies are in the row labeled Exp. r_{D-O} and r_{O-O} are the distances from the starred D to the O it is H-bonded to and the corresponding oxygen-oxygen distances. A weaker H-bond is longer, and a stronger H-bond is shorter.

0.10 M. Above this concentration, the viscosity increases. At 0.15 IMF, the viscosity of the CsCl solution is greater than that of pure water but less than the viscosities of LiCl and NaCl at the same concentration (Fig. 1B).

Aqueous solutions of CsCl, NaCl, and LiCl have viscosities that are linearly correlated with components of the OHD-OKE decays (38, 42). However, the relationships differ significantly. In NaCl solutions, the slowest component of the triexponential PPCF decay, which is not present in pure water, is linearly correlated with the viscosity (38). The PPCFs of LiCl solutions are tetra-exponential with two slow components that do not exist in pure water. The viscosity is linearly correlated to a combination of the third and fourth components of the decays (42). In both NaCl and LiCl solutions, t_1 and t_2 , the two components that are present in pure water, are not involved in the description of the viscosity trend. In contrast to both LiCl and NaCl, the viscosity of the CsCl solutions tracks the second PPCF component, t_2 (Fig. 3), which occurs in pure water and is caused by water H-bond rearrangement dynamics. In LiCl aqueous solutions, simulations (43) and OHD-OKE (42) studies showed that the growth in size and abundance of large ion/water clusters and extended networks cause the increase in viscosity. As these structures grow in size with increasing concentration, their dynamics slow, and the viscosity increases. The relationship of the viscosity to the PPCFs of CsCl solutions is very different from that of NaCl and LiCl. The CsCl decays are triexponential, but the concentration-dependent viscosity is correlated with the second decay component, t_2 . In addition, the amplitude of the CsCl third decay component, C_3 , is small; it is ~0.03 at the highest concentration, 0.29 IMF, where there are only 5 water molecules per CsCl.

The large differences between CsCl, NaCl, and LiCl solutions can be understood through a series of DFT calculations; the results of which are shown in Fig. 7. These calculations are intended to illustrate the substantial differences in interactions rather than provide precise values. They are not expected to be completely accurate because they use an implicit water model for solvent beyond the explicitly calculated solvation shells. The differences between the results for LiCl and NaCl vs. CsCl are so large that

moderate errors in the calculations will not change the qualitative understanding of the distinct characteristics of CsCl solutions.

Fig. 7A shows Morse potential calculations for NaCl, LiCl, and CsCl ion pairs. The energies were calculated for a series of inter-ionic distances to obtain the potential energy curve. LiCl and NaCl display deep minima at separations of 2.1 and 2.5 Å and dissociation energies of 22.3 kcal/mol and 18.1 kcal/mol, respectively. In stark contrast, CsCl has a very broad minimum at 3.5 Å with a depth of only 1.3 kcal/mol. Although these results are qualitative, the enormous difference in the depth of the potential minima between the CsCl curve and the other two curves shows the weak nature of Cs⁺-Cl⁻ ion pair. The DFT calculations indicate that LiCl and NaCl form strongly associated contact ion pairs. These results agree with simulations that have demonstrated that LiCl forms strong contact ion pairs (43). CsCl should form very weak contact ion pairs with a large Cs⁺-Cl⁻ separation. The interaction is so weak that CsCl contact ion pairing is unlikely to be a significant contribution to the viscosity.

Fig. 7B provides insight into the formation of solvent-separated ion pairs, that is, a water bridging a cation and a Cl⁻. As in Fig. 7A, these are Morse potentials calculated using DFT with implicit water. The red curve labeled Li⁺-OH₂ is the potential for the oxygen of a single water molecule interacting with Li⁺. The distance between the Li⁺ and the water oxygen was scanned to produce the potential energy curve. The same procedure was used for the other two cations, Na⁺-OH₂ (blue) and Cs⁺-OH₂ (purple), and for the anion, Cl⁻-HOH (green). Na⁺ and Li⁺ cations have strong interactions with water oxygens, and Cl⁻ has a moderate interaction (~9 kT). The depths of the Li⁺-OH₂, Na⁺-OH₂, and Cl⁻-HOH potentials indicate that there should be substantial formation of solvent separated ion pairs for these cations. In LiCl aqueous solutions, contact ion pairs form at moderate concentrations, and at high salt concentrations, extended chains of Li⁺-Cl⁻ pairs are “bridged” by water molecules, forming solvent-separated ion pairs (43).

However, the Cs⁺-OH₂ potential minimum is exceedingly shallow and broad, with a depth of 0.4 kcal/mol, less than kT at room temperature, indicating a very weak interaction with the oxygen. Again, these results are not quantitative, but the large differences

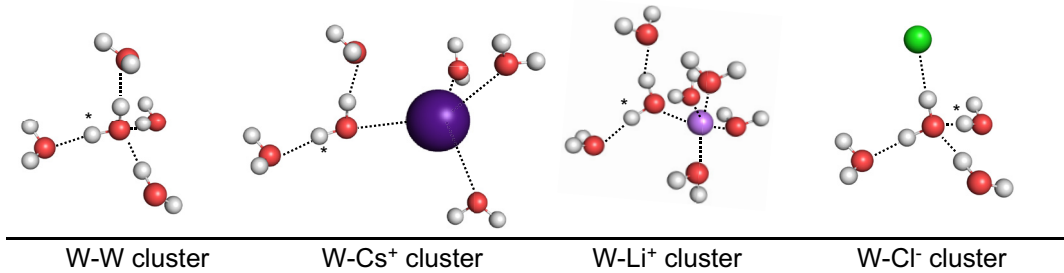


Fig. 6. Ion/water clusters used in the DFT calculations of bond lengths and ν_{OD} vibrational frequencies. Although an implicit solvent model was used, relevant waters were modeled explicitly to increase the accuracy of the calculations. The OD vibrational probe used to compute the frequencies is indicated with a*. Intermolecular/ionic interactions are denoted by dashed lines.

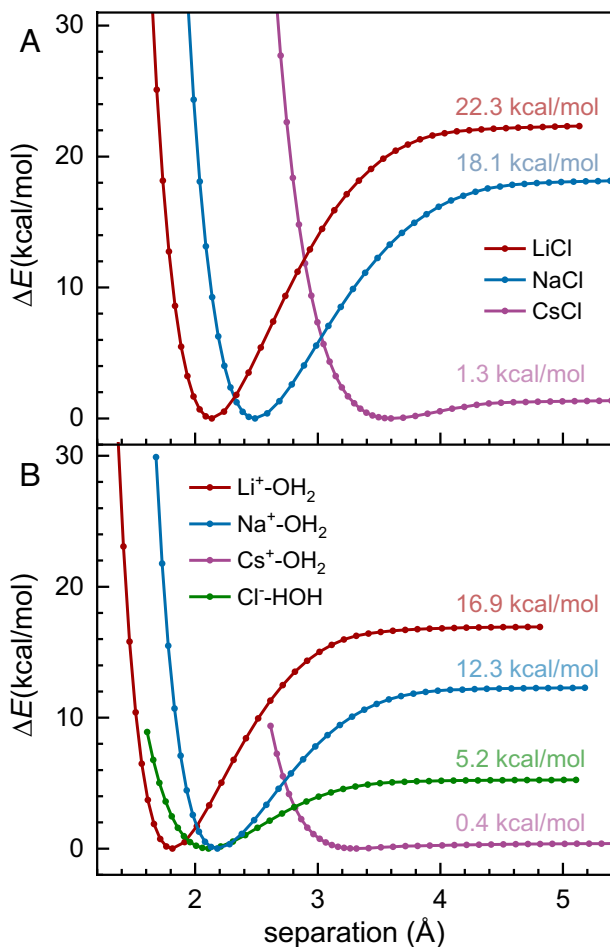


Fig. 7. Morse potentials for contact ion pairs and ion-water interactions calculated using DFT. (A) Contact ion pair potentials generated by computing energy for series of ion pair separations. Note the large separation and shallow potential well for CsCl. (B) Ion-water interaction potentials calculated using the same method. The calculation shows that Cs^+ has an almost negligible interaction with the water oxygen.

in the magnitudes of the $\text{Cs}^+\text{-OH}_2$ interaction compared with those of the other two cations suggest that solvent-separated ion pairs are far less stable in CsCl solutions than in LiCl and NaCl solutions, essentially to the point of nonexistence. The fact that Cs^+ forms very weak contact and solvent separated ion pairs is consistent with C_3 for CsCl solutions being $\leq 3\%$.

As discussed above, comparison to 2D IR experiments indicates that t_2 is the time constant for randomization of the H-bond network. The DFT calculations in Fig. 7 suggest that water-water H-bonds are much stronger and form more readily than contact CsCl ion pairs or solvent separated ion pairs. Rather than chains of contact ion pairs bridged by infrequent water separated pairs as occur in concentrated LiCl solutions, there are irregular clusters of water molecules H-bonded in a manner similar to pure water but modified by the presence of weakly interacting Cs^+ cations and H-bonding to Cl^- anions.

At very low CsCl concentrations, there is a sufficient number of water molecules to form many more than two solvation shells for each Cs^+ cation. In this regime, as the salt concentration increases, the number of Cs^+ first to second-shell water-water H-bonds increases, and these are weaker than those in pure water. These weak H-bonds result in faster H-bond rearrangement and lower viscosity than that of pure water. At very low concentrations, the viscosity decreases linearly with salt concentration. At some higher salt concentration, on average, there will be just enough

water molecules to form two solvation shells per Cs^+ and to solvate the Cl^- . An estimate of the number of water molecules in the Cs^+ first and second solvation shells is 40; adding 8 waters to solvate the Cl^- results in an IMF of ~ 0.042 (1.2 m). This corresponds to an interionic Cs^+ to Cs^+ separation of 13.2 Å if the cations are uniformly distributed (see SI). Above this concentration, adding more CsCl will no longer linearly increase the number of second solvation shell weak H-bonds because second solvation shells will not be complete.

However, the Cs^+ are not uniformly distributed. At 0.042 IMF, many Cs^+ are closer together than 13.2 Å and have overlapping second solvation shells. In the dilute limit, there is a negligible number of Cs^+ closer than 13.2 Å. Only at these very low concentrations will the viscosity decrease linearly with increasing concentration. To estimate how low the concentration must be to be in the linear regime, we will say that if the fraction of Cs^+ that are closer than 13.2 Å is $\leq 10\%$, the decrease in viscosity is linear in CsCl concentration. While the choice of 10% is arbitrary, for larger percentages, the effect on observables should be nonnegligible. To determine this concentration, we employ the fact that the distribution of Cs^+ distances about the average distance is a Poisson distribution. We determined the concentration at which there is a 10% probability of having an ion separation less than required for each Cs^+ on average to have two complete solvation shells (SI Appendix, Text S2). This concentration is 0.02 m (3.6e-4 IMF), which corresponds to a most probable ion separation of 28 Å. Therefore, the linear decrease in concentration occurs only at very low concentrations. Above this 10% concentration, deviations from linearity will become nonnegligible due to prevalence of shared Cs^+ second solvation shells. This explains the sublinear decrease in viscosity at concentrations well below the turnover concentration of 0.1 IMF.

Above 0.1 IMF, the viscosity increases and t_2 slows. The identical trend in these two observables (Fig. 3) is most likely caused by the slowing of water dynamics under conditions of nanoconfinement. Experiments on AOT (dioctyl sulfosuccinate sodium) reverse micelles (RMs) provided detailed information on the effects of nanoconfinement on water dynamics (50, 51). AOT has approximately monodispersed spherical water nanopools. When the nanopools are tens of nanometers in diameter, they have two distinguishable subensembles: a core with fast bulk water dynamics and a shell with water molecules at the AOT surface having significantly slower dynamics. For such large-sized nanopools, the core and surface dynamics are independent of size. The core water has the bulk orientational relaxation time of 2.6 ps, and the water at the interface has a reorientation time of ~ 18 ps (51). When the nanopool becomes small, ~ 4 nm, the RMs still have distinct core and surface dynamics, but the core dynamics are slower than those of bulk water, and the surface dynamics are slower than those of larger RMs. Below ~ 2 nm diameter (~ 40 water molecules), there are no longer two dynamical subensembles, surface, and core. The water molecules behave as a single ensemble with very slow dynamics, undergoing complete orientational relaxation on a time scale > 100 ps (51).

At the turnover point of the viscosity and t_2 (0.1 IMF) there are 18 water molecules per ion pair. If all the water molecules were uniformly distributed solvating the ions, 18 water molecules per ion pair would be just enough to form the first solvation shells of the Cs^+ (~ 8) and the Cl^- (~ 6), with a few water molecules remaining. However, water molecules have substantially stronger interactions with each other than they do with the ions (Fig. 7). At 0.1 IMF and somewhat lower concentrations, it is unlikely that the ions will have fully formed first solvation shells. There will be some water clustering. At the highest concentration studied, IMF = 0.29,

there are 5 water molecules per ion pair. In LiCl solutions, at these very high concentrations, there are long chains of contact ion pairs bridged by water-separated ion pairs (43). The Li interactions with water oxygens are stronger than the water oxygen interaction with hydroxyls. As discussed above, for CsCl the interactions that would lead to contact ion pairs and water-separated ion pairs are extremely weak. Water–water H-bonds are the strongest intermolecular/ionic interactions in the CsCl/water system. At salt concentrations above the turnover point, water should cluster. However, unlike RMs, the CsCl/water systems will not have monodispersed spherical nanopools. There will be water aggregates interwoven among weakly interacting ions. The water H-bond dynamics, reflected in t_2 , slow, and the viscosity increases (Fig. 3) as the CsCl concentration increases.

In bulk water, structural and orientational relaxation occur via “jump” H-bond rearrangements (46). Bulk water orientational relaxation involves concerted switching of H-bond configurations among many water molecules. Except for a very brief (~ 100 fs) transition period, the rearrangement switches from one approximately tetrahedral configuration to another. In RMs, water molecules at the AOT interface have fewer pathways for jump rearrangements, which slows configurational organization. The interaction with the interface is reasonably strong, and its effect propagates out some distance. When the RMs are <2 nm in diameter, the entire nanopool is affected by the interfacial reduction in the number of rearrangement paths, leading to very slow dynamics.

In the high concentration CsCl solutions, the small number of water molecules will form clusters and chains among the ions. The waters will undergo structural reorganization, but differently from bulk water or small RMs. As discussed above (Fig. 7), the interactions of water with the Cs^+ are very weak, and the $\text{Cs}^+\text{-OH}_2$ distance is large. The $\text{Cs}^+\text{-Cl}^-$ interactions are also weak. The very weak interactions with Cs^+ enhance a particular type of water-rearrangement pathway. Water can move between a Cs^+ ion and a water oxygen. This process has been referred to as replacement. Replacement was observed in LiCl solutions, where the CN stretch of methylSCN was used as a vibrational probe (52). Li^+ associates with nitrogen lone pairs. A water molecule moves between the N and Li^+ and replaces the Li^+ . When water is bound, an Li^+ replaces a water H-bonded to the N lone pair. However, because the interactions are strong in the LiCl/MeSCN system, the time scales are slow, in the range of 40 ps. In the CsCl/water solutions, the water interactions with the cation are very weak, and the cation–water separation is large, significantly increasing the rate of replacement. The replacement will cause the Cs^+ to move, which in turn will cause rearrangement of surrounding water molecules, Cl^- s, and other Cs^+ . Thus, water structural rearrangements also drive ion rearrangements. As the salt concentration increases, the number of water rearrangement pathways decreases, slowing the water dynamics and the overall structural changes that determine the viscosity. The net result is that, at higher concentrations where the number of water molecules per ion pair is small, as the CsCl concentration increases, the H-bond dynamics (t_2) slow, and the viscosity increases, as shown in Fig. 3.

Conclusions

The viscosity of CsCl, and to a lesser extent, RbCl and KCl, decreases as the salt concentration is initially increased from zero. For CsCl, the minimum viscosity is reached at a concentration of 0.10 IMF, after which it begins to increase. The experiments and DFT calculations presented above provide a detailed molecular-level explanation for the anomalous behavior of CsCl solutions.

Ultrafast optical OHD-OKE experiments were used to measure the structural dynamics of the CsCl/water solutions. The PPCF obtained from the experiments contained three exponentially decaying components. The equivalents of the fastest two decay components, t_1 and t_2 , occur in pure water. A third, low amplitude component was observed; it is not present in pure water. The viscosity is correlated with t_2 (Fig. 3), the time constant for randomizing the water H-bond network. This result is in stark contrast to other salt solutions previously studied by OHD-OKE experiments, such as LiCl (31) and NaCl (38) and LiBr (31). In these salt solutions, the viscosity tracked the slowest components of the OHD-OKE decays. These slow decay components arise from the dynamics of ion/water ion pairs, clusters, and extended ion/water networks.

The difference between CsCl and the other salts is attributed to the large size and very low charge density of the Cs^+ cation. Because of the low charge density, Cs^+ interacts with water molecules much more weakly than water molecules interact with each other. At low CsCl concentrations, the very weak $\text{Cs}^+\text{-OH}_2$ interactions result in weaker H-bonding with the second solvation shell than water–water H-bonding. This effect causes faster H-bond rearrangement, as shown by the OHD-OKE experiments. The faster concerted H-bond rearrangements reduce the solution's viscosity. To confirm the weaker H-bonding with the addition of CsCl, ultrafast IR PSPP experiments were performed to measure Lifetime Amplitude Spectra of hydroxyls, i.e., the OD stretch of dilute HOD in the CsCl/ H_2O solutions. These experiments revealed that Cs^+ perturbed ODs exhibit stretch vibrational frequencies that are significantly blue shifted compared to those in pure water. The observed blue shift of the Cs^+ perturbed OD stretch frequency is a hallmark of weak H-bonding. The blue shift of the OD stretch frequency and the weak interactions with water were confirmed by DFT calculations.

When there are fewer than 18 water molecules per ion pair (>0.1 IMF), the viscosity begins to increase from its minimum. At the same high concentrations, the viscosities of LiCl and NaCl solutions are substantially greater. In concentrated LiCl solutions, the dynamics are related to the rearrangements of extended networks of ion pairs. DFT calculations were used to show that CsCl contact ion pairs and solvent-separated ion pairs are exceedingly weak, unlike those of LiCl and NaCl. As a result, in CsCl solutions, water–water interactions are stronger than the interaction of water with Cs^+ and Cl^- . The interaction of Cs^+ with water oxygen is so weak compared to the water–water interaction that it is almost negligible. The strong water–water interactions lead to water clustering, which slows the water H-bond rearrangement dynamics compared to pure water. Replacement of water molecules in ion solvation shells couples the water H-bond network rearrangement to the structural dynamics of the ion/water system. Thus, at both high and low concentrations, the solution viscosities are determined by H-bond dynamics.

Materials and Methods

Sample Preparation. CsCl was purchased from Sigma Aldrich and used without further purification. Samples were prepared gravimetrically with ultrafiltered deionized water purchased from Fischer. For optical Kerr effect experiments, CsCl solutions were filtered through a $0.02\ \mu\text{m}$ filter into a cuvettes with path lengths from 1 to 4 cm. The cuvettes were sealed with Teflon stoppers and used immediately for experiments. The laboratory was maintained at $24.4 \pm 0.1^\circ\text{C}$ for all optical Kerr effect measurements. CsCl solutions used in IR PSPP experiments were prepared analogously; however, D_2O was added to produce 5% HOD in deionized ultrafiltered water. The OD stretch of HOD was used as a vibration probe

to eliminate vibrational excitation transfer that occurs when the OH stretch is excited in pure water. The solutions were loaded into a custom-built CaF_2 sample cell with a 12 μm path length.

OHD-OKE Experiments. The ultrafast laser systems used to perform OHD-OKE and IR PSPP experiments have been described in detail in previous publications (50, 53). In brief, the OHD-OKE experiment is a nonresonant pump-probe spectroscopy in which a strong, linearly polarized pump pulse induces a transient birefringence in the sample which is probed by a weak probe pulse polarized 45° with respect to the pump after a variable time delay. The birefringence induced by the pump causes a small percentage of the probe to become elliptically polarized. The probe pulse passes through crossed polarizers before and after the sample, so that only light correlated with the incidence of the pump pulse is measured.

A home-built 5 kHz Ti:Sapphire regenerative amplifier seeded by a mode-locked 90 MHz Ti:Sapphire oscillator produced short (120 fs) and intense 800 nm pulses. A 98/2% beamsplitter generated the pump and probe paths, and the latter was guided through a mechanical delay line. The pump and probe beams were focused and spatially overlapped in the sample, after which the probe beam passed through an analyzing polarizer and was directed toward a balanced detector. Optical heterodyne detection and phase and polarization cycling were implemented to improve the signal-to-noise ratio and to reject scattered light. The nonlinear signal was demodulated and amplified by a lock-in amplifier synchronized to the modulation frequency of the phase cycling scheme. The OHD-OKE signal provided the time derivative of the PPCF, $R'(t)$, which was fit to a multiexponential decay:

$$R'(t) = \sum_{i=1}^N A_i e^{-t/\tau_i} \quad [3]$$

Here, τ_i represents the time constant of a dynamical process and A_i is the amplitude. The number of exponential terms, N , is determined by the number of independent dynamical processes that cause the PPCF to decay. The PPCF was obtained by integration of Eq. 3.

$$R(t) = \int R'(t) dt = \sum_{i=1}^N A_i \tau_i e^{-t/\tau_i} \quad [4]$$

The normalized correlation function coefficients, C_m , provide the normalized statistical weight of the m th dynamical process and are given by

$$C_m = \frac{A_m \tau_m}{\sum_{i=1}^N A_i \tau_i} \quad [5]$$

All experiments were performed in triplicate and fit to the model independently. The parameters (i.e., decay constants and coefficients) were computed separately for each replicate. For each sample, the parameters from the replicates were averaged and the error bars were generated by computing the SD.

IR PSPP Experiments. IR PSPP experiments were conducted with the output of a home-built optical parametric amplifier (OPA) pumped by a 2 kHz Ti:Sapphire regenerative amplifier. The signal and idler of the OPA were overlapped in an AgGaS_2 crystal, generating 65 fs mid-IR pulses at 4 μm via difference-frequency generation (DFG). The DFG stage output was split into a strong pump and a weak probe. The pump was chopped at 1 kHz, and the differential signal between the pump on shot and the pump off shot was acquired. The probe was horizontally

polarized, and the pump polarization was set 45° with respect to the probe. The pump and probe were overlapped in the sample, and the transmitted probe passed through an electronically controlled resolving polarizer to collect the parallel ($+45^\circ$) and perpendicular (-45°) signals. The signal frequency components were resolved by a spectrograph and detected by a cryogenic 32-element HgCdTe array. To correct for polarization bias in the monochromator, a final polarizer was used to equalize the amplitudes of the parallel and perpendicular polarization-dependent probe spectra.

The parallel ($S_{\parallel}(t)$) and perpendicular ($S_{\perp}(t)$) signals recorded in the PSPP experiment were used to compute the population relaxation, $P(t)$.

$$P(t) = [S_{\parallel}(t) + 2S_{\perp}(t)]/3, \quad [6]$$

$P(t)$ was fit to exponential decays to quantify the time constants and amplitudes of the population relaxation dynamics. A long-lived isotropic heating signal was removed using a well-documented procedure to resolve the dynamics of interest accurately (54, 55).

The multiexponential vibrational population decays exhibited frequency-dependent amplitudes, enabling the calculation of lifetime amplitude spectra (LAS), the spectra of each lifetime component. The frequency-dependent population decays were fit to the following equation:

$$P(t; \omega) = \alpha_1(\omega) e^{-t/\tau_1} + \alpha_2(\omega) e^{-t/\tau_2} \quad [7]$$

In these experiments, two populations with different frequency-independent decay times were identified. The first population, with time constant τ_1 , decayed with the same time constant as an OD hydrogen-bonded to a water oxygen in pure water. The second population decayed with a longer, concentration-dependent time constant, τ_2 , that arose from an OD interacting with a Cl^- anion (37).

Density Functional Theory Calculations. Geometry optimizations and vibrational frequency calculations of water ion complexes were performed using the Gaussian 16 quantum chemistry package (56) with the CAM-B3LYP functional with mixed basis sets and SMD implicit solvent model (57) of water. One of the hydrogens on a central water molecule was replaced with deuterium to replicate the experimental HOD probes. H/D, O, and Li atoms were calculated using the aug-cc-pVTZ basis set (56, 57), which has been shown to reproduce water IR spectra accurately (58). Cs^+ is treated with LANL2DZ basis set with effective core potential (59). All optimized structures were confirmed as stable structures with zero imaginary frequency.

Data, Materials, and Software Availability. All study data are included in the article and/or *SI Appendix*.

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Author affiliations: ^aDepartment of Chemistry, Stanford University, Stanford, CA 94305; and ^bNano-Science Center and Department of Chemistry, University of Copenhagen, Copenhagen 2100, Denmark

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