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Hydrogen bonds in aqueous electrolyte solutions: Statistics and dynamics based on both geometric and energetic criteria

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We have investigated the statistics and dynamics of hydrogen bonds in a concentrated aqueous electrolyte solution and also in pure water by means of molecular dynamics simulations. Both geometric and energetic definitions are employed for the existence of a hydrogen bond. The present study extends our earlier work on the structure and dynamics of hydrogen bonds where only the geometric definition was used [A. Chandra, Phys. Rev. Lett. **85**, 768 (2000)]. In the presence of ions, like the earlier results for geometric definition, the energetic definition is also found to give a lower number of hydrogen bonds per water molecule and a wider distribution, a slightly faster rate of breaking and a slower rate of structural relaxation of hydrogen bonds. The results are explained in terms of a decrease of the potential of mean force between water molecules, an enhanced population of hydrogen bonded water pairs in the vicinity of the dividing surface that separates the hydrogen bonded and nonbonded states and an increase of the friction on translational and rotational motion of water molecules in the presence of ions.

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I. INTRODUCTION

This paper is concerned with the hydrogen bond properties of aqueous electrolyte solutions at room temperature. Hydrogen bonds are known to play a critical role in determining various macroscopic properties of water and aqueous solutions and hence studies of the equilibrium and dynamical aspects of hydrogen bonds have remained a subject of longstanding interest in physical chemistry [1–4]. Most of the existing studies of hydrogen bonds consider pure water [5–32]. However, in many experimental situations, one deals with aqueous electrolyte solutions where the presence of ions may significantly modify the behavior of these hydrogen bonds.

There have been very few studies on the dynamics of hydrogen bonds in aqueous electrolyte solutions. On the experimental side, Tominaga and coworkers [33,34] employed the low frequency Raman spectroscopy to study the dynamical structure of water in the presence of alkali-metal and halide ions. They found a reduction of the water-water intermolecular stretching frequency with increasing ion concentration. However, no explicit evaluation of the water-water hydrogen bond dynamics could be made in their studies. Kropman and Bakker [35] investigated the dynamics of anion-water and water-water hydrogen bonds in aqueous solutions by using femtosecond midinfrared spectroscopy. These authors found a significant slowing down of the relaxation of anion-water hydrogen bonds as compared to the dynamics of hydrogen bonds between two water molecules in the bulk. On the theoretical side, Chandra [36] investigated the distribution and dynamics of hydrogen bonds in concentrated aqueous ionic solutions by means of molecular dynamics simulations. The hydrogen bonds were defined by using a set of configurational (or geometric) criteria. It was found that the average number of hydrogen bonds per water molecule decreases with ion concentration. The rate of hydrogen bond breaking was found to increase slightly, whereas the rate of hydrogen bond structural relaxation was found to slow down with increasing ion concentration. Xu and Berne [37] also employed molecular dynamics simulations and the same set of geometric criteria for the definition of a hydrogen bond to explore the dynamics of water-water hydrogen bonds in an aqueous solution of a negatively charged polypeptide and positive counterions. It was found that the kinetics of breaking and forming of hydrogen bonds is slower in the first solvation shell of the polypeptide. Around the positive counterions, however, the hydrogen bonds were found to break at a somewhat faster rate. As mentioned above, both these simulation results were obtained by using only one definition of the hydrogen bond (i.e., geometric) and it is not clear whether the general behavior remains the same when a different definition is used for the existence of a hydrogen bond. This is especially important because it has been shown earlier that many of the calculated equilibrium and dynamical properties of hydrogen bonds can depend significantly on the way a hydrogen bond is defined [15,21].

For pure water, mainly two kinds of definitions have been employed for hydrogen bonds: Geometric and energetic [14–27]. In the 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, ones uses a cutoff on the pair interaction energy between two water molecules to decide whether or not they are hydrogen bonded. Sometimes, additional configurational criteria such as a cutoff on oxygen-oxygen distance is employed in the energetic definition to make the definition of the hydrogen bond more strict. Of course, other kinds of definitions are also available in the literature, an example being the temporal definition of a hydrogen bond [28–31]. All studies of hydrogen bond dynamics in aqueous electrolyte solutions have so far been carried out by using only the geometric definition of hydrogen bonds and, to the best of our knowledge, no study has yet been carried out for hydrogen bond dynamical properties of elec-

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TABLE I. Values of Lennard-Jones and electrostatic interaction potential parameters. e represents the magnitude of electronic charge.

Atom (or 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

trolyte solutions where a different (such as energetic) definition of hydrogen bonds is employed. Such a study is presented in this paper where, in addition to the geometric definition, an energetic definition is also employed to investigate both the statistics and dynamics of hydrogen bonds in aqueous electrolyte solutions. An interpretation of the observed behavior is given in terms of the potential of mean force between water molecules, relative population of hydrogen bonded water pairs in the vicinity of the dividing surface that separates the hydrogen bonded and nonbonded states and molecular frictions on translational and rotational motion of water molecules in the aqueous electrolyte solution as compared to those in pure water.

The rest of the paper is organized as follows. In Sec. II, we have presented the simulation details and, in Sec. III, we have presented the results of hydrogen bond statistics. The results of the dynamics of hydrogen bonds are included in Sec. IV and our conclusions are summarized in Sec. V.

II. SIMULATION DETAILS

In this work, we have carried out molecular dynamics (MD) simulations of pure water and an aqueous NaCl solution of 3.3m concentration. The water molecules are characterized by the extended simple point charge (SPC/E) potential [38] and the sodium and chloride ions are modeled as charged Lennard-Jones particles [39,40]. In these models, the interaction between atomic sites (or ions) is expressed as

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

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 $\epsilon_{ij}=\sqrt{\epsilon_i\epsilon_j}$. The values of the potential parameters q_i, σ_i, and ϵ_i for water and Na^+ and Cl^- ions are summarized in Table I.

The MD simulations were carried out in the microcanonical ensemble at an average temperature of 298 K. A cubic box of 256 molecules including water and ions, the experimental density of the solutions [41] and periodic boundary conditions with minimum image convention were employed. The simulations were performed with pure water and a 3.3m solution of NaCl in water. We employed a spherical truncation of the Lennard-Jones interaction potential at 0.5L where L is the edge length of the simulation box. The long range electrostatic interactions were treated using the Ewald method with the dielectric constant of the surrounding medium $\epsilon'=\infty$ and the convergence parameter $\alpha=6.4/L$ [42]. The real space portion of the Ewald sum was evaluated by employing a spherical cutoff at 0.5L. We employed the quaternion formulation of the equations of rotational motion and, for the integration over time, we adapted the leap-frog algorithm with a time step of 10^{-15} s (1 fs). In the starting configuration, the water molecules and ions were located on a face-centered cubic lattice with random orientations of water molecules. MD runs of 400 ps were used to equilibrate each system and then the simulations were run for another 400 ps for the calculation of various equilibrium and dynamical quantities.

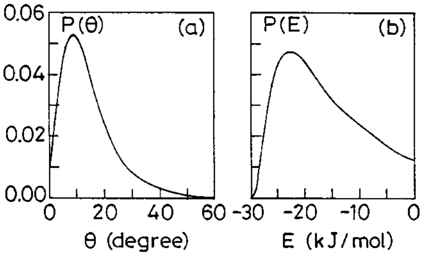

FIG. 1. The probability distribution of (a) the angle θ for a water pair having oxygen-oxygen and oxygen-hydrogen distances less than 3.5 and 2.45 Å, respectively, and (b) the pair interaction energy E of a water pair having oxygen-oxygen distance less than 3.5 Å. The results are for pure water.

III. DISTRIBUTION OF HYDROGEN BONDS

The analysis of the hydrogen bond statistics is based on a calculation of the percentages f_n of water molecules that engage in n hydrogen bonds and the average number of hydrogen bonds per water molecule n_{HB}. Here we have adopted two different definitions for the existence of a hydrogen bond between a water pair. The first definition is based on a configurational criteria and the second one is based on a combination of configurational and energetic criteria. In the configurational criteria, two water molecules are considered hydrogen bonded if their interoxygen distance is less than 3.5 Å and simultaneously oxygen-hydrogen distance is less than 2.45 Å and the oxygen-oxygen-hydrogen angle is less than 30° [20,21,36]. In the combined configurational energetic criteria, two water molecules are considered hydrogen bonded if their interoxygen distance is less than 3.5 Å and at the same time their pair interaction energy is less than -10 kJ mol^{-1} [15,17–19]. In the present paper, we refer to the first definition as the geometric and the second one as the energetic definition of a hydrogen bond.

We note that the critical distances of 3.5 and 2.45 Å are essentially the positions of the first minimum in the oxygen-oxygen and oxygen-hydrogen radial distribution functions. The angular criterion reflects the directional character of hydrogen bonds. In Fig. 1(a), we have shown the quantity $P(\theta)$ that describes the distribution of oxygen-oxygen-hydrogen angle θ for water pairs with oxygen-oxygen distance less than 3.5 Å and hydrogen-oxygen distance less than 2.45 Å. Clearly, the distribution of θ is rather narrow with its maximum at around $\theta\sim 9°$ which shows the slightly bent charac-

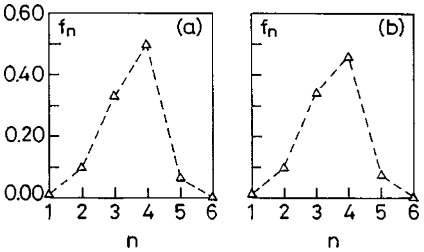

FIG. 2. The fraction of molecules with n number of hydrogen bonds for (a) geometric and (b) energetic definitions. The results are for pure water.

ter of the most favorable hydrogen bonds in liquid water. The distribution of interaction energy (E) of two water molecules with oxygen-oxygen distance less than 3.5 Å is shown in Fig. 1(b). The maximum is found to be at $E\sim -23\ \mathrm{kJ\,mol^{-1}}$. In the definition of the hydrogen bond, one puts the cutoff at $\theta=30°$ (geometric) or at $E=-10\ \mathrm{kJ\,mol^{-1}}$ (energetic) to allow some fluctuations from the most favorable configuration or the most favorable pair interaction energy.

The values of f_n $(n=1,2,...,5)$ for pure water are shown in Fig. 2 for both the definitions. The corresponding values of the average number of hydrogen bonds per water molecule (n_{HB}) are included in Table II. Both geometric and energetic definitions are found to produce very similar results. It is clear that pure water is dominated by molecules that form four hydrogen bonds. However, fractions of molecules with two, three, or five hydrogen bonds are also significant. We now discuss the results for 3.3*m* NaCl solution. In Fig. 3, we have shown the distribution of the angle θ and the pair interaction energy E for the NaCl solution. As before, the angle θ is calculated for water pairs having oxygen-oxygen and oxygen-hydrogen distances less than 3.5 Å and 2.45 Å, respectively, and the pair interaction energy is calculated for water pairs with oxygen-oxygen distance less than 3.5 Å. In both cases, the probability distributions are found to be slightly wider than those in pure water. The corresponding results for the f_n and n_{HB} are shown in Fig. 4 and Table II, respectively. In the ionic solution, the value of f_n at its maximum is found to be less than that in pure water. One observes a widening of the distribution and a decrease of the average number of hydrogen bonds per water molecule in the presence of ions. Thus, the presence of ions modifies the distribution of water-water hydrogen bonds by breaking some of the hydrogen bonds that were present in pure water.

TABLE II. Values of the average number of hydrogen bonds per water molecule, the average lifetime of a hydrogen bond, and the hydrogen bond structural relaxation time for both pure water and 3.3*m* aqueous NaCl solution. (The standard deviations, which were calculated by using block averages over 75 ps, are about 1.5%, 2.5%, and 2.5% of the final values reported above for n_{HB}, τ_{HB}, and τ_R, respectively.)

Solution	Definition	n_{HB}	τ_{HB}	τ_R
0.0*m*	Geometric	3.50	0.54	6.58
3.3*m*	Geometric	2.75	0.50	6.92
0.0*m*	Energetic	3.45	0.40	6.45
3.3*m*	Energetic	2.65	0.37	7.12

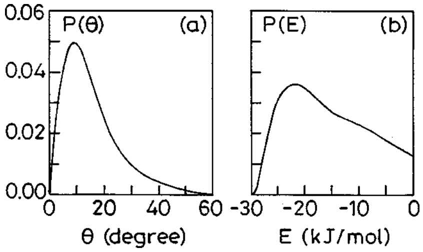

FIG. 3. The probability distribution of (a) the angle θ for a water pair having oxygen-oxygen and oxygen-hydrogen distances less than 3.5 and 2.45 Å, respectively, and (b) the pair interaction energy E of a water pair having oxygen-oxygen distance less than 3.5 Å. The results are for 3.3*m* aqueous NaCl solution.

IV. DYNAMICS OF HYDROGEN BONDS

In the dynamical equilibrium of aqueous solutions, the hydrogen bonds break and reform due to librational and translational motion of water molecules. The analysis of the dynamics of hydrogen bonds is based on the construction of two hydrogen bond population variables $h(t)$ and $H(t)$: $h(t)$ is unity when a particular tagged pair of water molecules is hydrogen bonded at time t according to an adopted definition and zero otherwise, whereas $H(t)=1$ if the tagged pair of water molecules remains continuously hydrogen bonded from $t=0$ to time t and zero otherwise. For the analysis of the H-bond breaking dynamics, we calculate the time correlation function [17]

$$S_{\mathrm{HB}}(t)=\langle h(0)H(t)\rangle/\langle h\rangle \qquad (2)$$

where $\langle\cdots\rangle$ denotes an average over all pairs. Clearly, $S_{\mathrm{HB}}(t)$ describes the probability that an initially hydrogen bonded pair remains bonded at all times upto t. The associated relaxation time τ_{HB} can be interpreted as the average lifetime of a hydrogen bond [43]. We note that both librational and translational or diffusional motion contribute to the decay of $S_{\mathrm{HB}}(t)$. In Fig. 5 we have shown the results of $S_{\mathrm{HB}}(t)$ for pure water and the 3.3*m* NaCl solution. For each system, the associated hydrogen bond relaxation time τ_{HB} is obtained as the time integral of $S_{\mathrm{HB}}(t)$. At long times, the dynamics of $S_{\mathrm{HB}}(t)$ is described well by a single exponential function for both pure water and the aqueous solution. The relaxation

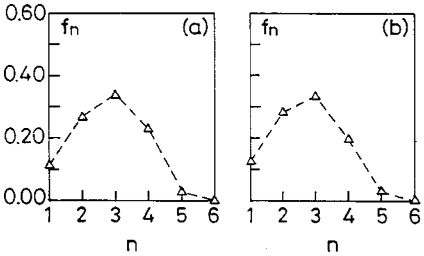

FIG. 4. The fraction of molecules with n number of hydrogen bonds for (a) geometric and (b) energetic definitions. The results are for 3.3*m* aqueous NaCl solution.

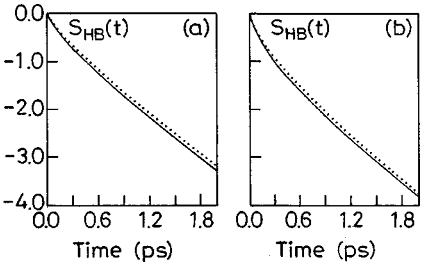

FIG. 5. The time dependence of the continuous hydrogen bond correlation function $S_{\mathrm{HB}}(t)$ for (a) geometric and (b) energetic definitions. The dotted and the solid curves are for pure water and 3.3*m* aqueous NaCl solution, respectively. The values of $S_{\mathrm{HB}}(t)$ are plotted in the logarithmic scale.

time τ_{HB} is calculated by explicit integration of $S_{\mathrm{HB}}(t)$ from simulations until 3.0 ps and by calculating the integral for the tail from the fitted exponential functions. In Table II, we have included the results of τ_{HB} for both geometric and energetic definitions of hydrogen bonds. For both definitions, the decay rate of $S_{\mathrm{HB}}(t)$ is found to accelerate slightly in presence of ions. This indicates that the H-bonded water pair in ionic solutions is less strongly held compared to that in pure water. To gain more insight into this dynamical behavior, we have calculated the potential of mean force (PMF) between two neighboring water molecules and the results are shown in Fig. 6 [44]. It is seen that the well depth and also the force constant or the curvature at the minimum of PMF decreases in presence of ions. We note that this decreasing force constant is consistent with the experimental results of Tominaga and coworkers [33,34] where a reduction of the water-water intermolecular stretching frequency with increasing ion concentration was observed. Also, for pure water, the present results of the relaxation time of $S_{\mathrm{HB}}(t)$ agree well with the experimental hydrogen bond correlation time constant of 0.5 ± 0.2ps reported by Kropman and Bakker [35] in their femtosecond midinfrared laser study and with the relaxation time of 0.56 ps reported by Tominaga and coworkers [33] in their low frequency Raman studies. In the latter study, the relaxation time was attributed to the lifetime of hydrogen bonded tetrahedral structure of water and it was found to increase with the increase of salt concentration, whereas the present results show a slightly faster breaking of the hydrogen bonds in the presence of ions. As noted in Ref. [36], it is possible that the lifetime observed by Tominaga and coworkers at finite ion concentrations also included contributions from anion-water hydrogen bonds that have a slower time scale of relaxation [35,45]. In the present study, of course, only water-water hydrogen bonds are considered.

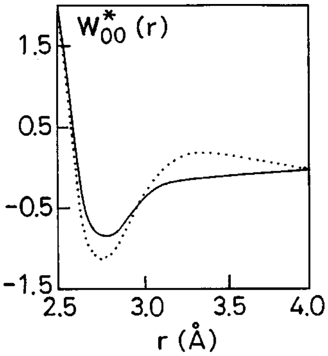

FIG. 6. The distance dependence of the oxygen-oxygen potential of mean force between two neighboring water molecules $[W^*_{\mathrm{OO}}(r)=W_{\mathrm{OO}}(r)/k_BT]$. The different curves are as in Fig. 5.

The ion induced changes of the PMF between two neighboring water molecules can affect the rate of hydrogen bond breaking in two different ways. The reduction of the well depth means a relatively weaker effective interaction between two neighboring water molecules in the presence of ions compared to that in pure water. 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 that tends to inhibit diffusion. The second effect is that, in the ionic solution, the value of PMF is lower near the dividing surface (i.e., $R_{\mathrm{OO}}\sim3.5$ 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 cross over to the nonbonded state and this also leads to an enhancement of the rate of hydrogen bond breaking. In order to verify whether a reduction of the PMF leads to a faster rate of relative diffusion of a water pair, we have calculated the relaxation of the correlation function of relative velocity of two initially hydrogen bonded water molecules, which is defined as [46]

$$C^{(12)}_{v;\mathrm{H_2O}}(t)=\langle v_{12}(t)v_{12}(0)\rangle/\langle v_{12}(0)^2\rangle, \tag{3}$$

where $v_{12}(t)$ is the relative velocity of two water molecules at time t, which were hydrogen bonded at time $t=0$. It may be noted that the correlation function of relative velocity can be decomposed into two parts: The autocorrelation of single particle velocity and the cross correlation of velocities of two particles. The cross part plays an important role in the momentum transfer between neighboring molecules [47–51]. The time dependent relative diffusion coefficient of two initially hydrogen bonded water molecules is defined as the time integral of the relative velocity correlation function of two hydrogen bonded molecules

$$D_{12}(t)=\frac{k_BT}{M}\int_0^t C^{(12)}_{v;\mathrm{H_2O}}(t')dt', \tag{4}$$

where M is the reduced mass of the water pair. We note that, in the absence of any cross velocity correlation, $D_{12}(t)=2D_{\mathrm{H_2O}}(t)$, where $D_{\mathrm{H_2O}}(t)$ is the time dependent self-diffusion coefficient of water molecules. We also note that the relative diffusion coefficient as defined by the integral of Eq. (4) is different from the so-called mutual diffusion coefficient [52]. The mutual diffusion coefficient is traditionally defined only for multicomponent systems through an integral of the collective velocity variables [53–56] and it describes the mutual diffusion of molecules of one species against those of another species in the mixture. In the present work, the integral of Eq. (4) is a microscopic quantity that de-

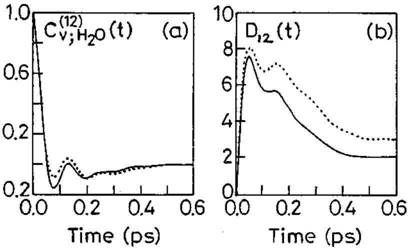

FIG. 7. The time dependence of the (a) relative velocity correlation function and (b) relative diffusion coefficient of two initially hydrogen bonded water molecules. The different curves are as in Fig. 6.

scribes how fast a pair of initially hydrogen bonded water molecules diffuse away from each other and hence we call it the relative diffusion coefficient. In Fig. 7, we have shown the time dependence of $C_{v;\mathrm{H_2O}}^{(12)}(t)$ and $D_{12}(t)$ for both pure water and the 3.3*m* NaCl solution. The decay of $C_{v;\mathrm{H_2O}}^{(12)}(t)$ shows an enhanced caging effect at the intermediate time in the presence of ions. The value of $D_{12}(t)$ is found to be smaller for the ionic solution at all times. The long time or the zero-frequency values of D_{12} are 3.0×10^{-5} cm^2 sec^{-1} and 2.0×10^{-5} cm^2 sec^{-1} for pure water and the ionic solution, respectively. We note that the relative diffusion coefficient is related to the inverse of the friction that acts on the relative motion of a hydrogen bonded water pair. Thus, the enhanced caging of $C_{v;12}(t)$ and the lower value of D_{12} show the presence of an enhanced friction on the motion of water molecules in the electrolyte solution as compared to that in pure water. The additional friction originates from the ions present in the solution. Thus, although the reduction of PMF tends to increase the relative diffusion of two water molecules, the existence of ionic friction plays a more important role that gives rise to a slowing down of the relative diffusion even at short times. Thus, 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 the concentrated ionic solution as compared to that in pure water.

The correlation function $S_{\mathrm{HB}}(t)$ describes the dynamics of hydrogen bond breaking as it depends on the continuous presence of a hydrogen bond. We calculate the correlation function $C_{\mathrm{HB}}(t)$ that does not depend on the continuous presence of a hydrogen bond [20,21]

$$C_{\mathrm{HB}}(t)=\langle h(0)h(t)\rangle/\langle h\rangle. \tag{5}$$

The correlation function $C_{\mathrm{HB}}(t)$ describes the probability that a hydrogen bond is intact at time *t*, given it was intact at time zero, independent of possible breaking in the interim time. $C_{\mathrm{HB}}(t)$ relaxes to zero as the probability that a specific pair of molecules is hydrogen bonded in a macroscopic system at equilibrium is negligibly small. The dynamics of $C_{\mathrm{HB}}(t)$ describes the structural relaxation of hydrogen bonds. The temporal behavior of $C_{\mathrm{HB}}(t)$ is shown in Fig. 8. The relaxation of $C_{\mathrm{HB}}(t)$ is found to occur at a slower rate with increasing ion concentration. The overall dynamics of hydrogen bond structural relaxation is found to be an order of magnitude slower than that of hydrogen bond breaking. Even at long times, the relaxation of $C_{\mathrm{HB}}(t)$ is highly nonexponential and no long-time exponential time constant could be found for the decay of these quantities. However, for the purpose of comparative analysis, one can obtain an average relaxation time τ_R from the available simulation data [36]. In the present study, the average relaxation time τ_R is defined by $C_{\mathrm{HB}}(n\tau_R)=e^{-n}$ where the value of n is determined from the lowest value of $C_{\mathrm{HB}}(t)$ obtained in the simulations. We stress that this definition is made only to make a comparison of the relative time scales of relaxation 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 $C_{\mathrm{HB}}(t)$. The results of τ_R are also included in Table II. For both geometric and energetic definitions, the hydrogen bond structural relaxation time increases in the presence of ions. Since the function $C_{\mathrm{HB}}(t)$ does not depend on the continuous presence of a hydrogen bond and it allows for the recrossing of the dividing surface from an intermittant nonbonded state to the bonded state, its dynamics is not expected to depend significantly on the small changes of the population of water pairs in the vicinity of the dividing surface. Rather, its dynamics is controlled by the long-time diffusion and orientational motion of water molecules. The presence of ions leads to a decrease of the diffusion coefficient and an increase of the orientational relaxation times of water due to additional electrolyte frictions that act on both translational and rotational motion of water molecules [36,46]. This slowing down of the translational and rotational diffusion of water molecules is believed to be responsible for the slowing down of hydrogen bond structural relaxation in the presence of ions.

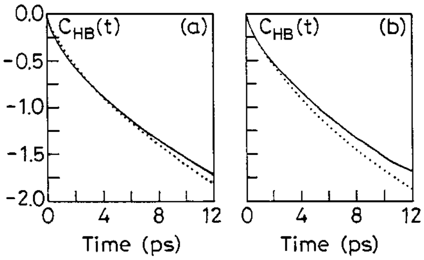

FIG. 8. The time dependence of the hydrogen bond correlation function $C_{\mathrm{HB}}(t)$ for (a) geometric and (b) energetic definitions. The dotted and the solid curves are for pure water and 3.3*m* aqueous NaCl solution, respectively. The values of $C_{\mathrm{HB}}(t)$ are plotted in the logarithmic scale.

It has been argued earlier that the long-time dynamics of $C_{\mathrm{HB}}(t)$ is invariant with respect to any reasonable definition of the hydrogen bond [20,21]. However, the dynamics of $S_{\mathrm{HB}}(t)$ depends significantly on the definition of the hydrogen bond due to the frequent crossing of the dividing surface. This frequent crossing of the diving surface leads to a faster relaxation of $S_{\mathrm{HB}}(t)$. 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 $S_{\mathrm{HB}}(t)$ would show a different behavior when a large cutoff is used to define a hydrogen bond. Thus, $C_{\mathrm{HB}}(t)$ appears to be a better function for studying the hydrogen bond dynamics. However, the relative changes of the relaxation of $S_{\mathrm{HB}}(t)$ in the presence of ions that are discussed here are likely to hold for any reasonable definition of the hydrogen bond.

V. CONCLUSION

In this paper, we have presented results for the distribution and dynamics of hydrogen bonds in water and 3.3*m* aqueous NaCl solution for two different definitions of the hydrogen bond. The first definition is based on a set of configurational criteria and the second one is based on a combination of configurational and energetic criteria. It is shown that both definitions give very similar results for the hydrogen bond distribution and the average number of hydrogen bonds per molecule. For pure water, majority of water molecules are having four hydrogen bonds although fractions of molecules having two, three, or five hydrogen bonds are also significant. As ions are dissolved in water, the hydrogen bond distribution becomes wider and also its value at the maximum decreases leading to a decrease of the average number of hydrogen bonds per water molecule. Thus, the presence of ions is found to modify the hydrogen bonded structure of water by breaking some of the hydrogen bonds that exist in pure water.

The two definitions are also found to give qualitatively similar results for the dynamics of breaking and structural relaxation of hydrogen bonds in water and the 3.3*m* aqueous NaCl solution. The breaking of hydrogen bonds is found to be a very fast process with subpicosecond time scale and its rate slightly increases in the presence of ions. Although the calculation of the potential of mean force shows a reduction of the effective strength of hydrogen bonds in the ionic solution, a calculation of the time dependent relative diffusion coefficient of a hydrogen bonded pair shows a slowing down of the relative motion of the two water molecules even at short times due to the presence of additional electrolyte friction. The slightly faster dynamics of hydrogen bond breaking observed in the present study is, at least in part, due to a higher population of hydrogen bonded water pairs in the vicinity of the dividing surface between the bonded and nonbonded states as the two molecules of such a pair need to travel only a short relative distance between them to break the hydrogen bond and cross over to the nonbonded state. The dynamics of hydrogen bond structural relaxation involves a much longer time scale (few picoseconds). Its rate of relaxation slows down in the presence of ions which can be attributed to the additional electrolyte frictions that act on the long-time orientational and translation motion of water molecules in the presence of ions.

The present work can be extended in many different directions. For example, in an aqueous ionic solution, anion-water hydrogen bonds are also present apart from water-water hydrogen bonds. In the present work, we have focused only on the water-water hydrogen bonds and it would certainly be very interesting to investigate the statistics and dynamics of anion-water hydrogen bonds [35]. It would also be worthwhile to study the equilibrium and dynamical properties of hydrogen bonds in aqueous ionic solutions at nonambient conditions such as at low temperature or high pressure. We hope to address these issues in the near future.

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[44] The oxygen-oxygen potential of mean force is calculated from the relation: $W_{\mathrm{OO}}(r) = -k_B T \ln g_{\mathrm{OO}}(r)$, where $g_{\mathrm{OO}}(r)$ is the oxygen-oxygen radial distribution function.

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