Dynamical Behavior of Anion−Water and Water−Water Hydrogen Bonds in Aqueous Electrolyte Solutions: A Molecular Dynamics Study

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The dynamics of breaking and structural relaxation of Cl⁻−water, Br⁻−water and water−water hydrogen bonds in aqueous alkali halide solutions are investigated by means of molecular dynamics simulations. The hydrogen bonds are defined by using a set of configurational criteria with respect to the anion(oxygen)−oxygen and anion(oxygen)−hydrogen distances and the anion(oxygen)−oxygen−hydrogen angle for an anion-(water)−water pair. The results of the hydrogen bond dynamics are obtained for a smaller cutoff and also for a larger cutoff for the angular criterion. In both cases, the dynamics of anion−water hydrogen bonds are found to be slower than that of water−water hydrogen bonds. However, the extent of slowing down is not as great as observed in recent experiments. The relaxation of anion−water hydrogen bonds is found to slow with an increase of ion concentration which is in agreement with the trend observed in experiments. The diffusion coefficients and the orientational relaxation times of water molecules in the vicinity of halide ions and also in the bulk phase are calculated, and the relative changes of these quantities are compared with those of the hydrogen bond dynamics for anion−water and water−water pairs.

1. Introduction

The dynamics of hydrogen bonds in aqueous solutions of charged particles has been a topic of great interest over past several years. Earlier experiments[1−3] and some of the recent simulations[4−6] focused mainly on the effects of ions on the water−water hydrogen bonds, and now, the attention is being shifted to the dynamics of ion(or macroion)−water hydrogen bonds in these solutions.[7,8] On the experimental side, Kropman and Bakker[7] employed the femtosecond mid-infrared spectroscopy to investigate the dynamics of anion−water hydrogen bonds in aqueous solutions of alkali halides. These authors found a significant slowing down of the dynamics of anion−water hydrogen bonds as compared to that of water−water hydrogen bonds in the bulk. For example, the length of the hydrogen bond between a water molecule and a halide ion was found to change with a characteristic time constant of 12−25 ps which is 20−50 times longer than the characteristic time constant of the water−water hydrogen bonds in liquid water. On the theoretical side, all of the existing studies on halide ion−water hydrogen bonds have focused on their structural and energetic aspects,[9−11] and we are not aware of any direct investigation of the dynamical properties of anion−water hydrogen bonds in aqueous alkali halide solutions. Very recently, Raugei and Klein[12] carried out ab initio molecular dynamics simulations of a bromide ion dissolved in liquid water. These authors calculated the hydrogen bonded solvation structure around the bromide ion and also the residence time of water molecules in the inner solvation shell. The inner solvation shell of the bromide ion was found to be asymmetric on the time scale of the simulation, and the residence time of a water molecule in the inner solvation shell was found to be significantly longer than that given by a classical molecular dynamics (MD) simulation using a nonpolarizable model of water and the same system size as used for ab initio MD. The ab initio MD result of the residence time of water in the bromide ion solvation shell agreed with the

experimentally measured time constant of bromide ion−water hydrogen bond dynamics. Regarding the classical molecular dynamics studies of hydrogen bond dynamics near charged particles, we note the work of Xu et al.[5,6] and of Balasubramanian et al.[8] Xu and Berne[5] investigated the dynamics of hydrogen bonds in an aqueous solution of a negatively charged polypeptide and positive counterions. The relaxation of water−water hydrogen bonds was calculated at various distances from the polypeptide. It was found that the kinetics of breaking and forming of hydrogen bonds is slower in the first solvation shell of the polypeptide. The later work of Xu et al.[6] considered the relaxation of hydrogen bonds between a water molecule in the bulk and another one in the hydration shells of the sodium and chloride ions and compared the dynamics with that in bulk water excluding the solvation shells. However, in both studies, the dynamics of anion−water hydrogen bonds, which is the focus of the present work, was not investigated. Balasubramanian et al.[8] investigated the dynamics of hydrogen bonds at the surface of a charged micelle. In this work, the lifetime of a hydrogen bond between a negatively charged headgroup of the micelle and a water molecule was found to be much longer than that between two water molecules. This behavior is believed to be a general feature of charged surfaces of organized assemblies and is likely the reason for slow relaxation of water molecules at such interfaces that has been observed both experimentally and theoretically.[13−18]

In the present work, we have carried out MD simulations of aqueous alkali halide solutions at infinite dilution and also at a higher concentration to investigate the dynamics of hydrogen bonds between water and halide ions. We have also calculated the relaxation of water−water hydrogen bonds so that the dynamics of anion−water hydrogen bonds can be readily compared with that between two water molecules in the bulk. To the best of our knowledge, such an MD study of the dynamics of halide ion−water hydrogen bonds is presented here for the first time.

TABLE 1: Values of Lennard-Jones and Electrostatic Interaction Potential Parameters[a]

atom/ion	σ (Å)	ϵ (kJ/mol)	charge (e)
O	3.169	0.6502	−0.8476
H			+0.4238
Na⁺	2.583	0.4184	+1.0
Cl⁻	4.40	0.4184	−1.0
Br⁻	4.54	0.4184	−1.0

[a] e represents the magnitude of electronic charge.

We have organized the rest of the paper as follows. In section 2, we describe the models and the details of simulations. We define the water−water and anion−water hydrogen bonds in section 3 and the hydrogen bond correlation functions in section 4. In section 5, we present the results for aqueous solutions at infinite dilution. The results for a concentrated ionic solution are discussed in section 6. In section 7, we have compared our simulation results with those of recent experiments and other related studies. Our conclusions are briefly summarized in section 8.

2. Models and Simulation Details

In this work, we have carried out molecular dynamics simulations of aqueous solutions containing a single chloride or a single bromide ion and also of a concentrated solution of 3.35 M NaCl in water (M = molarity). The water molecules are characterized by the extended simple point charge (SPC/E) potential[19] and the ions are modeled as charged Lennard-Jones particles.[20,21] In these models, the interaction between atomic sites or ions are expressed as

$$u(r_i, r_j) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \qquad (1)$$

where q_i is the charge of the ith atom (or ion). The Lennard-Jones parameters σ_{ij} and ϵ_{ij} are obtained by using the combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$ where σ_i and ϵ_i are the Lennard-Jones diameter and well-depth parameter for the ith atom or ion. The values of the potential parameters q_i, σ_i, and ϵ_i for water and also for chloride, bromide, and sodium ions are summarized in Table 1.

The MD simulations were carried out in the microcanonical ensemble at an average temperature of 298 K. A cubic box with a total of 256 molecules (water plus ions), the experimental density of the aqueous solutions at infinite dilution and at 3.35M NaCl concentration,[22] and periodic boundary conditions with minimum image condition were employed. The long-range electrostatic interactions were treated using the Ewald method.[23,24] We employed the quaternion formulation of the equations of rotational motion, and for the integration over time, we adapted the leapfrog algorithm with a time step of 10^{-15} s (1 fs). MD runs of 400 ps were used to equilibrate each system and then each system was further run for another 400 ps for the calculation of hydrogen bond properties and other relevant quantities.

3. Definition of the Hydrogen Bonds

In the literature, the existence of a hydrogen bond between two water molecules is usually determined by using either a set of configurational criteria, an energetic criterion, or a combination of the both.[25−39] In the configurational or geometric definition, two water molecules are assumed to be hydrogen bonded if they satisfy some configurational criteria with respect to oxygen−oxygen and oxygen−hydrogen distances and the oxygen−oxygen−hydrogen angle. In the energetic criteria, one uses a cutoff on the pair interaction energy between two water molecules to decide if they are hydrogen bonded. Sometimes, the energetic criterion is combined with additional configurational criterion such as a cutoff on oxygen−oxygen distance. Of course, other kinds of definitions are also available in the literature, an example being the temporal definition of hydrogen bonds.[40−43] In the present study, we have employed the geometric definition of hydrogen bonds because the configurational criteria that are used to define a water−water hydrogen bond can be easily extended to define the anion−water hydrogen bonds.

In the configurational criteria considered here, a hydrogen bond between two water molecules or between a water molecule and an ion exists if the following distance and angular criteria are satisfied

$$R^{(\mathrm{XO})} < R_{\mathrm{c}}^{(\mathrm{XO})}$$

$$R^{(\mathrm{XH})} < R_{\mathrm{c}}^{(\mathrm{XH})}$$

$$\theta < \theta_{\mathrm{c}} \qquad (2)$$

where X denotes the oxygen atom of the first water molecule in the case of water−water hydrogen bonds and it denotes the Cl⁻ or Br⁻ ion in the case of anion−water hydrogen bonds. Thus, $R^{(\mathrm{XO})}$ and $R^{(\mathrm{XH})}$ denote the oxygen−oxygen (or anion−oxygen) and oxygen−hydrogen (or anion−hydrogen) distances, and the corresponding quantities with the subscript "c" denote the cutoff values. The angle θ ($=\theta^{(\mathrm{XOH})}$, X = O, Cl⁻, Br⁻) is the oxygen(anion)−oxygen−hydrogen angle and θ_{c} is the upper limit that is allowed for a hydrogen bond to exist. The hydrogen atom that appears in all of the above distances and angle is the one that participates in the hydrogen bond in the tagged water−water or anion−water pair.

In case of water−water hydrogen bonds, many of the earlier studies considered the following cutoff values for the oxygen−oxygen[4−6,8,29−33] and oxygen−hydrogen[4,8,32] distances: $R_{\mathrm{c}}^{(\mathrm{OO})}$ = 3.5 Å and $R_{\mathrm{c}}^{(\mathrm{OH})}$ = 2.45 Å, and we continue to use these values in the present study. We note that these critical distances of 3.5 and 2.45 Å are essentially the positions of the first minimum of the oxygen−oxygen and oxygen−hydrogen radial distribution functions. We have used similar criteria for the anion−water critical distances. That is, the cutoff values for anion−oxygen and anion−hydrogen distances are determined from the positions of the first minimum of the corresponding radial distribution functions. The values thus obtained are $R_{\mathrm{c}}^{(\mathrm{XO})}$ = 3.90 and 3.95 Å and $R_{\mathrm{c}}^{(\mathrm{XH})}$ = 3.05 and 3.15 Å for X = Cl⁻ and Br⁻, respectively. Now it remains to decide the cutoff angle θ_{c}. For water−water hydrogen bonds, many of the earlier studies have used a cutoff of 30° for this angle[4−6,8,28,30−33] although higher values have also been used to give more flexibility to the hydrogen bond.[29,32] To find the appropriate values for this critical angle for both water−water and anion−water hydrogen bonds, we have calculated the probability $P(\cos \theta)$ for water−water, water−chloride ion, and water−bromide ion pairs which satisfy the two distance criteria as mentioned before, and the results are shown in Figure 1. It is clear that the distribution of the hydrogen bond angle is rather narrow for both water−water and anion−water pairs. The maximum of the probability at $\cos \theta = 1$ shows the predominantly linear character of both water−water and anion−water hydrogen bonds in aqueous solutions. We note that, in ref 44, the hydrogen bond angle distribution was expressed in terms of $P(\theta)$ rather than $P(\cos \theta)$. However, more accurate information on the intrinsic
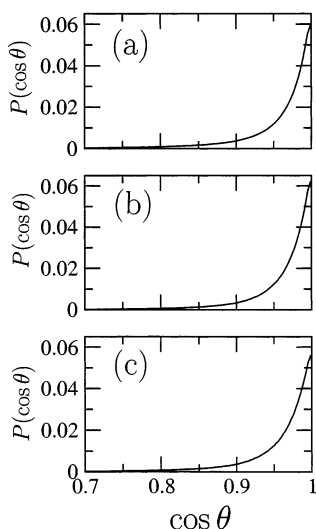
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Figure 1. Probablility distribution of the cosine of the hydrogen bond angle θ for water−water and anion−water pairs which satisfy the two distance criteria given by eq 2. The plots a, b, and c are for water−water, Cl⁻−water and Br⁻−water pairs, respectively.

linearity of hydrogen bonds can be obtained by calculating the probability function $P(\cos \theta)$ as was done earlier in ref 45 for pure water. This latter work[45] also reported the preferential presence of linear hydrogen bonds in liquid water similar to the ones found in the present work.

As mentioned before, for water−water hydrogen bonds, many of the earlier studies put the cutoff at $\theta_c = 30°$ to allow some fluctuations from the most favorable configuration. Because the overall behavior of the hydrogen bond angular distribution functions for water−water and anion−water pairs are rather similar, we have used the same cutoff of $\theta_c = 30°$ for both water−water and anion−water hydrogen bonds. However, because the primary goal of the present study is to investigate the relative time scales of the dynamics of water−water and anion−water hydrogen bonds, we have also used a higher cutoff of $\theta_c = 45°$ to give more flexibility to the existence of hydrogen bonds. We call the definition with $\theta_c = 30°$ as the "stricter" definition and the one with $\theta_c = 45°$ as the "less strict" definition of the hydrogen bonds.[46] We note that for $\theta = 30°$ angular fluctuations would contribute significantly to the breaking of hydrogen bonds. For the less strict definition, however, diffusion would play a more important role in the breaking of hydrogen bonds although orientational fluctuations would still contribute to the breaking process to some extent due to the presence of anion(oxygen)−hydrogen distance criterion. Clearly, the lifetime of a hydrogen bond for the less strict definition would be longer than that for the stricter definition. Because, the integrated probability has essentially reached its saturation value at $\theta = 45°$ for both water−water and anion−water pairs, any further increase of the cutoff angle θ_c would have practically no effect on the lifetimes or the dynamical behavior of the hydrogen bonds.

4. The Hydrogen Bond Time Correlation Functions

Following previous work,[4−6,8,27−33] we investigate the dynamics of hydrogen bonds by calculating the relaxation of two different hydrogen bond time correlation functions: A continuous hydrogen bond correlation function $S_{HB}(t)$ and an intermittent hydrogen bond correlation function $C_{HB}(t)$.

The construction of these time correlation functions is based on two hydrogen bond population variables $h(t)$ and $H(t)$: $h(t)$

is unity when a particular water−water or anion−water pair is hydrogen bonded at time t according to the adopted definition as discussed before and zero otherwise, whereas $H(t) = 1$ if the water−water or anion−water pair remains continuously hydrogen bonded from $t = 0$ to time t and zero otherwise. The continuous time correlation function $S_{HB}(t)$ is defined as

$$S_{HB}(t) = \langle h(0)H(t)\rangle/\langle h\rangle \tag{3}$$

where $\langle \cdots \rangle$ denotes an average over all water−water or anion−water pairs. Clearly, $S_{HB}(t)$ describes the probability that an initially hydrogen bonded water−water or anion−water pair remains bonded at all times up to t. The associated integrated relaxation time τ_{HB} can be interpreted as the average lifetime of a hydrogen bond between two water molecules or between an anion and a water molecule.[47]

The correlation function $S_{HB}(t)$ describes the dynamics of hydrogen bond breaking as it depends on the continuous presence of a hydrogen bond. The intermittent hydrogen bond correlation function $C_{HB}(t)$ does not depend on the continuous presence of a hydrogen bond and is defined as

$$C_{HB}(t) = \langle h(0)h(t)\rangle/\langle h\rangle \tag{4}$$

Clearly, the correlation function $C_{HB}(t)$ describes the probability that a water−water or anion−water hydrogen bond is intact at time t, given it was intact at time zero, independent of possible breaking in the interim time. $C_{HB}(t)$ relaxes to zero as the probability that a specific pair of molecules is hydrogen bonded in a macroscopic system at equilibrium is negligibly small. Because the function $C_{HB}(t)$ allows recrossing of the dividing surface that separates the bonded and nonbonded states, its relaxation describes the structural relaxation of hydrogen bonds. Earlier work on hydrogen bond dynamics in aqueous alkali halide solutions considered the above correlation functions only for water−water hydrogen bonds,[4] whereas in the present study, these quantities are calculated also for Cl⁻−water and Br⁻−water hydrogen bonds in aqueous solutions. Thus, a comparison of the relative time scales of relaxation of water−water and anion−water (anion = Cl⁻, Br⁻) hydrogen bonds could be made in the present study.

5. Results for Aqueous Solutions at Infinite Dilution

We first discuss the results for solutions containing either a single chloride or a single bromide ion. We have computed the above correlation functions for both stricter ($\theta_c = 30°$) and less strict ($\theta_c = 45°$) definitions of the hydrogen bonds and the results are shown in Figure 2. Overall, the decay of $S_{HB}(t)$ occurs at a slower rate for the less strict definition of hydrogen bonds as one would expect. For both the definitions, it is found that the decay of $S_{HB}(t)$ is somewhat slower for anion−water hydrogen bonds as compared to the water−water hydrogen bonds. Thus, the anion−water hydrogen bonds have a longer lifetime than the water−water hydrogen bonds. In Table 2, we have included the average lifetimes τ_{HB}, which are defined as the time integrals of $S_{HB}(t)$, for both water−water and anion−water hydrogen bonds and for both stricter and less strict definitions. We note that the value of 0.54 ps for τ_{HB} for water−water hydrogen bonds (stricter definition) agrees well with the characteristic hydrogen bond time constant of 0.50 ± 0.2 ps reported by Kropman and Bakker[7] in their femtosecond mid-infrared laser studies and with the relaxation time of 0.56−0.72 ps reported by Tominaga and co-workers[3] in their low-frequency Raman studies.

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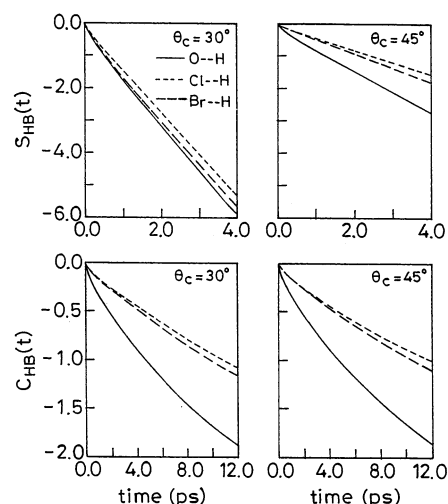
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Figure 2. Time dependence of the continuous correlation function ($S_{HB}(t)$) and the intermittent correlation function ($C_{HB}(t)$) of water–water, Cl⁻–water and Br⁻–water hydrogen bonds for stricter ($\theta_c = 30°$) and less strict ($\theta_c = 45°$) definitions. The results are for solutions containing a single chloride or a single bromide ion. The solid, short-dashed and long-dashed curves are for water–water, Cl⁻–water, and Br⁻–water hydrogen bonds, respectively. The values of the y-axis correspond to the logarithm of the correlation functions.

TABLE 2: Mean Lifetimes (τ_{HB}) and the Structural Relaxation Times (τ_R) of Anion–Water and Water–Water Hydrogen Bonds[a]

quantity	θ_c (deg)	Cl···H	Br···H	O···H
τ_{HB}	30	0.64	0.58	0.54
τ_{HB}	45	2.40	2.15	1.30
τ_R	30	11.4	10.2	6.6
τ_R	45	12.0	10.8	6.8

[a] The results are for aqueous solutions with a single chloride or a single bromide ion at 298 K. The values of τ_{HB} and τ_R are expressed in ps.

The lifetimes of the anion–water hydrogen bonds are found to be somewhat longer than that of water–water hydrogen bonds. The difference is found to be more significant for the less strict definition of the hydrogen bonds. For example, the lifetime of Cl⁻–water hydrogen bond is only 1.2 times that of water–water hydrogen bonds for the stricter definition, whereas it is 1.85 times the lifetime of water–water hydrogen bonds for the less strict definition. We note that for the stricter definition the hydrogen bonds break primarily by fast orientational or librational motion, whereas they also break by relatively slower diffusional motion for the less strict definition. The presence of the ionic field slows down both the translational and orientational motion of water molecules. However, the heavier mass of the chloride and bromide ions further slows down the relative diffusion of an anion–water pair as compared to that of a water–water pair, and as a result, we observe a significant difference in the lifetimes of anion–water and water–water hydrogen bonds for the less strict definition. We also note that, for both definitions, the lifetime of Br⁻–water hydrogen bond is found to be smaller than that of the Cl⁻–water hydrogen bond. This can be attributed to the larger size and hence weaker electric field of the bromide ion which leads to a faster relaxation of the water molecules in its vicinity as compared to the relaxation near a chloride ion. This issue is discussed in further details in the later part of this section.

The temporal behavior of $C_{HB}(t)$ is also shown in Figure 2 for both water–water and anion–water hydrogen bonds. The overall dynamics of hydrogen bond structural relaxation is found to be an order of magnitude slower than that of hydrogen bond breaking. Also, unlike the case of $S_{HB}(t)$, both stricter and less strict definitions lead to very similar dynamics for the relaxation of $C_{HB}(t)$ for both water–water and anion–water hydrogen bonds, especially at long times. The dynamics of $S_{HB}(t)$ depends significantly on the definition of the hydrogen bond because of the frequent crossing of the dividing surface. This frequent crossing of the dividing surface leads to a faster relaxation of $S_{HB}(t)$. However, when the cutoff is short, the same hydrogen bond is restored in most cases after the initial crossing of the dividing surface and the hydrogen bond was not broken in the chemical sense. Clearly, the relaxation of $S_{HB}(t)$ occurs at a slower rate when a large cutoff is used to define a hydrogen bond. The function $C_{HB}(t)$, on the other hand, describes structural relaxation of the hydrogen bonds by allowing reformation of a hydrogen bond after it was broken initially. For two different but physically reasonable definitions of the hydrogen bonds, the dividing surfaces in the configuration space which separate the bonded and nonbonded states are different but lie not too far from each other. Trajectories cross and recross such nearby surfaces rather frequently. A change of the dividing surface will thus alter the amount of recrossings and the decay of $C_{HB}(t)$ at very short times, but its long time dynamics will not change significantly as has been observed in the present study. We note that this issue of the invariance of $C_{HB}(t)$ with respect to physically reasonable hydrogen bond definitions was discussed earlier in the context of water–water hydrogen bonds.[31]

Even at long times, the relaxation of $C_{HB}(t)$ is highly nonexponential, and no long-time exponential time constant could be found for the decay of these quantities. This could be attributed to the coupling of hydrogen bond dynamics with diffusion which introduces a continuum of relaxation times.[31] However, for the purpose of comparative analysis, one can obtain an average time constant τ_R from the available simulation data.[4] In the present study, the average time constant τ_R is defined by $C_{HB}(n\tau_R) = e^{-n}$ where the value of n is determined from the lowest value of $C_{HB}(t)$ obtained in the simulations. We stress that this definition is made only to make a comparison of the relative time scales of structural relaxation of water–water and anion–water hydrogen bonds and it avoids the use of fitting of the tail by some function which is required when the average relaxation time is defined as the integral of $C_{HB}(t)$. The results of τ_R are also included in Table 2. For both definitions, it is found that the value of τ_R for Cl⁻–water and Br⁻–water hydrogen bonds are, respectively, about 1.75 and 1.6 times greater than that of water–water hydrogen bonds. Thus, the structural relaxation of anion–water hydrogen bonds is about 60–75% slower than the relaxation of water–water hydrogen bonds in the aqueous solutions considered in this study. We note in this context that Xu et al.[6] defined the relaxation time of $C_{HB}(t)$ as $C_{HB}(\tau_R) = e^{-1}$ and reported a value of 4.2 ps for the relaxation time of water–water hydrogen bonds in bulk water. The present study gives a value of 4.5 ps for the same quantity and for the same definition. The agreement is rather good considering the fact that the hydrogen bonds were defined in ref 6 in a slightly different manner than the one used in the present study.

The relatively slower structural relaxation of anion–water hydrogen bonds is likely to be correlated with the slowing down of long time diffusion and orientational relaxation of water molecules in the vicinity of anions as compared to those in bulk water. The long time diffusion coefficient, D, is obtained by integrating the normalized velocity–velocity autocorrelation function $\langle v(t)v(0)\rangle/\langle v(0)^2\rangle$ of a single water molecule and

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TABLE 3: Diffusion Coefficients and Orientational Relaxation Times of Water Molecules in the Vicinity of Chloride and Bromide Ions and in the Bulk at 298 K[a]

region	D	τ_1^μ	τ_1^{HH}	τ_1^{OH}
vicinity of Cl⁻	2.10	5.40	5.70	5.80
vicinity of Br⁻	2.20	5.05	5.40	5.45
bulk	2.65	3.95	3.90	3.90

[a] The results are for aqueous solutions with a single anion. The diffusion coefficient and the relaxation times are expressed in units of 10^{-5} cm^2 sec^{-1} and ps, respectively.

multiplying the integral by $k_B T/m$ where k_B is Boltzmann constant, T is the temperature, and m is the mass of a water molecule. For calculation of the diffusion coefficient of water molecules in the vicinity of a negative ion, the correlation function $\langle v(t)v(0) \rangle$ is averaged over only those water molecules which are found in the first solvation shell of the negative ion at time $t = 0$. The values of $\langle v(t)v(0) \rangle$ up to $t = 0.75$ ps were sufficient to obtain converged values of the time integral as the decay of the velocity correlation function occurs quite fast. We note that this time scale of 0.75 ps is significantly smaller than the average residence time of a water molecule around a chloride or a bromide ion which was found to be around 10 ps.[48,49] Clearly, the trajectory of a water molecule, which was in the first solvation shell of an anion, is likely to remain in the vicinity of the negative ion over the time scale of its velocity relaxation. For the calculation of the diffusion coefficient of bulk water molecules, the velocity correlation function was averaged over all water molecules excluding those in the solvation shells of ions. The orientational relaxation time τ_l^α is obtained as the time integral of the orientational correlation function: $C_l^\alpha(t) = \langle P_l[e^\alpha(t) \cdot e^\alpha(0)] \rangle / \langle P_l[e^\alpha(0) \cdot e^\alpha(0)] \rangle$, where P_l is the Legendre polynomial of rank l and e^α is the unit vector which points along the αth axis in the water molecular frame. We have calculated τ_l^α for $l = 1$ and 2 and for three different e^α, the molecular dipole vector μ, the H−H vector and the O−H vector. These orientational relaxation times were obtained by explicit integration of $C_l^\alpha(t)$ from simulations until 6 ps and by calculating the integral for the tail from the fitted exponential functions. As discussed before, the averages were carried out separately for bulk and solvation shell water molecules in order to obtain the orientational relaxation times of water molecules in the bulk phase and in the vicinity of an anion. In Table 3, we have shown the results of the diffusion coefficients and orientational relaxation times for $l = 1$. The values of τ_2^α show a similar trend and hence are not included in the table. Note that the values of the orientational relaxation times reported here for the bulk water differ slightly from the values reported earlier in refs 4 and 30. This slight difference is due to the fact that in the earlier work the decay of orientational correlation functions was explicitly calculated up to 3 ps, whereas in the present work, these quantities are explicitly calculated and hence used in the integration to find τ_l^α up to 6 ps. It is seen from Table 3 that both diffusion and orientational relaxation of water molecules slow down in the vicinity of the negative ions. The extent of slowing down is found to be in the similar ballpark as it was observed for the hydrogen bond dynamics. Also, the extent of slowing down is more in the vicinity of a chloride ion than that in the case of a bromide ion which can be attributed to the somewhat smaller size and a stronger solvation of the chloride ion. These results have direct consequences on the observed anion−water hydrogen bond dynamics where a greater slowing down of the relaxation was found for Cl⁻−water hydrogen bonds than the ones between a bromide ion and water.
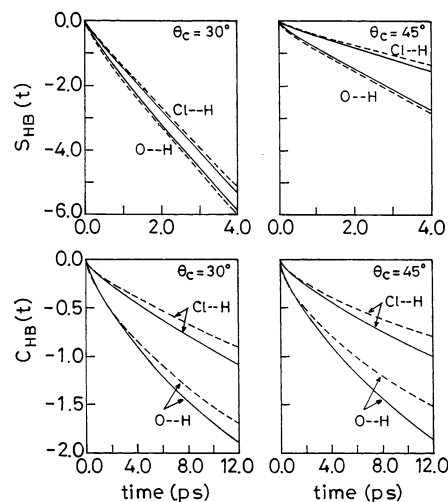

Figure 3. Time dependence of the continuous and intermittent correlation functions of water−water and Cl⁻−water hydrogen bonds for the stricter and less strict definitions. The solid curves are for aqueous solution containing a single chloride ion and the dashed curves correspond to the concentrated solution of 3.35 M NaCl in water. The values of the y-axis correspond to the logarithm of the correlation functions.

TABLE 4: Mean Lifetimes (τ_{HB}) and the Structural Relaxation Times (τ_R) of Anion−Water and Water−Water Hydrogen Bonds in a 3.35 M Aqueous NaCl Solution at 298 K[a]

quantity	θ_c (deg)	Cl···H	O···H
τ_{HB}	30	0.68	0.50
τ_{HB}	45	2.55	1.25
τ_R	30	13.0	6.95
τ_R	45	13.9	7.30

[a] The values of τ_{HB} and τ_R are expressed in ps.

6. Effects of Finite Ion Concentration

The above results were obtained for aqueous solutions with a single chloride or a single bromide ion. We have also investigated the hydrogen bond dynamics of a concentrated NaCl solution. The goal was to study the effects of ion concentration on the dynamics of water−water and anion−water hydrogen bonds. In Figure 3, we have shown the results for $S_{HB}(t)$ and $C_{HB}(t)$ for a 3.35 M aqueous NaCl solution. We have also included the results for infinite dilution for comparison. The corresponding hydrogen bond time constants are included in Table 4. For both stricter and less strict definitions, it is found that the decay of $S_{HB}(t)$ occurs at a slightly faster rate for water−water hydrogen bonds and at a slightly slower rate for anion−water hydrogen bonds for the concentrated NaCl solution. To understand this dynamical behavior, we calculated the potential of mean force (pmf) between two neighboring water molecules and also between a chloride ion and a water molecule in its solvation shell. The changes of water−water pmf with ion concentration and their effects on the breaking of water−water hydrogen bonds have already been discussed earlier,[4] so here, we briefly mention the main points. The well-depth of the water−water pmf decreases as the ion concentration is increased. The reduction of the well-depth means relatively weaker water−water hydrogen bonds in the concentrated ionic solutions compared to that in pure water or at infinite dilution. This effect may lead to an enhancement of the relative diffusion of the water pair (which, in turn, leads to a faster rate of hydrogen bond breaking) if it can overcome the effects of additional ionic friction which tends to inhibit diffusion. The second effect is that, in the ionic solution, the value of pmf is lower near the

TABLE 5: Diffusion Coefficients and Orientational Relaxation Times of Water Molecules in the Vicinity of Chloride Ions and in the Bulk in a 3.35 M Aqueous NaCl Solution at 298 K[a]

region	D	τ_1^μ	τ_1^{HH}	τ_1^{OH}
vicinity of Cl$^-$	1.30	7.45	7.05	7.15
bulk	1.70	5.70	5.30	5.35

[a] The diffusion coefficient and the relaxation times are expressed in units of 10^{-5} cm^2 sec^{-1} and ps, respectively.

dividing surface (i.e., $R_{OO} \sim 3.5$ Å), and therefore, the population of water pairs in the vicinity of this dividing surface is higher. The two water molecules of such a pair need to travel only a short relative distance between them to break the hydrogen bond and crossover to the nonbonded state, and this also leads to an enhancement of the rate of hydrogen bond breaking. A calculation of the time dependent relative diffusion of a water pair of initially hydrogen bonded molecules showed a slower diffusion for the concentrated solution at all times. Thus, although the reduction of pmf tends to increase the relative diffusion of two water molecules, the presence of ionic friction slows down the relative diffusion even at short times. The higher population of water pairs near the dividing surface between the bonded and nonbonded states appears to play a more important role in the slight enhancement of the rate of hydrogen bond breaking that is observed in aqueous ionic solution as compared to that in pure water. The well-depth of the anion−water pmf remains essentially unchanged with an increase of ion concentration to 3.35 M, and also, the value of pmf is only marginally lower for the concentrated solution near the critical distance which separates the bonded and nonbonded states. Thus, in this case, the effective strength of the hydrogen bond remains essentially unchanged and also the population of anion−water pairs near the dividing surface changes only marginally and thus plays a less significant role in affecting the lifetime of anion−water hydrogen bonds in the concentrated solution. Clearly, for anion−water hydrogen bonds, the slowing down of relative diffusion of the anion−water pair and the orientational relaxation of water molecules at finite ion concentration play more important role and leads to a slightly longer lifetime of these hydrogen bonds.

The relaxation of $C_{HB}(t)$ is found to occur at a slower rate in the concentrated solution for both water−water and anion−water hydrogen bonds. Because the function $C_{HB}(t)$ does not depend on the continuous presence of a hydrogen bond and it allows for the recrossing of the dividing surface from an intermittent nonbonded state to the bonded state, its dynamics is controlled mainly by the long time diffusion and orientational motion of water molecules. The values of these diffusion coefficients and the orientational relaxation times for the concentrated solution are included in Table 5. It is found that the presence of ions in the concentrated solution reduces the diffusion coefficients and increases the orientational relaxation times. This slowing down of the translational diffusion of ions and water molecules and the rotational diffusion of water molecules is believed to be responsible for the slowing down of the structural relaxation of water−water and anion−water hydrogen bonds in the concentrated ionic solution as compared to that at the infinite dilution limit.

We note, in the present context, the recent MD simulations of Xu et al.[5,6] where a slightly faster breaking of the water−water hydrogen bonds was found in the vicinity of Na$^+$ ions for the same nonpolarizable SPC/E model[19] and also for the TIP4P model[50] of water. The above slightly faster relaxation, however, became slower compared to that in the bulk when the polarizable TIP4P/FQ model[51] was employed. In the latter case, the large induced dipole in the water molecule near the Na$^+$ ion was found to strengthen the water−water hydrogen bond and, as a result, its lifetime became longer. Thus, the slightly shorter lifetime of water−water hydrogen bonds in the concentrated NaCl solution that has been observed in our work could be due to the use of a nonpolarizable water model.

7. Comparison with Recent Experiments and Other Related Work

The present simulations reveal that the dynamics of anion−water hydrogen bonds for chloride and bromide ions at room temperature can be, at the most, about two times slower than that of water−water hydrogen bonds. The recent experiments of Kropman and Bakker[7] have, however, shown an order of magnitude slower dynamics for anion−water hydrogen bonds for the same anions considered here. For example, it was found that in a 1 M NaCl solution the hydrogen bond distance of a Cl$^-$−water pair changes with a characteristic time constant of 12 ± 4 ps, whereas that of a water−water hydrogen bond changes with a time constant of 0.5 ± 0.2 ps. The hydrogen bond length of a Br$^-$−water pair was found to change with a time constant of 18 ± 5 ps in a 1 M NaBr solution. Because the diffusion or even the orientational motion of a water molecule in the solvation shell of an anion would alter the anion−water hydrogen bond distance, both orientational and translational motion of water molecules in the hydration shell of the anion was thought to be essentially frozen, and the picture of a rigid solvation structure was put forward. In a later experiment,[52] the orientational relaxation of water molecules in bulk and in the solvation shell of a chloride ion in a 3 M NaCl solution was investigated. For water molecules in the solvation shell, the orientational relaxation was found to occur with a time scale of 9.6 ± 0.6 ps. Because this time constant was faster than the time scale of Cl$^-$−water hydrogen bond dynamics (which is 14 ± 2 ps for the same salt concentration) and because any rotation of an individual water molecule in the solvation shell would change the anion−water hydrogen bond distance, the experimentally observed rotational relaxation time was believed to be not of the rotation of individual water molecules in the solvation shell, rather it was attributed to the rotation of the entire solvation shell with its rigid anion plus water structure. In other words, it was inferred that any rotational motion of individual water molecules in the solvation shell of a chloride ion could occur only with a time scale equal to or longer than 14 ± 2 ps for the above salt concentration. For bulk water, this orientational time constant was found to be 2.6 ± 0.2 ps which can be compared with the value of 1.9 ps found in the present study.[53] We note that the orientational relaxation time measured in this experimental study is the second rank time constant τ_2, and we also note that the experimental relaxation time is for HDO molecules in D$_2$O. Taking this small isotopic effect into account, it is clear that, for bulk water, the present simulation results for the time constants of orientational relaxation and hydrogen bond dynamics of bulk water agree reasonably well with the experimental findings of Bakker and co-workers. However, it's a different scenario for the orientational relaxation in solvation shell and for the dynamics of anion−water hydrogen bonds where the present results seem to differ significantly from those of refs 7 and 52.

The main drawback of the present study is the neglect of polarizability. The polarization effects give rise to many body interactions and make the water−water or ion−water interactions dependent on the surrounding environment. This many body effect can influence both the strength and kinetics of

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hydrogen bonds. Recently, Xu et al.[6] investigated the role of polarizability in the dynamics of water−water hydrogen bonds in pure water and in a 0.5 M aqueous NaCl solution by employing the polarizable TIP4P/FQ model[51] of water in their molecular dynamics simulations. The results of the polarizable model were compared with those of the corresponding fixed charge nonpolarizable TIP4P model.[50] It was found that the polarizability enhances the strength of hydrogen bonds and increases the hydrogen bond relaxation time by about 60% for hydrogen bonds in bulk water and by about 100% for hydrogen bonds between a water molecule in the bulk and another water molecule in the solvation shells of the ions. We note that the work of Xu et al.[6] considered the dynamics of water−water hydrogen bonds in the vicinity of an ion, whereas the focus of the present study is on the dynamics of anion−water hydrogen bonds, i.e., the hydrogen bonds that are formed between a water molecule and the anion itself. Like the case of water−water hydrogen bonds, the polarization effects are also expected to increase the relaxation times of anion−water hydrogen bonds, and it remains to be seen if there is any dramatic change in the relative time scales of relaxation of the water−water and anion−water hydrogen bonds when polarizable force fields are employed for both water and ions. Clearly, it would be worthwhile to carry out further studies to quantify the effects of polarizability on the anion−water hydrogen bond kinetics.

The effects of polarization and many body interactions enter naturally in ab initio molecular dynamics simulations.[54,55] Among the ab initio MD studies of aqueous solutions, we note, in particular, the recent work of Raugei and Klein[12] on the aqueous HBr solution. The residence time of a water molecule in the inner solvation shell of the bromide ion was calculated, and it was found to be about 19 ps. This value was compared with the experimentally measured Br$^-$−water hydrogen bond time constant of 19 ± 5 ps for a 2 M NaBr solution. These authors also carried out a classical MD simulation with the same system size (31 water molecules and one Br$^-$) and nonpolarizable SPC model[56] of water, and the above residence time was found to be only 5 ps. Based on this result and an earlier result of Impey et al.,[57] who found a value of 4.5 ps for the residence time of water in the solvation shell of a chloride for the nonpolarizable MCY model,[58] it was concluded that the nonpolarizable models are inadequate in properly describing the dynamics of water in aqueous solvation shells. We note in this context the work of ref 48 where the residence time of water in the chloride ion solvation shell was found to be around 10.8 ps for the nonpolarizable SPC/E model. A very similar residence time was also found by Lyubartsev and Laaksonen[49] for the flexible (but nonpolarizable) SPC model.[59] We note that the two latter studies considered much bigger simulation systems. We also stress that the actual value of the residence time depends, to some extent, on how it is defined.

We also note that although the ab initio MD result of the residence time of water in Br$^-$ solvation shell (for a chosen definition of the residence time) agrees with the experimentally observed time constant of the relaxation of Br$^-$−water hydrogen bond distance, such a comparison also brings in a few related points. First, the experimental time constant (of 19 ± 5 ps) corresponds to the relaxation time of bromide ion−water hydrogen bond distance correlation, i.e., it describes the time scale at which the Br$^-$−water hydrogen bond distance changes, and it is not necessarily equal to the residence time of a water molecule in the solvation shell. A water molecule can remain in the solvation shell and still can alter the anion−water hydrogen bond distance through rotational motion. If the

residence time is indeed comparable to the experimentally observed hydrogen bond time constant, such a comparison is also expected to be valid for water−water hydrogen bonds. The residence time of water in the solvation shell of another water has been estimated to be around 5−6 ps,[48,49] whereas the experimentally observed characteristic time constant for water−water hydrogen bond dynamics is less than a picosecond.[7] Clearly, more work is needed to fully understand the dynamics of halide ion−water hydrogen bonds.

We also note in this context the recent simulation work of Balasubramanian et al.[8] where the lifetime of the hydrogen bonds between water and the polar headgroups (PHG) of a micellar surface was found to be an order of magnitude longer than that of water−water hydrogen bonds in the bulk. No such dramatic slowing down is observed in the present study for hydrogen bonds between water and the halide ions. As described by Balasubramanian et al.,[8] the longer lifetime of the PHG−water hydrogen bonds could originate from the bridge bonds that the water molecules at the micellar surface form with the PHGs and also from the coupling to the organized assembly of the micelle. Clearly, such complex features are absent in the aqueous solvation shell of a chloride or a bromide ion and that could be the reason for our not finding any dramatic difference between the lifetimes of anion−water and water−water hydrogen bonds in the present work.

8. Conclusions

In this work, we have investigated the dynamics of anion−water and water−water hydrogen bonds in aqueous alkali halide solutions by means of molecular dynamics simulations. The results are obtained for solutions containing a single chloride or a single bromide ion and also for a concentrated solution of 3.35 M NaCl in water. The dynamics of breaking and the structural relaxation of anion−water hydrogen bonds are found to be slower than that of water−water hydrogen bonds. However, the extent of slowing down is not as great as reported in recent experimental studies. The dynamics of anion−water hydrogen bonds in a concentrated NaCl solution is found to be slower than that at infinite dilution which is in qualitative agreement with the trend observed in experiments. It is concluded that more work is needed on this problem to fully understand the detailed dynamics of anion−water hydrogen bonds in aqueous alkali halide solutions.

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