

Range and sensitivity of ^{17}O nuclear spin-lattice relaxation as a probe of aqueous electrolyte dynamics

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The study of electrolytic solutions is of relevance for many research fields, ranging from biophysics, materials and colloid science, to catalysis and electrochemistry. The dependence of solution dynamics on the nature of electrolytes and their concentrations has been the subject of many experimental and computational studies, yet it remains challenging to obtain a full understanding of the factors that govern solution behavior. Here we provide additional insights into the behavior of aqueous solutions of alkali chlorides by combining ^{17}O relaxation data with diffusion and viscosity data and contrasting their behavior with ^1H NMR relaxation data. The main findings are that ^{17}O relaxation correlates well with viscosity data, but not with diffusion data, while ^1H relaxation correlates with neither. Certain ionic trends match known ion-specific series behavior, especially at high concentrations. Notably, we also examine the ranges of the interactions and conclude that the majority of the effects are tied to local water reorientation dynamics.

I. INTRODUCTION

NMR spectroscopy has a long history of providing information on dynamical processes in solutions.¹⁻⁴ NMR relaxation rates sense fluctuations induced by motion at specific frequencies. Relaxation of quadrupolar nuclei is often primarily the result of fluctuations of the electric field gradient (EFG) at the site of the spin under investigation. In this work, we focus on studies of ^{17}O relaxation in aqueous solutions of different alkali chlorides over a large concentration range.

^{17}O exhibits particularly fast relaxation due to a relatively large nuclear quadrupole moment, and a large spin value ($I = 5/2$).⁵⁻⁷ The spin-lattice relaxation rate is given by

$$\frac{1}{T_1} = \frac{3}{40} \left(\frac{e^2 q Q}{\hbar} \right)^2 \frac{2I+3}{I^2(2I-1)} \tau_c \quad (1)$$

in the fast motion regime, which applies for all the cases examined here ($\omega_0 \tau_c \ll 1$).³ In this expression, e is the unit charge, Q the nuclear quadrupole moment and eq the electric field gradient felt at the site of the nuclear spin. The two main properties that are being sensed by ^{17}O relaxation are therefore the average asymmetry of the charge distribution and the time scale at which it fluctuates. Due to the strong quadrupolar interaction, other relaxation mechanisms, such as dipolar couplings contribute very little to the relaxation rates.⁸⁻¹¹

We show here experimental data on ^{17}O relaxation from aqueous solutions of alkali chlorides over a relaxation range from 0.1 - 4 mol/kg to capture both the low and the high concentration regions. One type of interpretation of the results is based on the comparison with the Hofmeister series¹² and the lyotropic series¹³ and the related classification into structure-forming and structure-breaking salts. The Hofmeister series describes the influence of different ions (≥ 0.1 molar concentrations) on protein solubility, while the lyotropic series was based on the effect of ions on the properties of the solvents,

which can be quantitatively expressed by the lyotropic activity of ions, influencing phenomena such as salting out,¹⁴ gelation and solvation of lyophilic colloids, viscosity of salt solutions, etc.^{13,15} To date, the microscopic mechanisms underlying the series behavior are, however, not well understood. We further examine the correlation of the relaxation behavior with solution viscosity and water diffusion data. We find that ^{17}O relaxation correlates well with viscosity data even in the ‘anomalous’ low-concentration regions for ions such as KCl, RbCl, and CsCl (where both the relaxation rates and viscosity initially decrease with concentration increase). One surprising finding, however, is that ^{17}O relaxation does not correlate well with diffusion data in this region. Furthermore, we also examine the nature of these correlations for ^1H relaxation, and in this case, the relaxation data correlate with neither viscosity nor diffusion. These findings could help elucidate the nature of the connections between microscopic and macroscopic properties in ionic solutions.

II. METHODS

A. Solution Preparation

Five different electrolyte samples were prepared by weighing the salt and diluting with the proper water amount composed of 90% H_2O and 10% D_2O . The addition of 10% D_2O is to obtain a frequency lock in the NMR measurements. The samples were transferred to 5mm NMR glass tubes for measurements. The ion concentration of the electrolyte solution ranged from 0.1 to 4 mol/kg. The use of molality as a concentration unit is generally convenient in cases where density changes are observed as a function of concentration or other experimental parameters.

B. NMR relaxation measurement

All NMR experiments were performed using a Bruker 9.4 T NMR spectrometer (400 MHz ^1H frequency). ^{17}O NMR spectra were acquired using the following acquisition parameters: 512 averages, 6 kHz spectral width, 43 ms acquisition time, and 40 ms relaxation delay. The ^{17}O T_1 relaxation time constants were measured using an inversion-recovery sequence and represented in the following figures as rate constants ($R_1 = 1/T_1$). All measurements were performed at 298.15 K (25 °C). The temperature setting was calibrated using a sample of ethylene glycol, with ± 0.5 °C uncertainty of the NMR chemical shift thermometer.¹⁶ Temperature changes can be ruled out as a source of errors of relaxation measurements within this range.

C. Molecular dynamics simulations

Molecular dynamics simulations were performed using the OpenMM package v. 7.1 on NYU's high-performance computing platform as described previously.¹⁷ For convenience the main simulation parameters are listed here with relevant modifications: The system was created with the molality of the relevant electrolyte solutions using the SPCE water model in a $40 \times 40 \times 40 \text{ nm}^3$ box with periodic boundary conditions. Ion nonbonding parameters were modeled using the screened charges modification by Laage and Stirnemann¹⁸, which have shown to provide a good representation of polarization effects. Calculations were performed with a nonbonded cutoff of 1 nm, a particle mesh Ewald (PME) method, a time step of 2 fs, a temperature of 298.15 K (to match experiments), a pressure of 1 atm (Monte Carlo barostat with an interval of 25 steps), 100,000 equilibration steps, 200,000 production steps (400 ps), and a Langevin integrator were used. Following energy minimization and NPT equilibration, production runs were performed. The electric field gradients (EFGs) were calculated at the site of the oxygen atom and averages were performed over its correlation functions using the Python MDAnalysis package, as described previously.¹⁷ From these quantities, the correlation functions for the ^{17}O quadrupolar interaction were calculated.

III. RESULTS AND DISCUSSION

The ^{17}O spin-lattice relaxation rate constants in the different solutions are shown in Figure 1. Aqueous solutions of LiCl, NaCl, KCl, RbCl, and CsCl were investigated here. The anions of the electrolytes were fixed to chlorides so that the effect from the cations on ^{17}O relaxation could be analyzed in isolation. Data points were fitted with polynomial model curves as a guide to the eye and for later correlation with other quantities, such as proton relaxation and diffusion. The T_1 data shown here agree well with previous line width measurements by Fister and Hertz,¹⁹ indicating the observation of the fast motion regime over the whole concentration range. That regime was also observed previously, for example, for LiCl

solutions for concentrations up to 20 mol/kg¹⁷ and for NaCl solutions for up to 5 mol/kg.²⁰ When extrapolating the fitted curves to zero concentration, a standard deviation of 0.8% of the mean value (136.7 s^{-1}) is found, indicating acceptable accuracy (The measurement of a pure 90% H_2O / 10% D_2O solvent sample gave 137.0 s^{-1}).

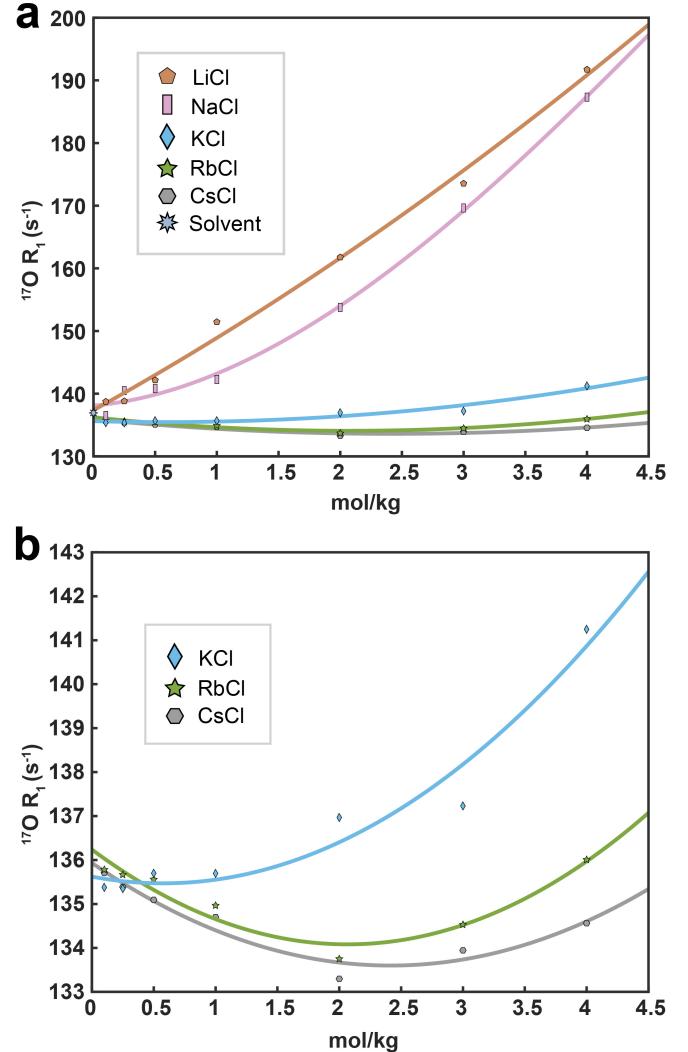


FIG. 1: Experimental results of the relaxation rate constant $^{17}\text{O} R_1$ in the respective aqueous electrolyte solutions vs. molality (mol/kg). The lines represent polynomial fits through the data sets. (a) Full-range figure including both structure-forming and structure-breaking salts. The point corresponding to the pure solvent indicates the measured $^{17}\text{O} R_1$ at infinite dilution. (b) A zoomed-in version is shown for structure-breaking salts only to highlight the anomalous region.

Figure 1 shows that for structure-forming salts (LiCl, NaCl) the relaxation rate strongly increases with increasing concentration. The structure-breaking salts (KCl, RbCl, and CsCl), by contrast, show the intriguing effect that the relaxation rate constants initially decrease before they increase again at

TABLE I: Comparison of the ion specificity with chloride as anion.

R_1^a	Reverse Hofmeister series ^b	Reverse lyotropic series ^c
Li^+	Li^+	Li^+
Na^+	Cs^+	Na^+
K^+	Rb^+	K^+
Rb^+	Na^+	Rb^+
Cs^+	K^+	Cs^+

^a Ions are ordered according to decreasing R_1 values from top to bottom.

^b The reverse Hofmeister series is listed from top to bottom (increasing effectiveness of precipitating proteins out of solution).

^c The lyotropic series is listed from top to bottom (decreasing lyotropic number).

higher concentration. The order of the relaxation rates from highest to lowest is $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$ overall when they are compared at the same concentrations in the range from 2 to 4 mol/kg. The structure-breaking effect of KCl is not as apparent as for RbCl and CsCl , but there is a clear distinction between this group and the NaCl and LiCl solutions.

The trend of ^{17}O relaxation rates in water for different electrolytes is similar to certain ion specificity series, for example those examined by Mazzini and Craig.²¹ Table I summarizes the observed order and compares it to the reverse Hofmeister series and the reverse lyotropic series. The order of the reverse lyotropic cation series is exactly the same as the trend of the ^{17}O relaxation rate constant in water. The order of the reverse Hofmeister cation series differs mainly in the relative position of the Caesium and Rubidium cations.

The relative ordering of the relaxation rates at high concentrations also matches the order of ion size. Larger ions have a lower charge density, which leads to a larger disruption of water structure, which has been linked to higher mobility, shorter correlation times τ_c , and consequently slower relaxation rates.²² Similar charge density arguments as above were made to explain the ion-specific effect for other water dynamic properties as well.^{23,24}

We note that it has been previously reported that a similar distinction of trends is observed for both viscosity²⁵ and diffusion.²⁶ The dynamic motion properties of ^{17}O in various aqueous electrolytes^{27–29} and the estimated ionic Jones-Dole B -coefficients³⁰ have been studied by NMR experiments. Much has been debated about the underlying reasons,^{31–38} but it appears that a clear general model still is elusive. The interplay between jump motion and frame reorientation has been investigated as a suitable criterion for demarcating the different regimes.^{18,39} Ion size clearly also plays a role as the charge-to-size ratio modulates the structure-forming/breaking propensities.⁴⁰

It is intuitive to suggest that at high concentrations, viscosity would increase due to crowding, and that one should find larger relaxation rates. The same consideration would apply for diffusion. Indeed, when considered separately, both diffusion and viscosity display the same qualitative trends.^{41,42} For structure-breaking salts this trend is also observed above

TABLE II: Slopes of linear fits to the curves in Fig. 3

Electrolytes	Slope (s)	R^2
LiCl	0.013	0.99
NaCl	0.010	0.99
KCl	0.009	0.93
RbCl	0.012	0.90
CsCl	0.022	0.91

concentrations of approximately 3 molal as seen in Fig. 1.

The rotational correlation time relevant for quantifying ^{17}O relaxation from Eq. (1) can be related by the Stokes-Einstein-Debye (SED) relation introduced by Bloembergen, Purcell, and Pound,⁴³ which can be expressed by $\tau_c = \frac{4\pi\eta a^3}{3k_B T}$ when assuming that molecules can be considered spheres with radius a . η is the dynamic viscosity of the solution. Similarly, viscosity can be related to the diffusion coefficient via the Stokes-Einstein equation. These expressions, however, are applicable only in the low concentration regime, are not derived for molecular-sized particles, and have been shown to require strong corrections for charged particles.⁴⁴ Nonetheless, these relationships often form the starting point of analyses, and also provide the context within which one can expect to find a relationship between viscosity and rotational and translational motion.

For these reasons, we decided that it would be suitable to examine the correlation between $1/D$ and the ^{17}O relaxation rate constant (which itself is proportional to the rotational correlation time) (Fig. 2). While the behavior is relatively linear in the high concentration range for the structure-making salts, this is not so in the low-concentration region, as seen in the zoomed-in version shown in Fig. 2b.

Next, we examine these same correlations with viscosity, and there we find a good linear correlation for all salts shown at Fig. 3. Although generally near-linear behavior is observed, the slopes vary for the different salts, and so viscosity is not a sole predictor for $^{17}\text{O} R_1$. The slopes and R^2 values of the η - $^{17}\text{O} R_1$ curves are shown in Table II.

It is further interesting to investigate how ^1H relaxation behaves in relationship to diffusion and viscosity. It is found that neither diffusion, nor viscosity correlates well with ^1H spin-lattice relaxation rates for the structure-breaking salts. It is of note that ^1H relaxation has a significant contribution from intermolecular dipolar couplings which extend out to longer length scales. It is therefore suggested that this length scale would be the distinguishing factor for the difference in the effects on ^1H vs. $^{17}\text{O} R_1$ data.

In order to substantiate this suggestion, we investigated the range of the factors affecting ^{17}O relaxation. As a first step, we investigated the change in the electric field gradient (EFG) as a function of cutoff distance in a water system with NaCl . All molecules with at least one atom within the cutoff distance from the oxygen atom under investigation were included in the calculation. Following that, the EFG was calculated using a point-charge model and the correlation functions were calculated over the trajectory, as described previously,^{17,20} by

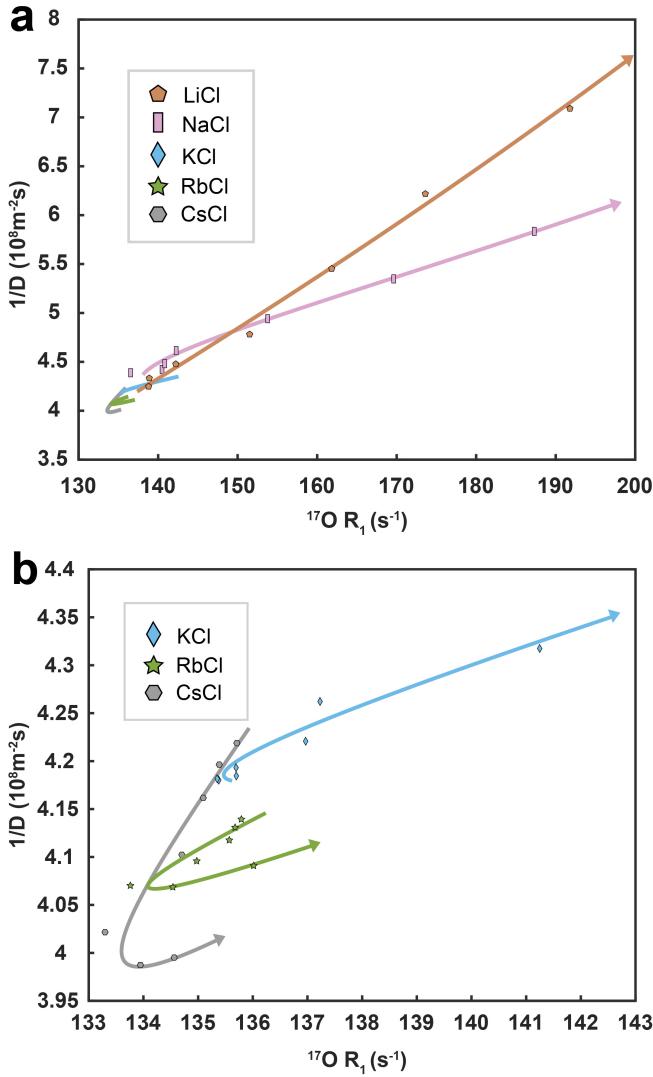


FIG. 2: Reciprocal self-diffusion coefficient of H_2O vs. $^{17}\text{O} R_1$. Self-diffusion data are obtained from Müller and Hertz.²⁶ The lines are obtained from polynomial fits through the data sets of self-diffusion coefficient and $^{17}\text{O} R_1$ both as functions of concentration. The experimental data points are plotted along with each set, and the arrows at the end of the curves indicate the direction of concentration increase. (a) Complete figure including data for both structure-forming and structure-breaking salts. (b) A zoomed-in version is shown for structure-breaking salts to highlight the anomalous region.

averaging over 1,000 oxygen atoms. The initial point in the EFG correlation function vs. cutoff distance is shown in Fig. 5a. It is clearly seen that the average EFG converges after a cutoff distance of approximately 3.5 Å. Within this initial convergence range the EFG value decreases by approximately 14 %, and therefore the majority of the quadrupolar relaxation effect is already determined by intramolecular effects within a single water molecule, with a minor additional contribution coming from the first coordination shell. Overall the change

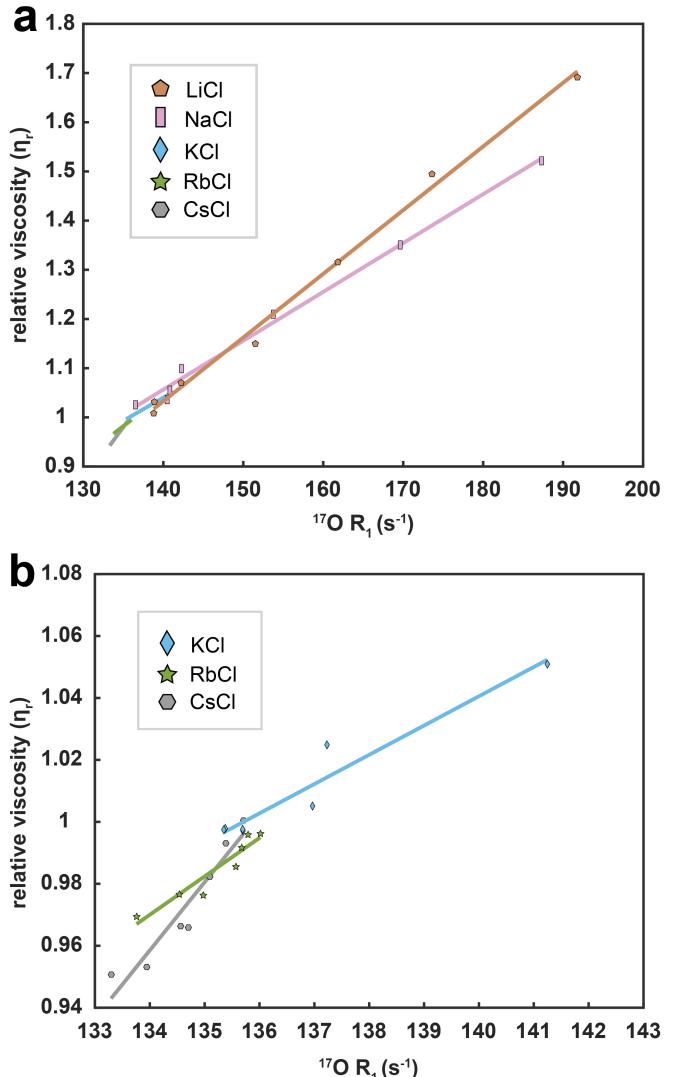


FIG. 3: Viscosity of alkali chloride solutions vs. $^{17}\text{O} R_1$ relaxation rate. Relative viscosity data adapted from Ostroff, Snowden, and Woessner.²⁵ The lines are obtained from linear fits through the data sets. The points on each figure correspond to the experimental $^{17}\text{O} R_1$ values. (a) Complete figure including both structure-forming and structure-breaking salts. (b) A zoomed-in version is shown for structure-breaking salts.

of the EFG contribution is very small as a function of concentration, and the major relaxation effect therefore must arise from the correlation time.

It is further of interest to examine the range effect of dynamic contributions to quadrupolar relaxation. For this purpose, the convergence of the correlation time was examined as a function of cutoff distance Fig. 5b. The correlation times were calculated from the correlation functions by integration as described previously.^{17,20} It is likewise observed that the correlation time, describing the time-scale of the dynamic effects, has an overall distance range similar to EFG alone (ap-

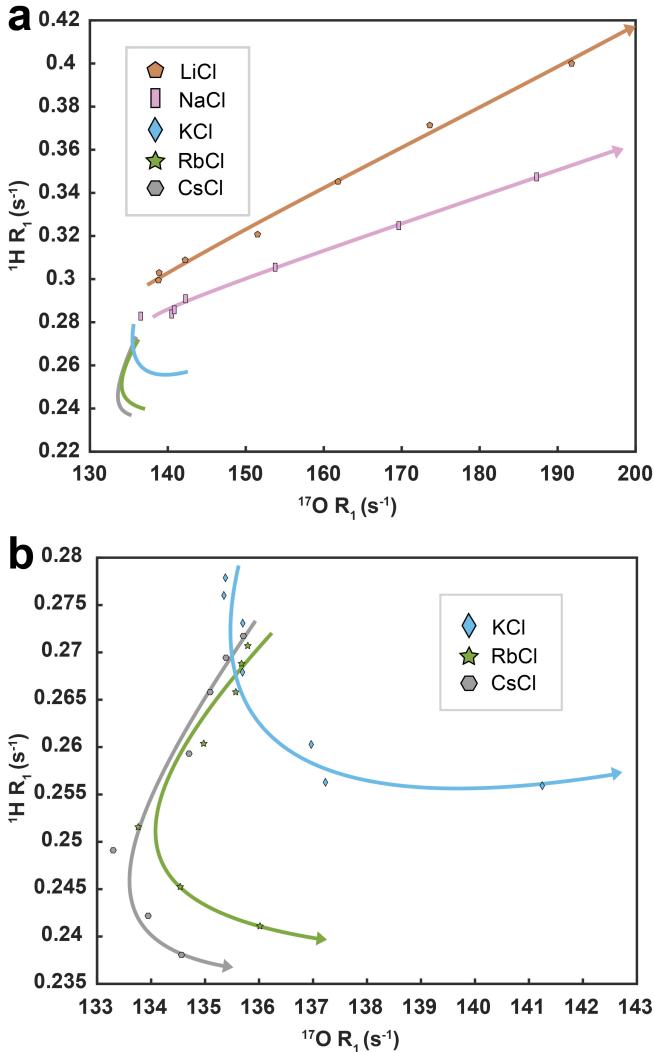


FIG. 4: ${}^1\text{H} R_1$ vs. ${}^{17}\text{O} R_1$. The ${}^1\text{H} R_1$ data are taken from Müller and Hertz.²⁶ Polynomial fits are used to obtain continuous curves for this representation. (a) Complete figure including data for both structure-forming and structure-breaking salts. (b) A zoomed-in version is shown for structure-breaking salts to highlight the anomalous region.

proximately 3.5 Å). This distance also represents the distance that includes all molecules of the first solvation shell. There is again only an approximately 10% overall decrease from calculations using a single water molecule. As a result, one may conclude that ${}^{17}\text{O} R_1$ relaxation is affected to at least $\sim 85\%$ by the rotational dynamics of a single water molecule, and to $\sim 15\%$ by contributions from the first solvation shell only. This result strongly supports the notion that ${}^{17}\text{O}$ spin-lattice relaxation probes very localized dynamics. It is all the more surprising that a very good correlation with viscosity is found, which is a much longer-range effect. The presence of ions in aqueous solution, therefore has a long-range effect on the dynamics of single water molecules.

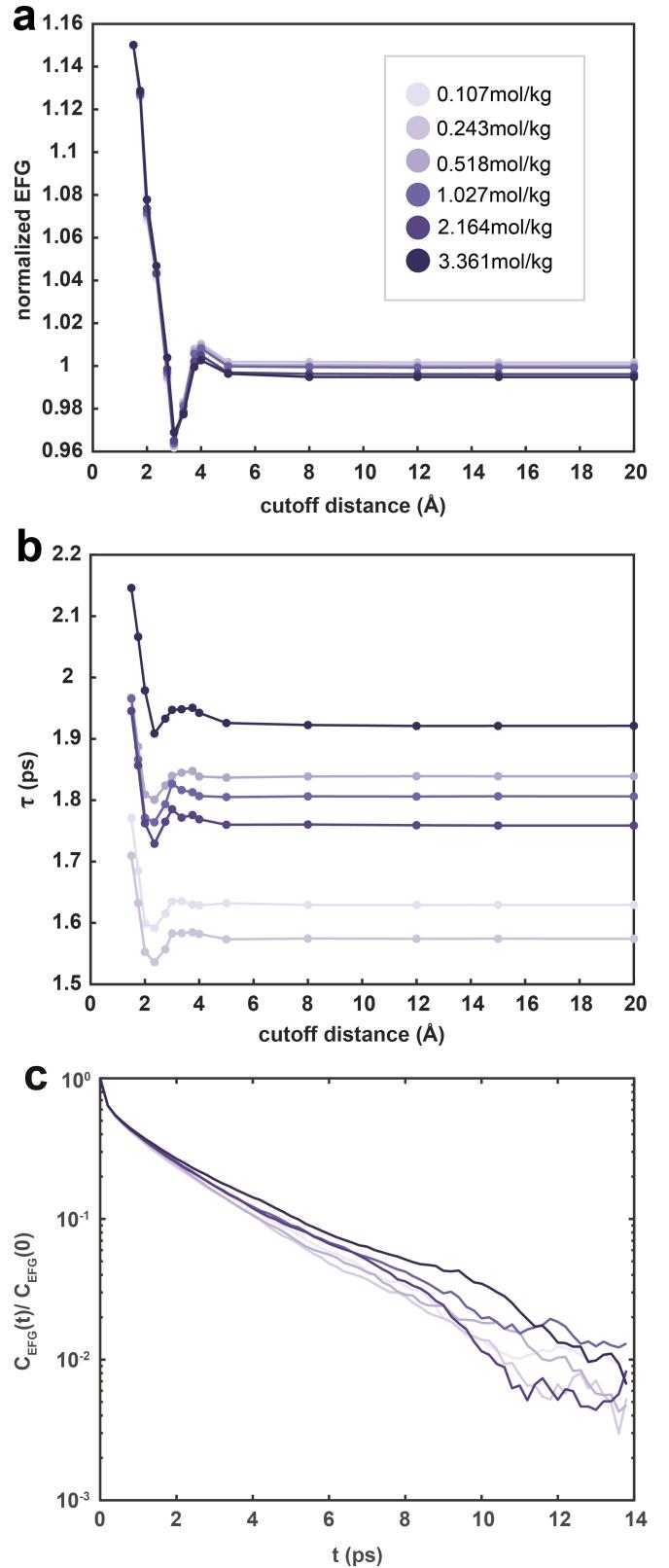


FIG. 5: Calculations of quadrupolar correlation times for NaCl solutions. (a) Initial point of the EFG correlation function vs. cutoff distance, normalized to the converged value at the lowest concentration. (b) Correlation times vs. cutoff distance. (c) Correlation functions, normalized to the first point. The color gradients indicate the concentration and correspond to the legend in (a).

IV. CONCLUSION

In this work, we examined ^{17}O relaxation in different aqueous electrolyte solutions. While for some salts, the relaxation rate increases with concentration (structure-forming salts), it initially decreases for others (structure-breaking salts). For all salts the rate increases at very high concentrations (generally above 2 mol/kg). The ^{17}O relaxation rate of the water was found to correlate well with solution viscosity, even in the anomalous low-concentration region. It is interesting that the correlation with inverse diffusion is not good. Further, we find that ^1H relaxation does not correlate well with either viscosity or diffusion in the low-concentration region. We also find that the range of the interactions involved can in part explain the difference in behavior. For ^{17}O relaxation the majority of the effect is found to be due to single water reorientation rates with only about 15% of the effect arising from the first coordination shell. We therefore conclude that ^{17}O relaxation rates are good reporters of how water reorientation itself is affected by the longer-range communication of structural changes in the solution.

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CONFLICT OF INTEREST STATEMENT

The authors have no conflicts to disclose.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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