**CHEMICAL PHYSICS**

**Polyelectrolytes induce water-water correlations that result in dramatic viscosity changes and nuclear quantum effects**

J. Dedic, H. I. Okur, S. Roke*

INTRODUCTION

Most biochemical reactions occur in aqueous environments, underlining the importance of water for life. More than just a passive background, water actively participates in various processes, such as enzyme and ion channel activity, protein folding and stability, self-assembly (1), molecular recognition (2, 3), charging (4), and lubrication (5). This is possible because water molecules are strongly responsive to electrostatic fields of simple ions, charged macromolecules such as polyelectrolytes, or polar groups. To understand the complex role that water plays in biochemical processes, it is necessary to study the interaction of ions and ionic groups with water on both the molecular and macroscopic levels. It has been found that various macroscopic properties of bulk aqueous solutions are influenced by ions, such as the dynamic viscosity and the surface tension (6–8). The changes in these properties have their origins within the molecular nature of the interactions between ions and water. The molecular-level interaction of ions with water has been investigated for electrolyte solutions with ionic strengths of >0.1 M using x-ray scattering (9), neutron scattering (10), infrared spectroscopy (11), Raman scattering (12, 13), terahertz spectroscopy (14), and molecular dynamics (MD) simulations (15–18), among others. These studies show that the molecular structure of water in the vicinity of ions is strongly influenced by the valence, polarizability, and size of the ion (19–21) and that significant perturbations of the structure and dynamics of liquid water are observed within the first three hydration shells. In addition, the ion-water interaction is influenced only minimally by nuclear quantum effects (22–25).

Recent femtosecond elastic second harmonic scattering (fs-ESHS) experiments performed by us (24, 26) and others (27), together with subsequent computational studies (15, 28, 29), have provided a new dimension to the understanding of water-ion interactions. fs-ESHS experiments are performed by illuminating an aqueous solution with 190 fs laser pulses at 1028 nm and detecting the light scattered at the second harmonic (SH) wavelength (514 nm). Coherently emitted SH light reports on orientational correlations between molecules and is thus sensitive to hydrogen (H)–bonding. Performing fs-ESHS experiments on 21 different aqueous electrolyte solutions spanning a concentration range from 1 μM to 0.1 M revealed a universal increase in the fs-ESHS intensity, but only for polarization combinations that contain coherent emission. This increase was further absent for neutral solutes and displayed remarkably different curves for H2O and D2O. It was proposed that the total long-ranged electrostatic field of the ions already present at low salt concentrations perturbs the water-water correlations in the H–bond network of water and is subject to a significant and as of yet unexplained nuclear quantum effect. Revisiting key elements of the experiments and interpretation here, Fig. 1A shows fs-ESHS data for NaCl in H2O and D2O solutions adapted from (24, 30). It can be seen that the fs-ESHS response already increases at a salt concentration of 10 μM and saturates at ~1 mM. In an fs-ESHS experiment, the nonlinear optical polarization of a liquid composed of noncentrosymmetric molecules is measured. This polarization arises from two sources (31–33): The first contribution arises from the polarization of individual molecules and gives rise to incoherent (hyper-Rayleigh) scattering (31, 34). It occurs in all polarization combinations of the in- and outgoing optical fields. The second contribution arises from the coherent addition of SH signal from different but orientationally correlated molecules. This coherent contribution can be measured only in certain polarization combinations of the optical fields, e.g., with all beams polarized parallel to the scattering plane (PPP polarization combination). The response in Fig. 1A therefore arises from water (because the ions used are centrosymmetric) and reports on orientational correlations between different water molecules. Because these correlations are already observed at ion separations of ~20 nm, the phenomenon reports on long-ranged interactions. The D2O solution in Fig. 1A displays the same trend but with a lower saturation value and higher onset concentration compared to H2O. Although the H2O curve in the PPP polarization combination in Fig. 1A can be modeled using a mean-field Debye–Hückel model that describes the influence of the total electrostatic field in the solution on the molecular orientational order (24, 26, 28, 29), this model fails to...
H$_2$O/D$_2$O difference therefore suggests that ions influence collective models that represent water only by a dielectric constant. The $I_{\text{salt}}/I_{\text{water}}$ ratio decreases from H$_2$O to D$_2$O, indicating a decrease in orientational order in the aqueous bulk solution. This decrease in orientational order is attributed to the breaking of H-bonds through rotation, which is stronger in H$_2$O than in D$_2$O. The breaking of H-bonds through rotation is predicted to be weaker in D$_2$O compared to H$_2$O, as indicated by the fs-ESHS data adapted from (24, 30).

Here, we report that long-range reordering of the H-bond network of water was connected to the Jones-Ray effect (35), which exhibits an anomalous and isotope-dependent ~0.3% reduction in the surface tension at the fs-ESHS saturation concentrations. The ion-induced increase in orientational order in the aqueous bulk solution gives rise to an entropic penalty, which causes a reduction in the surface tension (24, 35, 36). This long-range interaction of the ionic electrostatic field with water is a new and poorly understood phenomenon that warrants further investigation. One could ask how long-ranged and important water ordering can be because, until now, the reported effects cause only a minor (0.3%) change in macroscopic properties (37).

Here, we report that long-range reordering of the H-bond structure of water via weakly screened electrostatic interactions in polyelectrolyte solutions causes significant changes of the reduced specific viscosity. Anionic polyelectrolytes, poly(acrylic acid) (PAA), and poly(styrene sulfonate) (PSS) are shown to strongly enhance the orientational order of water, starting at polyelectrolyte concentrations as low as 1 nM and ionic strength of 1 μM. The molecular structures of PAA and PSS are displayed in Fig. 1C. The changes in the orientational order of water are more pronounced in H$_2$O than in D$_2$O, consistent with the behavior observed in the solutions of simple salts. The reduced specific viscosity of the polyelectrolyte solutions follows a similar trend as the water ordering, for both H$_2$O and D$_2$O, and changes of more than two orders of magnitude are observed. We conclude that long-range interactions between spatially correlated ion groups on the polyelectrolytes and the H-bond network have a significant impact on the reduced viscosity. Although traditional mean-field models based on inter- and intra-polyelectrolyte correlations can qualitatively explain the viscosity anomaly in H$_2$O, the models fail to predict the discrepancy between H$_2$O and D$_2$O (38, 39). This points to water-water correlations having an influence on the anomalous viscosity of polyelectrolyte solutions. In addition, our data suggest that H-bond breaking through rotations occurs more readily than through H-bond stretching (Fig. 1B) and is relatively more important for viscosity.

RESULTS AND DISCUSSION

Femtosecond snapshots of long-range order

The orientational correlations between water molecules in solutions of PAA and PSS were measured at different concentrations (ionic strengths). The ionic strength ($I$) of the solution, due to the dissolved and partially dissociated polyelectrolytes, was calculated as $I = 0.5c_m f$, where $c_m$ is the monomer concentration in M and $f$ is the percentage of dissociated counterions. According to Manning’s theory of counterion condensation (40, 41), the degree of ionization is $f = b/\lambda_B = 0.35$, where $b = 0.25$ nm is the distance between ionizable groups on the polyelectrolyte chain and $\lambda_B = e^2/4\pi\varepsilon_0 k_B T = 0.71$ nm is the Bjerrum length in water, with $e$ the elementary charge, $\varepsilon_0$ the vacuum permittivity, $\varepsilon = 78.5$ the dielectric constant of water, $k_B$ the Boltzmann constant, and temperature $T = 298$ K. Figure 1D shows the fs-ESHS response of PAA solutions of different ionic strength recorded at a scattering angle $\theta = 90^\circ$, with all beams polarized in the horizontal scattering plane. The intensities are normalized with respect to the fs-ESHS intensity of the pure solvent, and data for both H$_2$O and D$_2$O solutions are shown. It can be seen that the fs-ESHS response from H$_2$O solutions increases from a value of 1 at near-infinite dilution and reaches a maximum of 6.2, after which the intensity drops again and levels off above an ionic strength of ~1 mM. The increase in the scattered intensity with concentration might be intuitively interpreted in terms of increasing the number density of bare polyelectrolytes. This simple explanation is, however, contradicted by the subsequent decrease in fs-ESHS intensity. Moreover, incoherent fs-ESHS measurements [recorded with all beams polarized in the direction vertical to
the scattering plane (SSS)] of the same solutions, shown in fig. S1, display no increase in the fs-ESHS response at the concentrations used here. If the bare polyelectrolytes contributed significantly to the SH signal, we would expect to see an increase in the incoherent response in fig. S1. The reason why the contribution of the bare polyelectrolytes is insignificant compared to their hydration shells can be understood by noting that in a nonresonant fs-ESHS experiment, the emitted SH intensity scales quadratically with the number of molecules in the focal volume (42). Even at the highest polyelectrolyte concentration used here, there are still >1000 water molecules per monomer, leading to a theoretical 10⁶ higher contribution from the water than from the polyelectrolytes.

Figure 1D also shows that a significant discrepancy occurs when the same fs-ESHS experiment is conducted using D₂O as the solvent instead of H₂O. The fs-ESHS trend for D₂O is significantly altered compared to H₂O: The maximum intensity is 2.4× lower and appears at a 1.5× higher concentration (ionic strength) compared to H₂O. The presence of a saturation intensity at high concentration, a low-onset ionic strength, and the difference between H₂O and D₂O are reminiscent of the observations for aqueous salt solutions of Fig. 1A. The main difference here is the appearance of a pronounced peak in the concentration curve compared to electrolyte solutions. This behavior stems from the interactions between the electrostatic field of the ionic groups on polyelectrolytes and the H-bond network of water. At very low ionic strength, the polyelectrolyte chains are in an extended conformation due to strong intrachain electrostatic repulsion (43–46) and different polyelectrolytes are expected to be correlated with each other (38, 47–49). The ionized groups on the polyelectrolyte chains therefore do not move freely like simple electrolyte ions but are limited in their spatial arrangement by both the limited flexibility of the polyelectrolyte chains and the interactions between different chains. These intra- and interchain correlations affect the orientational order of water molecules that are associated with each ionic group as extended hydration shells. The long-range correlations in polyelectrolyte solutions arise from a combination of a high degree of ionization of the polyelectrolytes and a large Debye screening length. At an ionic strength of I = 10 µM, the Debye length is \( \lambda_D = (2k_B T/N_A) \approx 100 \text{ nm} \), where \( k_B \) is the Boltzmann constant and \( N_A \) is the Avogadro number. Because the ionic strength is a function of polyelectrolyte concentration, the increase in the polyelectrolyte concentration shortens the Debye length, which suppresses long-range spatial correlations (43, 44, 49).

The importance of Debye screening for the fs-ESHS response was confirmed by measuring the effect of varying ionic strength on the viscosity. The specific viscosity of PAA, on the other hand, shows no such behavior, underscoring the fact that long-range electrostatic interactions between the charged and the H-bond network in polyelectrolyte aqueous solutions play a role in this viscosity anomaly. Traditional viscosity models are based on a mean-field approximation of the solvent and therefore do not explicitly take into account changes in solvent structure. Experimentally performing specific viscosity and fs-ESHS measurements will show whether a long-range interaction between the electrostatic field and the H-bond network of water is playing a role in the viscous flow of polyelectrolyte solutions.

In what follows, we investigate the long-range correlations in aqueous polyelectrolyte solutions in more detail by measuring the integrated SH intensity scattered in the forward half-plane (Fig. 2A) and comparing it with the reduced specific viscosity of the solutions (Fig. 2B). In Fig. 2A, the measured integrated fs-ESHS intensity (\( S_{\text{int}} \)) is plotted as a function of polyelectrolyte concentration (bottom axis) and ionic strength (top axis) for PAA solutions in H₂O (red circles) and D₂O (blue squares) and for poly(ethylene glycol) (PEG), a neutral polymer dissolved in H₂O (green triangles). The fs-ESHS data for PSS are shown in fig. S3 and display a similar trend as the PAA. The concentration dependence of \( S_{\text{int}} \) is comparable to the fixed-angle measurements of Fig. 1D, but higher fs-ESHS intensities are recorded, allowing a more accurate comparison. The fs-ESHS intensity increases up to a value of 80 times the scattered intensity of pure water up to a concentration of ~9 nM (ionic strength of ~10 µM). The intensity drops with further addition of PAA, leveling off at a concentration of 220 nM (ionic strength of 240 mM). For D₂O solutions, the behavior is also similar compared to Fig. 1D and shows a curve that is reduced in maximum intensity by a factor of ~4 and shifted to eight times higher concentrations. The results for PSS (fig. S3) are qualitatively similar but display an even more pronounced difference between H₂O and D₂O. The fs-ESHS peak intensity is reduced from 80 to 8, and the peak polymer concentration is increased by a factor of 14. PEG, on the other hand, shows no such behavior, underlining the importance of the electrostatic interactions with water.

The measured reduced specific viscosity, \( \eta_{\text{red}} \), as a function of polymer concentration is shown for PAA solutions in H₂O (red) and D₂O (blue) in Fig. 2B. The reduced specific viscosity is calculated by

\[
\eta_{\text{red}} = (\eta_{\text{solution}} - \eta_{\text{water}})/c_m \eta_{\text{water}},
\]

where \( \eta_{\text{solution}} \) is the measured dynamic viscosity and \( c_m \) is the monomer concentration. The data for the PSS polyelectrolyte are plotted in the same manner and are shown in fig. S3. As a comparison, the specific viscosity of neutral PEG polymer chains in H₂O is also displayed (green trace). The \( \eta_{\text{red}} \) of PEG was theoretically calculated with details shown in section S4. The specific viscosity of
PAA and PSS shows a surprisingly similar behavior as the fs-ESHS data, starting at a low value and then going over a maximum with increasing concentration. The maximum occurs at the same ionic strength as the fs-ESHS maximum (~10 μM for H2O) and comprises a difference of two orders of magnitude in the reduced specific viscosity. The effect of D2O on the viscosity is similar: The peak intensity is shifted to higher ionic strength for D2O (~100 μM), and the peak value is reduced by ~20%. For PSS (fig. S3), the effect is even more pronounced: Switching from H2O to D2O, the peak concentrations are shifted from 3.2 to 100 nM (ionic strength of 2.8 to 85 μM), and the peak value of reduced specific viscosity is reduced by a factor of ~3.

The appearance of a peak in reduced specific viscosity as a function of polyelectrolyte concentration is in qualitative agreement with previously measured data for both PAA (60, 61) and PSS (38, 61) in H2O. To the best of our knowledge, the D2O measurements have not been reported before and are remarkably different from H2O in that the peak occurs at 10× higher concentration and with a smaller amplitude. The anomalous viscosity peak is known to rapidly disappear when excess salt is added to the solution due to Debye screening (62), which is consistent with the sensitivity of the fs-ESHS response to added salt shown in fig. S2. This points to long-range electrostatics as the source for the observed behavior in both the molecular structural (fs-ESHS) measurement and the macroscopic (reduced viscosity) measurement. The neutral PEG (and other neutral polymers) does not display the viscosity anomaly (63, 64). Likewise, there is no peak in the fs-ESHS response of PEG. This further confirms the importance of long-range electrostatic interactions in PAA (PSS) solutions, which are responsible for the strong enhancement of the fs-ESHS response and the reduced viscosity and are absent for neutral polymers such as PEG.

The behavior observed in Fig. 2 is interesting for the following reasons: First, the correlation between the fs-ESHS intensity and the reduced specific viscosity for both H2O and D2O and for both polyelectrolytes with different molecular weights and different chemical structures suggests that they derive (at least partially) from the same mechanism. Second, the isotope effect observed in the viscosity is unexpected. According to literature, the anomalous behavior of the specific viscosity of polyelectrolyte solutions stems solely from intra- and inter-polyelectrolyte correlations (38, 39, 48). These models are in agreement with the experimental data in H2O. However, because they are based on a mean-field approximation of water, they do not predict a significant difference in the reduced specific viscosity between H2O and D2O, as the dielectric constants of the two solvents differ by less than 0.4% (65). Using one of the existing mean-field models (66), we calculated the reduced specific viscosity and plotted it together with the measured data for H2O and D2O. The data are presented in fig. S4. Although the model reproduces the anomaly for PAA in H2O, it predicts nearly the same behavior for D2O. Yet, the measured reduced specific viscosity of PAA is significantly different for D2O, indicating that the enhancement of water-water correlations plays an important role.

As mentioned in the Introduction, the fs-ESHS data for simple electrolyte solutions in Fig. 1 A are different for H2O and D2O. This difference was attributed to nuclear quantum effects. H-bonds between water molecules can be broken along two different orthogonal axes. Figure 1B illustrates two H-bonded water molecules that are orientationally correlated, and the black arrows illustrate the two axes of motion: a stretching motion or a rotational motion. The stretching motion does not lead to differences in orientational correlations in contrast to the rotations, rendering fs-ESHS more sensitive to H-bond breaking via rotation. Because the H-bond bending mode is predicted to be stronger in D2O than in H2O (22, 67, 68), the fs-ESHS response of pure D2O is larger than that of H2O (24), as is its resistance to restructuring due to ions (24) or ionic groups on polyelectrolytes as is observed here. Because the fs-ESHS data and the specific viscosity data are similar, it is plausible that a similar decoupling effect also contributes to viscosity. Viscosity depends on the movement of molecules through water, and this
naturally involves the breaking of H-bonds (69). Our combined data suggest that the breaking of H-bonds by rotation plays a relatively larger role in determining the viscosity than the breaking of H-bonds by stretching. Namely, if both modes would contribute equally, no viscosity difference between H$_2$O and D$_2$O solutions would be observed. If the stretching mode would contribute more, then the D$_2$O/H$_2$O difference would be reversed. Our observation and assessment are in agreement with spectroscopic measurements, because the H-bond stretch mode was detected at ~183 cm$^{-1}$, while the H-bond bending mode was found to occur at lower frequencies of ~50 cm$^{-1}$ (for H$_2$O) (70, 71). Although both values are below the thermal energy (219 cm$^{-1}$ at room temperature), the bending mode is energetically more favorable and therefore may contribute more than the stretching mode. Such a mechanism could also explain an isotope effect observed in adhesion hysteresis (72). Thus, long-range interactions are present in more systems than simple electrolyte solutions and can lead to marked changes in macroscopic properties as well as unexpected significant nuclear quantum effects. As water plays an omnipresent role in diverse disciplines as physics, chemistry, biology, and medicine, the observed effects can have consequences for processes where charges are involved.

**SUMMARY AND CONCLUSIONS**

We investigated long-range interactions between polyelectrolytes and the H-bond network of water. We found an increase in the orientational order of water and an even larger difference between H$_2$O and D$_2$O solutions compared to simple electrolyte solutions. Upon increasing the polyelectrolyte concentration, the fs-ESHS intensity increases up to a maximum and then reduces and levels off. Qualitatively, this behavior can be explained by two parallel effects: increasing polyelectrolyte number density and screening of the electrostatic field by counterions. Macroscopically, we observed a similar behavior for the reduced viscosity. The reduced viscosity changes up to two orders of magnitude with increasing concentration, shifts by a factor of ~8 to 14 in the concentration, and decreases in maximum value (20 to 300%) when D$_2$O is used instead of H$_2$O. Traditional mean-field models cannot explain such a difference. We conclude that the anomalous viscosity of polyelectrolyte solutions cannot be entirely explained by intra- and inter-polyelectrolyte correlations but that changes in water-water orientational correlations also influence the reduced viscosity. Moreover, our data suggest that H-bond breaking through rotations occurs more readily than through H-bond stretching and is more important for viscous flow.

**MATERIALS AND METHODS**

**Chemicals and sample preparation**

PAA (molecular weight of 450 kDa; Polysciences Inc.), sodium PSS, sodium salt (molecular weight of 1000 kDa; Polysciences Inc.), and PEG (molecular weight of 400 kDa; Sigma) in powder were used as received. NaCl (99.999%) was purchased from Acros. Stock polymer solutions were prepared by dissolving the polymer in water (H$_2$O or D$_2$O). The samples were prepared by subsequent dilution of the stock solutions to obtain the desired polymer concentration. Stock NaCl solutions were filtered through Millipore Millex-VV 0.1-mm polyvinylidene difluoride membrane filters. Ultrapure H$_2$O with an electrical resistance of 18.2 MΩ·cm was obtained from a Milli-Q UF-Plus instrument (Millipore Inc.). For experiments with heavy water, the D$_2$O used was 99.8% D atoms with an electrical resistance of >2 MΩ·cm (Armar).

**fs-ESHS setup and measurements**

Laser pulses (190 fs) centered at 1028 nm with a 200-kHz repetition rate were used as the light source for fs-ESHS measurements. The polarization of the input pulses was controlled by a Glan-Taylor polarizer (GT10-B, Thorlabs) and a zero-order half-wave plate (WPH05M-1030). The incident laser pulses, filtered by a long pass filter (FEL0750, Thorlabs), with a pulse energy of 0.3 μJ (incident laser power $P = 60$ mW), were focused into a cylindrical glass cuvette cell (inner diameter of 4.2 mm; LS Instruments) with a waist diameter of 35 μm and a Rayleigh length of 0.94 mm. Scattered SH light was collected with a plano-convex lens ($f = 5$ cm) and then filtered with a 10- or 50-nm bandpass filter centered around 515 nm (ET515/10 and ET515/50, Chroma). A Glan-Taylor polarizer (GT10-A, Thorlabs) was used for the polarization analysis of the SH light. Last, the SH light was focused into a gated photomultiplier tube (H7421-40, Hamamatsu). More details on the setup can be found in (73).

The experimental conditions used for fixed-angle measurements were the same as in (24, 30, 57). The detection angle was set to 90° with an acceptance angle of 11.4°. Each data point is an average of three to five measurements. Each measurement is an average of 50 expositions of 1-s integration time, using $50 \times 2 \times 10^5$ pulses in total. The gate width was 10 ns.

To compare fs-ESHS response with reduced specific viscosity, we introduced a different metric: integrated fs-ESHS intensity ($S_{int}$). To obtain this quantity, a scattering pattern is recorded at 5° steps between $-90^\circ$ and $+90^\circ$ with an opening angle of $3.4^\circ$. The pattern is normalized at each angle $\theta$ with respect to pure water: $S(\theta) = (I_{PPP,solution}(\theta) - I_{PPP,water}(\theta))/I_{SSS,water}(\theta)$, where $I(\theta)$ stands for the average SH count rate at a scattering angle $\theta$ and the subscripts PPP and SSS stand for polarization combinations ($P$ = parallel and $S$ = perpendicular with respect to the horizontal scattering plane), denoted in this order: second harmonic, fundamental, fundamental. The integrated normalized fs-ESHS intensity is calculated as $S_{int} = \sum S(\theta)$ for all $\theta \neq 0^\circ$.

**Dynamic viscosity measurements**

Viscosities were measured using an Ubbelohde-type glass capillary viscometer (Paragon Scientific Ltd.) immersed in a temperature-controlled water bath (ET 15S, Lauda Scientific GmbH). The measurements were performed at 25.00° ± 0.01°C. The viscometer with the liquid was allowed to reach equilibrium with the bath for at least 4 min before a measurement. The elution times were measured with a time-stamped digital camera (720 pixels at 24 frames per second, Huawei Mi A1) that recorded the passing of the liquid’s meniscus between the two marked positions on the viscometer. Each sample was measured at least three times.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/12/eaay1443/DC1

Section S1. Hyper-Rayleigh scattering from polyelectrolytes

Section S2. Dependence of fs-ESHS from PAA on excess salt concentration

Section S3. fs-ESHS and reduced viscosity of PSS

Section S4. Calculation of the reduced specific viscosity of PEG

Section S5. Modeling the reduced specific viscosity of PAA

Fig. S1. Negligible contribution of polyelectrolytes to SH scattering.

Fig. S2. fs-ESHS response disappears with addition of salt.

Fig. S3. Polyelectrolytes induce strong orientational correlations leading to viscosity changes.

Fig. S4. Reduced specific viscosity calculation.
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