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Self-Diffusion and Viscosity in Electrolyte Solutions

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ABSTRACT: The effect of salt on the dynamics of water molecules follows the Hofmeister series. For some "structure-making" salts, the self-diffusion coefficient of the water molecules, *D*, decreases with increasing salt concentration. For other "structure-breaking" salts, *D* increases with increasing salt concentration. In this work, the concentration and temperature dependence of the self-diffusion of water in electrolyte solutions is studied using molecular dynamics simulations and pulsed-field-gradient NMR experiments; temperature-dependent viscosities are also independently measured. Simulations of rigid, nonpolarizable models at room temperature show that *none* of the many models tested can reproduce the experimentally observed trend for the concentration dependence of *D*; that is, the models predict that *D* decreases with increasing salt concentration for both structure-breaking and structure-making salts. Predictions



of polarizable models are not in agreement with experiment either. These results suggest that many popular water models do not accurately describe the dynamic nature of the hydrogen bond network of water at room temperature. The simulations are in qualitative agreement, however, with experimental results for the temperature dependence of water dynamics; simulations and experiment show an Arrhenius dependence of D with temperature, T, with added salt, that is, $\ln D \sim 1/T$, over a range of temperatures above the freezing point of water.

1. INTRODUCTION

The structure and dynamics of water in aqueous solutions are of fundamental interest and are important in many applications. Ions have specific effects on protein solubility and surface tension of the air—water interface, leading to their classification using the Hofmeister series. The concepts of structure-breaking and structure-making have also been used in order to obtain a qualitative understanding of ion effects on water dynamics, for instance, ionic specificity in the Jones—Dole viscosity *B* coefficient, and translational, rotational, and reorientational correlation times of water molecules.^{1–5} In this paper, we focus on the effect of ions on the self-diffusion coefficient of water molecules in aqueous electrolyte solutions.

Specific ion effects on water dynamics are also manifested in the change of water diffusion in aqueous salt solutions (see Figure 1). In aqueous solutions of a structure-making salt, such as NaCl, the self-diffusion constant of the water molecules decreases with increasing salt concentration. In contrast, in solutions of a structure-breaking salt, such as CsI, the selfdiffusion constant of the water molecules *increases* with increasing salt concentration. At a qualitative level, this makes sense because a structure-breaking salt should disrupt hydrogen bonding and thus make the water molecules more mobile, with the opposite being true of structure-making salts.

A molecular-level understanding of this phenomenon has been elusive. Simulations of atomistic models of aqueous NaCl solutions suggest that salts can be structure-breaking at low temperatures and structure-making at higher temperatures,⁷ although these results have not been experimentally tested. In this paper, we study the effect of salt concentration and



Figure 1. Experimental data, adapted from Müller and Hertz,⁶ for the ratio of the self-diffusion coefficient, *D*, of water in aqueous salt solution to that in pure water (D_0) at T = 298 K, as a function of salt concentration. For structure-breaking salts, D/D_0 increases with increasing concentration, and for structure-making salts, D/D_0 decreases with increasing concentration.

temperature on the dynamics of water molecules using computer simulation and experiment.

The presence of ions can have two compensatory effects on the dynamics of water molecules. The ions can disrupt the hydrogen-bonding network but also interact strongly with the water molecules. The balance between these two effects can

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cause either an increase or a decrease in the water self-diffusion. If the balance is subtle, the net effect can be temperaturedependent. The properties of water and aqueous electrolyte solutions have been extensively studied using computer simulations. Most water models employ point charges in the O and H atoms, representing the chemical geometry. Although some models incorporate flexibility and polarizability, hydrogen bonding enters purely through Coulombic electrostatic interactions. Although the experimental results for the water self-diffusion were reported more than 15 years ago, we are not aware of any simulations that investigated the effect of different salts on the dynamics of water molecules. For this important physical observable, none of these models have been tested by comparison to experiment, which is one of the goals of this work.

In this work, we study the effect of salt on the self-diffusion of water using molecular dynamics simulations of atomistic models. We study aqueous solutions of nine salts, namely, NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr, and CsI, with five models of water (SPC/E, TIP3P, TIP4P, TIP4P/2005, and TIP5P) and four force fields for the ions. In all cases, the simulation results predict that the increasing salt concentration results in a monotonic decrease in the water self-diffusion coefficient, in qualitative disagreement with the experimental results (where the trend depends on the nature of the salt). We also investigate two polarizable models of water, AMOEBA and SWM4-DP, which show only a slight improvement over the rigid models above.

Our earlier work⁷ has suggested that the structure-breaking effect is more significant at lower temperatures. We carry out experiments for the self-diffusion constant of water in NaCl, $CaCl_2$, and CsI at various temperatures and show that the temperature dependence is the same for water and the three electrolyte solutions. Experimentally, the temperature dependence of the self-diffusion coefficients correlates very well with the temperature dependence of the measured solution viscosities; the hydrodynamic radius calculated from the two quantities appears relatively constant with temperature. For the temperature dependence, the simulations are in good agreement with the experimental results.

The rest of this paper is organized as follows: The simulation details and experimental method are described in section 2, results are presented and discussed in section 3, and some conclusions are presented in section 4.

2. METHODS AND MODELS

2.1. Simulation Details. Simulations are performed for seven combinations of nonpolarizable water and ion models that are listed in Table 1. For water, we use the SPC/E,⁸ TIP3P, TIP4P,⁹ TIP4P/2005,¹⁰ and TIP5P¹¹ models. Force fields for

 Table 1. Combinations of Nonpolarizable Models of Water

 and Ions Employed in This Study

set	water model	ref	ion model	ref
1	SPC/E	8	HMN	12
2	SPC/E	8	D	13-16
3	SPC/E	8	JC	17
4	TIP3P	9	JC	17
5	TIP4P	9	JJ	18
6	TIP4P/2005	10	HMN	12
7	TIP5P	11	HMN	12

ions consistent with these water models have been reported, and we refer to them as HMN,¹² D,¹³⁻¹⁶ JC,¹⁷ and JJ¹⁸ (the acronymns are initials of the developers). The simulations of these ion models are performed with the water models for which they were developed, that is, HMN and D in SPC/E, JC in SPC/E and TIP3P, and JJ in TIP4P. For TIP4P/2005 and TIP5P, however, no force field is available for the ions, and the HMN model is used.

Molecular dynamics (MD) simulations for these nonpolarizable models are carried out with the GROMACS v3.3.1 program.^{19,20} The equations of motion are integrated numerically using a leapfrog algorithm with a time step of 1 fs. The Berendsen coupling method²¹ is used to keep the temperature at the desired value and the pressure at 1 bar, with coupling constants of 0.1 and 0.5 ps, respectively, and the SETTLE algorithm²² is used to keep the water molecules rigid. A cutoff distance of 1 nm is used for Lennard-Jones interactions, and the particle-mesh Ewald method^{23,24} is used for the long-range electrostatic interactions.

We also investigate two polarizable models: SWM4-DP^{25,26} and AMOEBA,²⁷ simulations of which are performed using the CHARMM²⁸ and TINKER²⁹ packages, respectively. We closely follow the protocol of the original papers, and the reader is referred to the original work for details.^{25–27}

Initial configurations of pure water with N = 512 molecules are created in cubic simulation cells with a linear dimension of about 25 Å. Initial configurations are equilibrated for 500 ps at the desired temperature, followed by a production run of 5 ns simulations for all models except the AMOEBA model, for which an equilibration of 200 ps is followed by a production run of 1.5 ns. Configurations are saved every 100 ps. For aqueous salt solutions, randomly chosen water molecules are replaced by ions, with the number of ions depending on the concentration. Initial configurations for each temperature are obtained from 2 ns equilibration runs in the same way as for pure water. Simulations are performed for temperatures ranging from 275 to 325 K using the same protocol as for room temperature. To calculate the viscosity of the systems, four independent simulations are performed for each temperature with the periodic perturbation method,³⁰ in which an external force (acceleration = 0.025 nm/ps^2) is applied to cause a velocity field.

All properties are calculated from the final production run and averaged over all independent simulations. The selfdiffusion coefficient is obtained from the mean-square displacement (MSD) using the Einstein relation.³¹ We calculate the MSD averaged over all water molecules irrespective of their location relative to ions in order to compare simulation results with those from experiments shown in Figure 1. It is interesting to correlate the dynamics of molecules with their proximity to ions. For example, it is tempting to think in terms of two species of water (coordinated and not coordinated with ions). In NMR experiments, the existence of two species cannot be distinguished if they are exchanging rapidly on the NMR time scale, as is the case here. Analysis of position-dependent dynamics in simulations (which we have carried out previously⁷) suffers from a sensitivity to details; water molecules are rarely completely coordinated with an ion over the time-scale for reorientation. We do not present such analyses here because it is not possible to compare these to experiment. The viscosity is directly attained from the velocity profile as an output of Gromacs. The hydrodynamic radius is calculated from the previously obtained diffusion coefficient D



Figure 2. Effect of finite simulation box size on (a) the self-diffusion coefficient and (b) the ratio D/D_0 . The large box has 4096 molecules, whereas the small one has 512 molecules.

and viscosity η , using the Stokes–Einstein relation $D = k_{\rm B}T/(6\pi R_{\rm H}\eta)$, where *T* is the temperature and $k_{\rm B}$ is the Boltzmann's constant.

Finite size effects can be significant for the self-diffusion coefficient, but the concentration dependence is not affected. Figure 2a,b depicts the self-diffusion coefficient of the water molecules, D, and the ratio of this to the self-diffusion coefficient of pure water at the same temperature (D_0) for CsI and NaCl and for two different system sizes. These simulations are for the SPC/E water model and the HMN model for ions. There is a significant size dependence in D, with the larger system giving a higher value of D, as has been pointed out by Yeh and Hummer.³² The ratio D/D_0 , however, is essentially independent of the system size (Figure 2b).

2.2. Experiments. Salts (NaCl, from ACP Montreal, and CaCl₂ and CsI, from Sigma Aldrich) were used as received. Salt solutions were prepared in 15 mL of fresh deionized water, mixed by vortexing and hand shaking, and allowed to sit in a sealed container overnight before experiments. The same batch was used for both diffusion and viscosity measurements.

Pulsed-gradient NMR experiments were carried out on a Bruker Avance 600 spectrometer equipped with a diff30 pulsedgradient probe and were temperature-controlled to better than 0.1 °C. NMR samples were prepared in 5 mm NMR tubes that were flame-sealed upon filling. Pulsed-field-gradient NMR experiments at room temperature were carried out using a stimulated echo pulse sequence, while experiments at all temperatures (including room temperature) were carried out using bipolar gradients for convection compensation. Nearly square gradient pulses (trapezoidal, with rise time of 100 μ s, much smaller than the gradient duration of 2 ms and the diffusion time window Δ) were employed, with gradient amplitude g being varied to control a generalized gradient strength parameter $k = (\gamma \delta g)^2 (\Delta - \delta/3)$, and the diffusion coefficients were obtained from fits to monoexponential signal attenuations, as described elsewhere.³³ The pulsed-gradient stimulated echo results at room temperature were used as cross-calibration.

Viscosities as a function of temperature were measured using an Anton Paar MCR 301 rheometer using a concentric cylinder measuring system. Temperature control was better than 0.1 °C, and an enclosure with a rubber seal minimized temperature gradients. Shear stress σ was measured as a function of the strain rate $\dot{\gamma}$. The relationship in all experiments was linear with a very close to zero intercept, and the viscosity was obtained from the plateau value of $\eta = \sigma/\dot{\gamma}$.

3. RESULTS AND DISCUSSION

3.1. Concentration Dependence of Self-Diffusion Coefficient. The simulation results do not reproduce the trend seen in experiment (Figure 1), where structure-breaking salts result in an increase in the self-diffusion constant and structure-making salts do the opposite. Figure 3 depicts



Figure 3. Simulation results for the variation of D/D_0 with salt concentration for various salts at 298 K, with the SPC/E model for water and the HMN model for the ions. The simulations predict that the self-diffusion constant always decreases with increasing salt concentration, in contrast to the experimental results (see Figure 1).

simulation results for D/D_0 for several salts, using the SPC/E model for water and the HMN model for the salt ions. In all cases, D/D_0 decreases with increasing salt concentration, in contrast to the experimental results. The trends are similar: for example, increasing the size of the ions results in an increase in the self-diffusion coefficient, but the magnitude of the effect is not captured.

The qualitative trends are similar with other nonpolarizable models for water and the ions. Figure 4 compares predictions for D/D_0 with various models for water and ions to experimental data for NaCl and CsI. Although there is considerable variation in the quantitative predictions with the different models, the qualitative features are similar and all models predict structure-making behavior for all the salts.

The simulation results suggest that the rigid, nonpolarizable water models do not reproduce experimental data. We attribute the origin of the discrepancy to the water models rather than to ion models since a variety of parameter sets for ions give similar results.



Figure 4. Comparison of predictions of various nonpolarizable rigid water models for D/D_0 for (a) NaCl and (b) CsI at 298 K. Experimental data from Figure 1 are replotted for comparison.



Figure 5. Variation of D/D_0 with concentration in (a) NaCl and (b) CsI solutions at 298 K for two polarizable models. Experimental data from Figure 1 are replotted for comparison.

The incorporation of polarizability into the models does not make a significant improvement in the results. Figure 5 compares the predictions of two polarizable models (SWM4-DP and AMOEBA) for the variation of the diffusion coefficient with concentration for NaCl and CsI at 298 K. The predictions of the SWM4-DP model are very similar to those of the nonpolarizable models in Figures 3 and 4. The AMOEBA model predicts values of D/D_0 that are higher than the other models, and in fact, $D/D_0 > 1$ for CsI at intermediate concentrations. However, this model predicts very small differences for D/D_0 in NaCl and CsI. Therefore, we conclude that the previously proposed water models, whether nonpolarizable or polarizable, are flawed in the description of ionic effects on the dynamical behavior of water molecules.

This is in line with a recent simulation study,³⁴ where it was shown that empirical polarizable interaction potentials may overestimate surface adsorption for iodide in the air–water interface. In comparison with results from an extended dielectric continuum theory,³⁵ this study suggests that simulations using interaction potentials based on quantum mechanics are necessary in the study of ionic effects in the air– water interface.

3.2. Temperature Dependence of the Self-Diffusion Coefficient. Experiments show that the self-diffusion constant of water has an Arrhenius temperature dependence in the presence of added salt over the temperature range studied. Figure 6 depicts experimental results for the variation of the self-diffusion coefficient (*D*), the solution viscosity (η), and the hydrodynamic radius ($R_{\rm H}$) as a function of temperature, for pure water, 1.5 M NaCl, 6 M CaCl₂, and 1.5 M CsI. The hydrodynamic radius is defined using the Stokes–Einstein relation, $D = k_{\rm B}T/(6\pi R_{\rm H}\eta)$. For a given temperature, D and η depend strongly on the salt type and concentration with the viscosity increasing and the self-diffusion constant decreasing as salt is added. The trend is similar at all temperatures, however, and $R_{\rm H}$ is essentially independent of temperature.

The simulation models are in qualitative agreement with experiment for the temperature dependence of the self-diffusion constant and viscosity. Figure 7 depicts simulation results with the TIP5P/HMN model for pure water, and with added salt. We do not present results for the same concentrations as in experiment because simulations with high concentrations of salt require large systems and the calculation of the viscosity with small statistical uncertainties becomes difficult. The conclusions we draw, however, are insensitive to the concentration of added salt. Consistent with experiment, the variation of D with temperature is Arrhenius. R_H in the figure is almost constant, except at low temperatures of $1000/T \ge 3.5$. We plot $R_{\rm H}$ in order to remove the simple temperature dependence of the viscosity and self-diffusion constant on temperature and are not assuming that the Stokes-Einstein relation is valid. Nuclear magnetic resonance and quasi-elastic neutron scattering experiments have demonstrated, for pure water, that the Stokes-Einstein relation is valid at temperatures above 290 K but a fractional Stokes-Einstein relation fits experimental data better at lower temperatures.³⁶ The relative insensitivity of $R_{\rm H}$ that we observe at higher temperatures and the stronger deviations from Stokes-Einstein behavior we see at lower temperatures are consistent with the earlier observations.³⁶

Over the range of temperatures studied, the data for D for all salts has an Arrhenius dependence on T and the data for different salts can be collapsed onto one curve by merely scaling



Figure 6. Experimental results (this work) for the variation of (a) water self-diffusion coefficient, (b) viscosity, and (c) hydrodynamic radius, with temperature.

D by a constant. This is true in both the experiments and the simulations. Figure 8 depicts D as a function of 1/T for various cases. The collapse of these curves shows that the temperature dependence in pure water and added salt solutions is not very different, in both simulations and experiment.

4. CONCLUSIONS

We study the effect of salt on the self-diffusion of water using experiment and computer simulations, with a goal of providing a molecular origin of the structure-breaking and structuremaking effect of ions. We are unable to achieve this goal because all the simulated models of water are in qualitative disagreement with the experimental results for the concentration dependence of the self-diffusion constant of water; that is, in the simulation models, all the salts are structure-creating and result in a decrease in water diffusion as the concentration of salt is increased.

Clearly, the interaction parameters either for the water molecules or for the ions (or both) must be flawed in some manner. However, all the water models show similar behavior. On the other hand, there is not much room to tweak the ion parameters because the charge on the ions is fixed and the van der Waals parameters were adjusted to reproduce thermodynamic properties. We, therefore, conclude that the *form* of the interaction potentials (not the specific values of the potential parameters) have to be re-examined. By "form", we refer to the use of a simple point charge model to treat hydrogen bonding (in water) and the Lennard-Jones potential to treat the nonbonded van der Waals interaction. These two features are present in all the models we have investigated. Interestingly, the temperature dependence of the diffusion constant and viscosity is reproduced quite well by the simulation models. One can think of ions having two different effects on the dynamics of the water molecules. The hydration of the ions causes a decrease in the diffusion constant of the bound water molecules, and the disruption of the hydrogen bond network by the (structure-breaking) ions causes an increase in the diffusion constant of the water molecules.

The actual self-diffusion constant is a result of a balance between these two effects, and the simulation models do not get this right, with all models overemphasizing the binding of water to the ions. The hydrogen-bonding network in the models is sufficiently weak to start with that the presence of ions does not have a significant effect. (We come to this conclusion because, near the freezing point of water, the simulation models predict that NaCl is structure-breaking, which is the opposite of what happens at room temperature.⁷) The models do capture the *change* of the hydrogen-bonding network as the temperature is changed, over the range of temperatures studied. Therefore, the models are accurate for the temperature dependence, but not for the concentration dependence.

The development of valid molecular models for water and aqueous solutions is of critical importance and has been a major challenge in understanding many physicochemical processes on a molecular scale. Indeed, it is well recognized that non-polarizable interaction potentials do not agree with experimental data in the study of the air–water interface of aqueous salt solutions.³⁷ More recently, the limitation of empirical polarizable models has also been suggested in the same



Figure 7. Simulation results (with the TIP5P/HMN model) for the variation of (a) water self-diffusion coefficient, (b) viscosity, and (c) hydrodynamic radius, with temperature.



Figure 8. Scaled plot of the self-diffusion coefficient: (a) experiment and (b) simulations. For each salt, D is multiplied by a temperatureindependent constant (as shown).

system.³⁴ In addition, results in this work show that current models are not acceptable for a very simple dynamic property, namely, the self-diffusion constant of water. In developing a new molecular model, one usually starts with standard forms for the interaction potentials and the parameters are adjusted by fitting to experimental data for static properties. There is no guarantee that this will result in acceptable results for the dynamic properties. Therefore, one should be cautious when interpreting data from simulations of electrolyte solutions, especially in simulations of the systems with biomolecules in which ionic effects must be very important.

We argue that the form of the interaction potentials might need to be reconsidered. One possibility is that the directional nature of the hydrogen-bonding interaction might be incorporated explicitly, as is done in the Mercedes-Benz.³⁸⁻⁴⁰ Another possibility is the Lennard-Jones interaction be replaced by a softer repulsion to more accurately mimic the overlap between electron clouds on different atoms, as is done in the BMW water model.⁴¹ These considerations might lead to a class of water models that are accurate for both the thermodynamic and the dynamic properties of water.

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