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Influence of Ions on Water Diffusion—A Neutron Scattering Study

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ABSTRACT: Using quasielastic neutron scattering spectroscopy, we measured the averaged translational diffusion of water in solutions of biologically relevant salts, NaCl, a kosmotrope, and KCl, a chaotrope. The analysis revealed the striking difference in the influence of these ions on water dynamics. While the averaged water diffusion slows down in the presence of the structure making (kosmotrope) Na$^+$ ion, the diffusion becomes faster in the presence of the structure breaking (chaotrope) K$^+$ ion. The latter means that, despite strong Coulombic interactions introduced by the K$^+$ ions, their disruption of the hydrogen-bonding network is so significant that it leads to faster diffusion of the water molecules.
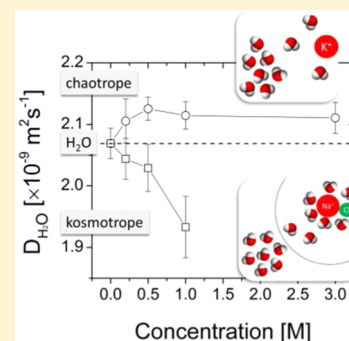
INTRODUCTION

An ion in aqueous solution is surrounded by a region of structurally and dynamically perturbed water molecules known as a hydration shell. The nature of these perturbations depends on the identity and concentration of the ions. These subtle differences are exploited in numerous biological processes, such as the selectivity of ion channels to sodium or potassium. Understanding the chemical/physical basis of these differences is, therefore, of great interest to fields ranging from neuro- and food sciences to ionic liquids and electrolytes research.

Na$^+$ and K$^+$ are both alkali metals, but their behavior in aqueous solution could not be more different. In a solution, Na$^+$ is known to possess a tight hydration shell of 3−5 water molecules, held electrostatically around the ion.[1,2] In contrast, K$^+$ does not form a classic hydration shell of tightly bound water molecules. The origin of the different interactions with water comes from the different surface charge densities[1,3] and relative sizes[4] of the respective ions. On the other hand, Cl$^-$ is only weakly hydrated in both NaCl and KCl aqueous solutions. However, it has been suggested that the water around it is well-ordered, with six water molecules coordinated to it, via hydrogen bonds.[5] Moreover, in aqueous solution, Na$^+$/Cl$^-$ form contact ion pairs, whereas K$^+$ and Cl$^-$ exist as separate moieties.[1] The formation of a contact pair requires that there is a partial dehydration of the two ions involved. This leads to a competition as to whether it is more energetically favorable to exist separately or to break hydrogen bonds (requiring energy) and form an ion pair (lowering the overall energy requirement). This is readily acceptable if both ions have similar affinities and has led to the suggestion of the "Law of Matching Water Affinities" by Collins et al.,[1] to classify the way different ions will exist in solution. This has led to the classification of ions as kosmotropes (structure forming) and chaotropes (structure breaking) for the alkalis (H$^+$ to Cs$^+$). In contrast, the halides (F$^-$ to I$^-$) were classified as strongly hydrated to weakly hydrated. Typically, Na$^+$ is classified as a kosmotrope and K$^+$ as a chaotrope,[1,2] and their behaviors are reproduced in simulations of solvation.[6]

On the other hand, neutron scattering studies have led to the conclusion that there does, in fact, exist a second coordination shell around these ions.[3,5,7−9] They reveal a significant difference in the structure of the hydration shell—perturbed water molecules—around K$^+$ and Na$^+$; the former has about 23 water molecules, whereas the latter has 18 water molecules[8] in both the first and the second hydration shells. More recent studies[10,11] have been either simulations or in confined systems. While these shells are not tightly bound, they represent perturbations in the local water structure. These results persist for concentrations as low as 0.67 M.[2] Dielectric studies also demonstrate marked differences in the water dielectric peak in aqueous solutions of NaCl and KCl,[12−14] at concentrations as low as 0.1 M. This peak is associated with the relaxation of the water cluster, implying that the ions do, in fact, have a structural effect, which might have a longer range than suggested in the literature. Recent pump−probe femtosecond spectroscopy[4] measurements have shown that rotational dynamics of water were affected only in the first hydration shell. The changes in viscosity, often associated with "structure making or breaking", could be simply the result of the size of the ion and its first hydration shell diffusing as a single unit. However, this assumes

that the reorientational dynamics that they probe are completely coupled to the diffusional motions. The diffusional dynamics of water may be also significantly modified by the altered network geometry induced by the ions. Recently, the difference between structure making and structure breaking ions was correlated to the volume difference between the hydrated ion and an equivalent water molecule in its place:[15] If the ion-to-oxygen distance is large than the oxygen—oxygen distance in pure water, then viscosity will decrease, whereas, if the ion-to-oxygen distance is smaller, the viscosity will increase. The consequent local fluctuations in energy and density would influence a diffusive step and the resultant viscosity. Thus, despite a long history of studies of aqueous ionic solutions, the nature of the ion—water complexes and their role in dynamics of the solutions remain a subject of discussion.

In this work, we study the dynamics of water in solution with K^+ and Na^+ ions using quasi elastic neutron scattering (QENS). This is an ideal technique to study these dynamics microscopically as we gain both spatial and temporal information about the atomic motions from the same experiment. In the current work, we use QENS to estimate the averaged diffusion coefficients of water molecules in salt solutions. Our study revealed that water diffusion slows down in the presence of structure forming Na^+ ions, whereas it is accelerated in the presence of the structure breaker K^+ ion. While the former is expected, observation of an increase in water diffusion coefficient due to disruption of the hydrogen-bonding network is intriguing and might have implications for studies of ion dynamics and some biological processes.

■ MATERIALS AND METHODS

Solutions of NaCl and KCl were prepared using triple distilled water. The 99.99% pure salts were purchased from Alpha Aesar and used directly without further purification. Molar solutions were prepared at concentrations of 0.0 M (pure water), 0.2, 0.5, and 1.0 M. QENS experiments were carried out on the backscattering spectrometer BASIS at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL).[16] The BASIS features a combination of a high-energy resolution (Q-averaged value of ca. 3.5 μeV, FWHM) and a wide and variable dynamic range of accessible energy transfers. BASIS choppers were operated at a frequency of 30 Hz, in order to give a dynamic range of approximately ±200 μeV. All samples were loaded into aluminum cans under an inert nitrogen atmosphere, sealed with indium, and measured immediately. The thinnest annular sample holder available, with the outer diameter of 29.0 mm and a thickness of 0.050 mm, was used to minimize multiple scattering. Sample transmission was 88.8%, suggesting that minimal multiple scattering will be present in the experimental spectra. The data reduction included normalization to a vanadium standard. The subtraction of the background, which is known to be sample- and temperature-dependent, is explained below. The output of the data reduction procedure was proportional to the dynamic structure factor, $S(Q,E)$. No multiple-scattering corrections have been applied. All the measurements were done at room temperature.

■ RESULTS

Hydrogen atoms have a neutron scattering cross section significantly larger than any other atom (the total scattering cross section[17] for H is 82.02 b compared to 3.28 b for Na). As a result, the neutron scattering spectra of hydrogen-containing

materials are usually dominated by contribution from hydrogen. Thus, the spectra obtained in our measurements represent motions of hydrogen atoms of water. In the accessible time window (between ∼5 and ∼300 ps), hydrogen motions reflect the averaged diffusion of water molecules. Thus, QENS provides a direct way to measure diffusion of water molecules in the aqueous salt solutions.

Neutron scattering measurements yield data in the form of the scattering function, $I(Q,E)$, which can be understood as the convolution of the dynamic structure factor with the instrumental resolution function (eq 1). In the incoherent approximation, this function is related to the self-correlation function of the water protons in time and space through the Fourier transform from frequency (energy) to time and from wave-vector Q space to real space. Figure 1 shows the measured $I(Q,E)$ for pure water at two Q values.
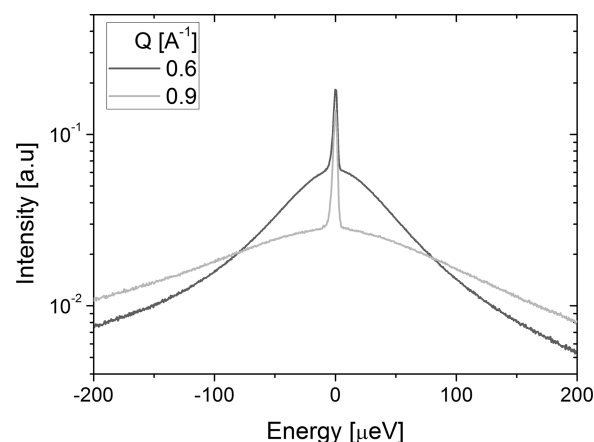

Figure 1. An example of the measured QENS intensity as a function of energy. The different curves represent the intensity measured as different Q. The sample was pure water.

The data may be fitted using the standard approach of a weighted δ function, to account for the elastic line, and a Lorentzian function for the quasielastic contribution

$$I(Q,E) = [x \cdot \delta(E) + (1-x) \cdot S(Q,E)] \otimes R(Q,E) + B \cdot E + C \tag{1}$$

where x is the weight of the elastic component, approximated by the δ function $\delta(E)$, $S(Q,E)$ is the dynamic structure factor corresponding to the sample, and $R(Q,E)$ is the resolution function of the spectrometer, which is numerically convoluted with the term in the square brackets. We used spectra of vanadium as the resolution spectra $R(Q,E)$. The broad background (characteristic for BASIS spectrometer) was fitted with a linear term of $(B \cdot E + C)$. The $S(Q,E)$ were fit using a single Lorentzian function where $\Gamma(Q)$ is the half width at half-maximum (HWHM)

$$S(Q,E) = \frac{1}{\pi} \cdot \frac{\Gamma(Q)}{E^2 + \Gamma^2(Q)} \tag{2}$$

An example of the data fit is presented in Figure 2. The same procedure was followed for the solutions of NaCl and of KCl with different salt concentrations. We also performed the fit of the data with a Cole−Cole function in the susceptibility formalism for the quasielastic contribution. However, there was no noticeable difference to the fit with a single Lorentzian (eqs
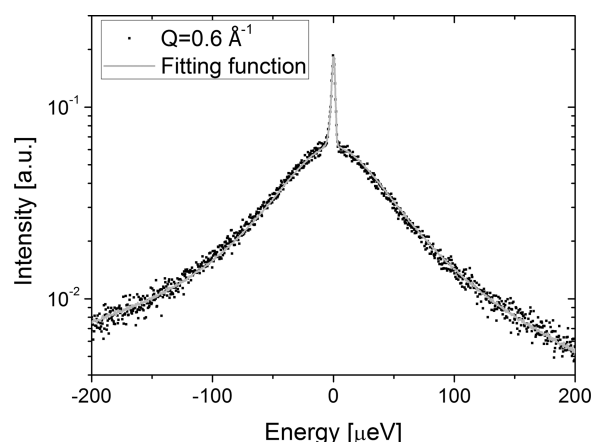
Figure 2. An example of the raw data for pure water (dots) and the fit curve (line) using eq 1.

1 and 2), and the stretching parameter α of the Cole−Cole function indicated no meaningful deviation from the single Lorentzian line shape. On the basis of this analysis, we concluded that a single Lorenzian function adequately fits the data in the studied energy range for all the samples. The fit provides estimates of the spectral broadening $\Gamma(Q)$.

■ DISCUSSION

The dynamic range of BASIS (3.5−200 μeV) is well-suited for studies of water diffusion.[18] The short-range, local fast dynamics of water yield a signal that is broad (faster)[19] compared to the dynamic range of the spectrometer and is accounted for by the linear background (eq 1) and, consequently, will not be discussed. The half width at half-maximum values, $\Gamma(Q)$, for NaCl and KCl are plotted in Figure 3 as a function of Q. The diffusion coefficient was calculated using

$$D_S(Q) = \frac{\Gamma(Q)}{\hbar Q^2} \tag{3}$$

The diffusion coefficient D_s is calculated by taking the averaged value of the $D(Q)$ in the range $0.5 < Q < 1.1$ Å^{-1}, where the plots show the expected Q-independent values (regular Fickian diffusion). For illustration, the values of $D_s(Q)$ for 0.5 M KCl and NaCl are plotted in Figure 4. For $Q < 0.5$ Å^{-1}, the diffusion coefficients deviate somewhat from the plateau level, being slightly higher than expected from the rest of the plateau points. Usually, such an overestimation of QENS broadening at low Q is a consequence of multiple scattering effects.[20] The thinnest available (0.050 mm) sample holder, providing 88.8% transmission through the sample, was sufficiently thin to reduce, but not completely eliminate, the effects of multiple scattering, which are most apparent at the lowest Q value. The data at Q above $Q > 1.1$ Å^{-1} correspond to diffusion that is faster than the energy window of the BASIS spectrometer, and the results of the fit are not reliable without making numerous assumptions. Moreover, some more local processes, such as rotations and local H-bonding rearrangements, also provide significant contributions at higher Q.

The derived diffusion coefficients present very different pictures for the two ions involved. The diffusion coefficient of water in a KCl solution is a rising function of concentration, saturating above 0.5 M. On the other hand, the diffusion coefficient of water in a NaCl solution is a constantly
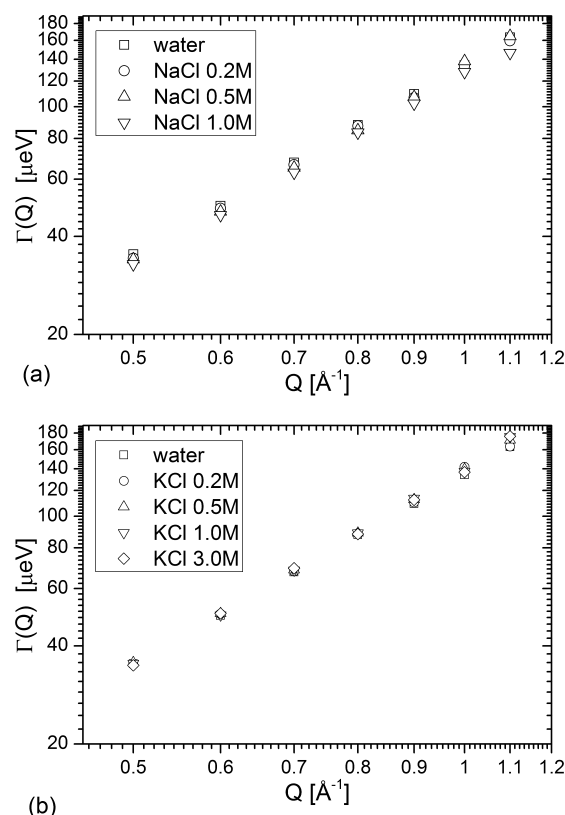

Figure 3. Half width at half-maximum, $\Gamma(Q)$, for (a) NaCl solutions and (b) KCl solutions as a function of Q, presented in the double logarithmic scale. For clarity, the error bars are not included.

decreasing function of concentration, at least in the measured range. The derived diffusion coefficient for pure water was 2.07 × 10^{-9} m^2 s^{-1}, which is consistent with known data for a room temperature of 22 °C.[19]

The observed difference in the concentration dependence points to very different local environments. The diffusion coefficients derived from the QENS data represent an averaged value of the diffusion coefficients of all water populations in the sample, including bulk water, water in and around the ion hydration shell, and their exchange. In the case of NaCl, it is accepted that there exists a tight hydration shell around the ions, regardless of whether they exist in contact pairs or not. In a two-component system, the diffusion can be represented by a single consolidated rate,[23] known as the mutual diffusion coefficients of the ions involved. As a comparison, these coefficients for NaCl and KCl, measured by free diffusion Rayleigh interferometry, are provided in Figure 5b.[21,22] Strong similarity in the behavior of mutual diffusion of ions (Figure 5b) and of the water diffusion (Figure 5a) provides strong support to our interpretation. The Na$^+$ ion forms a tight hydration shell that slows down its diffusion and the averaged diffusion coefficient of water molecules. In contrast, the structure breaking K$^+$ ion disrupts the hydrogen-bonding network in water. This leads to a faster averaged diffusion of water molecules and also diffusion of the K$^+$ ion significantly faster than that of the Na$^+$ ion.

To understand the importance of the obtained results, one must return to the physical situation of the ions in solution. It is usually considered that Na$^+$ will exist in conjunction with Cl$^-$ as a contact pair, partially dehydrated with a joint and relatively static hydration shell around them.[1,2] In any case, there exists a
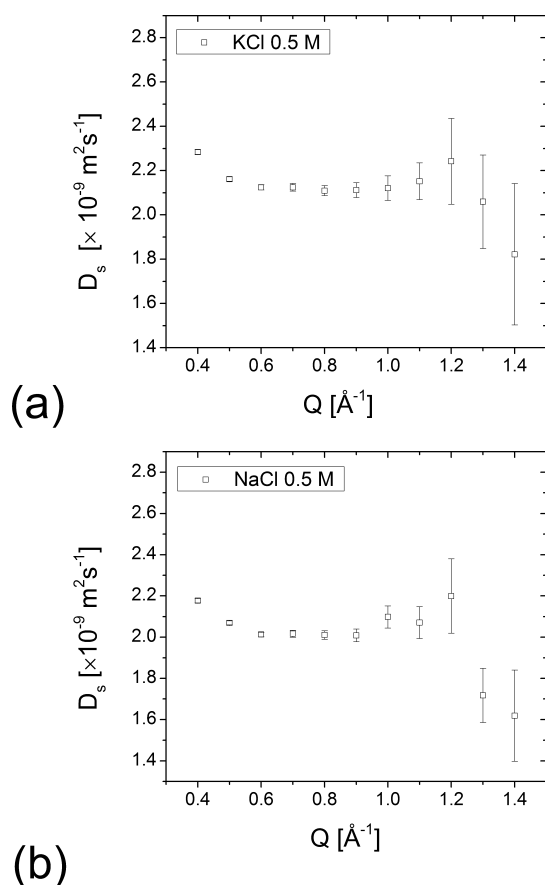
Figure 4. Self-diffusion coefficient as a function of Q for 0.5 M concentrations of KCl (a) and NaCl (b). The increase for $Q < 0.5$ is due to multiple scattering. The dynamic range of the BASIS is adequate for water dynamics at $Q < 1.1$ Å^{-1}. At higher Q, the spectrum is getting broader than the accessible spectral range. This leads to large error bars.

Figure 5. (a) The Q-averaged diffusion coefficients for NaCl and for KCl as a function of concentration. The error bars are the standard deviations. There is a marked difference between the diffusion of water molecules in the presence of potassium or sodium. Plotted for comparison in (b) are the volume fixed mutual diffusion coefficients for NaCl and KCl, taken from refs 21 and 22.

relatively stable hydration shell around the ion. As the concentration of ions increases, the averaged diffusion coefficient drops as more water molecules are included in the hydration shell of the ions. The K$^+$ ion, on the other hand, does not have a classic hydration shell and does not form a contact pair with the Cl$^-$ ion.[1,2,24] Furthermore, there is evidence to suggest that the residence times of water molecules around free Cl$^-$ ions actually decreases[2] while the potassium ion is structure breaking in its immediate vicinity.[1] These two observations are consistent with our results showing a rising diffusion coefficient with increasing concentration for KCl in Figure 5. As these two trends begin to balance, one notes saturation in the diffusion coefficient. It is interesting to note that this plateau occurs around biological concentrations of K.

These observations suggest a general scenario for cation diffusion in aqueous media where there is a strong effect of slowing down for kosmotropes, but only a relatively weak effect of speeding up for chaotropes. Kosmotropes slow down the diffusion of the surrounding water molecules, which, additionally, interact with the hydration shell of the kosmotrope, thereby yielding a strong cumulative effect of slowing down. Chaotropes speed up the diffusion of the surrounding water molecules, and then follow the enhanced diffusion dynamics of the solvent without forming any significant hydration shell. It would be interesting to investigate the diffusion slowing down for a kosmotrope with a weaker bound hydration shell. We
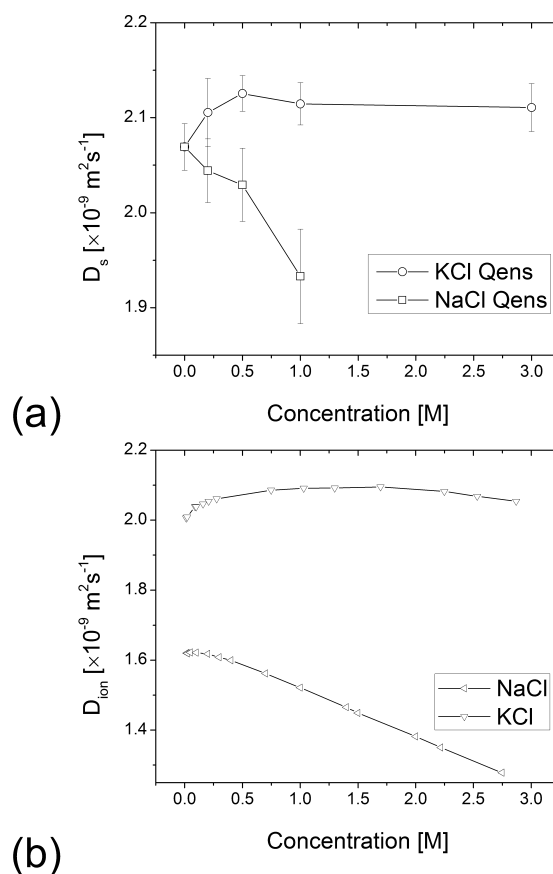
predict that there should be smaller separation between the diffusion of ions and the diffusion of solvent water molecules in this case.

One could also relate the observed difference in diffusion rates, to the selectivity of the respective ion channels, a major topic in biological/neuroscience research. Potassium channels selectivity comes from the small size of the pore through which the ion passes.[25−27] The potassium ion is fully dehydrated when it passes through the selectivity filter of the channel. This is consistent with the picture from our data. The same lack of a stable hydration shell structure that gives rise to the increased rate of diffusion for the hydration water of potassium contributes to the small energetic penalty in the dehydration of potassium as it passes through the ion channel. This is in contrast to the case of voltage-gated sodium ion channels. Sodium is a smaller ion, yet the selectivity filters for this ion are larger than those for potassium. This is because the sodium ion remains partially hydrated when it passes through the channel.[28] This partial hydration is consistent with our finding of a stable shell of slowly diffusing water surrounding the sodium ion. The high energetic penalty for disruption of this hydration structure forms the basis for the selectivity of the ion channel.

■ CONCLUSION

Using quasielastic neutron scattering spectroscopy, we were able to measure the averaged diffusion coefficient of water in the presence of ions. This analysis reveals a significant difference in the influence of the ions from the opposite sides of the Hoffmeister series on the diffusion of water molecules. The very different local environment induced by each ion works as an effective friction force in the case of Na^+ ions or an apparent lubricant, in the case of K^+ ions. These differences can be related to the different ionic sizes and charge densities of each ion, leading to different electrostatic environments. The diffusion coefficient of the water molecules in a solution is a relatively steep function of concentration for NaCl, but only weakly concentration-dependent for KCl. We suggest that this observation reflects the general difference between kosmotrope and chaotrope solutes. Because the former features more or less strongly bound hydration shells, the effect of diffusion slowdown for kosmotrope ions is cumulative, whereas that of diffusion aceleration for chaotrope ions is not.

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Notes

■ ACKNOWLEDGMENTS

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