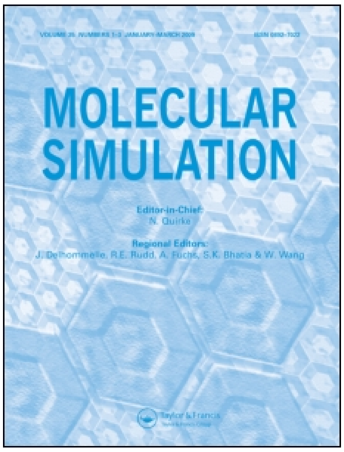

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Molecular Dynamics Simulation of OH^- in Water

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We have simulated the hydration and diffusion of the OH^- ions in water as well as the OD^- ions in heavy water by classical molecular dynamics. We find that the dynamics of the solvation complex continuously fluctuates among $H_3O_2^-$, $H_5O_3^-$, $H_7O_4^-$, $H_9O_5^-$ and $H_{11}O_6^-$ hydration structures. We have observed that the structures $H_5O_3^-$ and $H_7O_4^-$ are more frequent than the others. The diffusion coefficient of OH^- agrees with experimental values. The use of deuterium in the simulation instead of hydrogen has altered the results clearly, the hydration structures of the OD^- in heavy water are more stable, more compact and they diffuse more slowly than the corresponding structures in H_2O. The results are in good agreement with previous quantum simulations.

Keywords: Hydroxyl ions; Heavy water ions; Diffusion coefficients of water ions; Water ions hydration

INTRODUCTION

The hydroxyl ions are fundamental actors in many chemical processes which take place in water; many of them are biological importance. In particular, the OH^- ion is one of the main components in "pure" water at non-neutral pH. The OH^--ion formation in water is a very well studied problem [1–3]. However, there is as yet no computational model that reproduces convincingly its hydration and dynamics.

The OH^- ion is involved in the process of transport of protons in water. During this process one of the protons is transferred from a water molecule or hydronium (OH_3^+) to the OH^- along hydrogen bonds. This process is considered as an example of the Grothus chain mechanism, where the proton moves from one place to another along interconnected water molecules. This mechanism is faster than normal ion diffusion, which is considered as a process of secondary importance. However, the OH^- ion has a half life of around 2 or 3 ps period during which it does not have proton transfer.

Tuckerman *et al.* [4] have studied the process of transport of protons in water with *ab initio* molecular dynamics. They found two hydration structures of the OH^- in water: $H_7O_4^-$ with three water molecules surrounding the oxygen of the OH^-, and $H_9O_5^-$ with four water molecules around it. Water molecules are linked by hydrogen bonds to the OH^- oxygen. The OH^- proton is linked by a hydrogen bond to a water oxygen. Also, according to these authors, the $H_7O_4^-$ structure is more integrated to the solvent environment; thus the proton transfer is favoured. In the $H_9O_5^-$ structure the hydrogen bonds are in a plane perpendicular to the O–H axis of the OH^-. This planar conformation hinders the transfer of protons since it does not fit in the water structure. The $H_9O_5^-$ is a well defined anionic structure which does not diffuse during the simulation, in contrast to $H_7O_4^-$, which diffuses over appreciable distances. These authors used a box with 31 water molecules and one OH^-.

Hashimoto and Hiwatari [5] have studied the problem using classical molecular dynamics simulation (MD) with the Kumagai-Kawamura-Yokokawa (KKY) model potential [6] which allows analysing molecule dissociations. They simulated 64 molecules of water with one OH^- ion during 24 ps. These authors found only the $H_9O_5^-$ structure in their simulation, but the planar configuration of the hydrogen bonds reported in Refs. [4,5] was not

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observed and the proton transfer did not take place during the simulation time.

However, in the above mentioned works, the simulation method used has two disadvantages. On the one hand, their high computational cost forces very short simulation times; therefore, the conclusions regarding molecule solvation must be taken with caution. The calculation of the radial distribution functions requires simulation times much longer than those used by these authors to ensure that the system visits most of the possible configurations. On the other hand, in both works deuterium is used instead of hydrogen. This substitution is justified by the difficulties of the simulation methods used. However, the use of deuterium instead of hydrogen in the computational model of water significantly alters the results.

In this work, we have studied the hydration and diffusion of OH^- in water using classical MD methods. Although this method does not allow the study of the transfer of protons, the computer requirements of classical MD are much lower than those demanded by *ab initio* methods. Thus MD allows us to carry out longer simulations with a larger systems, therefore yielding a more refined vision of these phenomena.

METHOD

Molecular Dynamics. Computational Details

We have two systems, where one is obtained from the other by replacing all hydrogen atoms with deuterium atoms *System 1*: the system where the water is the solvent, and OH^- ions the solutes, and *System 2*: the system with OD^- ions dissolved in heavy water. In both systems there are 212 solvent molecules and 4 solute molecules, in a cubic box with periodic boundary conditions.

To model the solvent we used SPC/E water [10] in System 1, and SPC/HW [11] in System 2. In both models the geometry is the same, namely the O–H distance is 0.1 nm, and the $\hat{HOH}$ angle is 109.47°. The potential reads

$$U_{i,j} = \left[\frac{C_{12}}{r_{00}(i,j)}\right]^{12} - \left[\frac{C_6}{r_{00}(i,j)}\right]^{6} + \sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} \frac{q_\alpha(i) q_\beta(j)}{r_{\alpha\beta}(ij)} \quad (1)$$

The van der Waals interaction involves only the oxygen atoms [the Lenard-Jones parameters were, for both systems, $C_6 = 0.37122(\mathrm{kJ/mol})^{1/6}\,\mathrm{nm}$ and $C_{12} = 0.3428(\mathrm{kJ/mol})^{1/12}\,\mathrm{nm}$]. In SPC/E the oxygen atom charge is $-0.8476\,e$, and the hydrogen atom charge $0.4238\,e$. In SPC/HW the values are $-0.87\,e$ and for oxygen and $0.435\,e$ for deuterium. The OH^- (OD^-) ions model is based on the corresponding water model deleting one hydrogen (deuterium) atom, keeping the O–H (O–D) distance and the charges.

As the initial configuration for System 1 (respectively System 2) we used an SPC/E (SPC/HW) configuration in which we eliminated four hydrogen (deuterium) atoms belonging to different water molecules.

We carried out 20 steps of energy minimization in both systems while keeping the solute positionally restrained, until the absolute change in the total (potential) energy became smaller than $0.1\,\mathrm{kJ\,mol^{-1}}$. Then, we relaxed each system by 200 steps of energy minimization without constraints, obtaining a unit cell of $1.86 \times 1.86 \times 1.86\,\mathrm{nm^3}$ with a final density of water of $0.991\,\mathrm{g\,cm^{-3}}$ in System 1, and a unit cell of $1.87 \times 1.87 \times 1.87\,\mathrm{nm^3}$ with a density of heavy water of $1.083\,\mathrm{g\,cm^{-3}}$ in System 2.

In MD the equilibration criterion was to require constant potential energy density and a coupling thermal coefficient (*i.e.* the coefficient that multiplies the velocities to adjust the temperature to the reference) equal to 1 ± 10^{-6} in an average of 20 ps.

Although the radial distribution function is satisfactorily obtained using a time step of 1 fs, the analysis of hydration structures requires a time step shorter than the lifetime of the structures. We have reduced the time step gradually to obtain the larger value that allows description of the hydration structure, which turns out to be 0.5 fs.

We used the isobaric–isothermal ensemble by weakly coupling of the system to thermal and hydrostatic baths using Berendsen's thermostat [8]. We have set the thermal bath to a reference temperature of 300 K and a time constant $\tau_s = 5\,\mathrm{fs}$ and for the constant pressure a reference pressure of $1.013 \times 10^5\,\mathrm{Pa}$ (1 atmosphere), and a pressure time constant $\tau_p = 50\,\mathrm{fs}$.

To compute the interactions we used a twin range method [12] which evaluates the potential at every step for short distances (less than $R_S = 1.1\,\mathrm{nm}$) and less frequently at longer distances (up to the cut-off radius $R_W = 1.4\,\mathrm{nm}$). Additionally, a reaction field is included to approximate the contribution of the electrostatic interaction beyond the larger radius. We ran the simulation with the GROMOS package [7].

We calculated the radial distributions and the diffusion coefficients with a total time of 600 ps. We used 2.4×10^6 MD steps of 0.5 fs in the calculation of the life time of the solute hydration structures and the angular distribution functions of solvent atoms around solute atoms.

The Life Time

A hydration structure of the solute continues until one of the molecules of the solvent that surrounds it moves away from the first hydration shell. The solute considered in this work has two atoms, so the distinction of the possible structures is simple: one needs to analyze what happens around the O* (solute oxygen), and around the H* or D* (solute hydrogen or solute deuterium).

The duration of a hydration structure is not constant but depends on the residence time (t_r), this being the life time of a bond between molecules (hydrogen bonds in our case). A histogram of the number of times that a structure is observed (N_s) as function of the residence time can be fitted with a single exponential, a characteristic of a Poissonian process [9], as:

$$N_s(t_r) = N_s(0)\exp(t_r/\tau) \qquad (2)$$

where τ is the lifetime (residence time) in which $N_s(t)$ decays at $1/e$ of its value in $t_r = 0$.

The Diffusion Coefficient

For the calculation of the diffusion coefficient we used Eq. (3), where n is the number of molecules and $r_i(t)$ is the position at time t. This formula is used only for large times, when the diffusive regime is reached

$$D = \lim_{t\to\infty}\frac{1}{6t}\frac{1}{n}\left\langle \sum_{i=1}^{n}[r_i(0) - r_i(t)]^2 \right\rangle \qquad (3)$$

RESULTS AND DISCUSSION

Hydration Structures

We have analysed the hydration around the oxygen atom of the solute (indicated with O*). In System 1, the simplest hydration structure we found was $H_3O_2^-$, formed by the OH^- and one molecule of water together with a hydrogen bond to the O*. Other more complex structures we observed were: $H_5O_3^-$, $H_7O_4^-$, $H_9O_5^-$, and $H_{11}O_6^-$. We saw the same kind of structures for heavy water. For simplicity we called Structure A the structure with one solute molecule and one solvent molecule, structure B the structure with one solute molecule and two solvent molecules, and so on (Fig. 1).

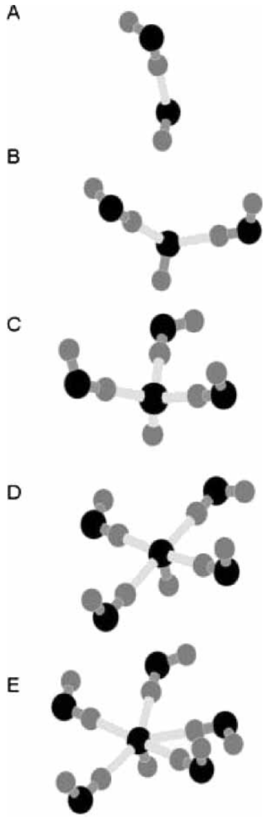

FIGURE 1 Hydration structures formed by the OH^- ion in aqueous solution. The small grey spheres represent hydrogen atoms. The oxygen atoms are indicated by black spheres. The O–H bonds are indicated by light grey cylinders and the hydrogen bonds by dark grey cylinders. The relative positions and angles correspond to mean values. Water molecules that are not part of the first solvation shell have been omitted.

A comparative analysis of the occurrence of the structures is shown in Fig. 2. In both systems the structures B ($H_5O_3^-$ and $D_5O_3^-$), and C ($H_7O_4^-$ and $D_7O_4^-$) were more frequent than the others. We can see that for heavy water the structures C ($D_7O_4^-$ and $D_{11}O_6^-$) are more frequent than the corresponding ones for regular water.

We observe that the H* spends long periods of time (up to 50 fs) without forming hydrogen bonds with the molecules of the surrounding water, showing that the behaviour of the hydrate structure H* is totally asymmetric with respect to the hydrate structure O*. Similar results hold for System 2.

Radial Distribution Functions

Figure 3 shows the oxygen–oxygen radial distribution functions [$g_{OO}(r)$] for the SPC/E water, the experimental results for water [13], and the hydration structures around OH^- and OD^- in water and in heavy water, respectively. The discrepancies between simulation and experiments on water have been discussed in Ref. [13]. As regards the hydration

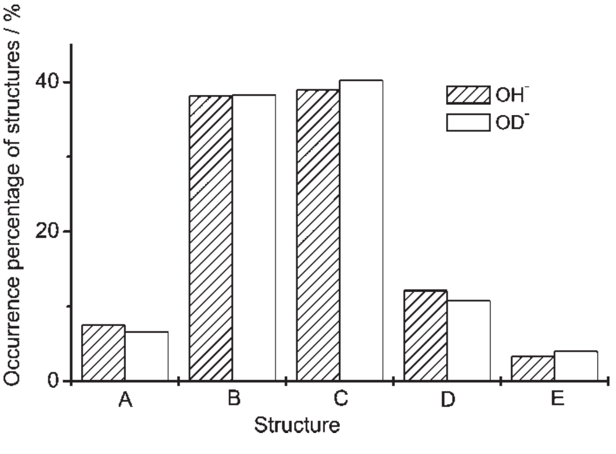

FIGURE 2 Occurrence percentage of observed hydration structures. Data are average over the complete run.

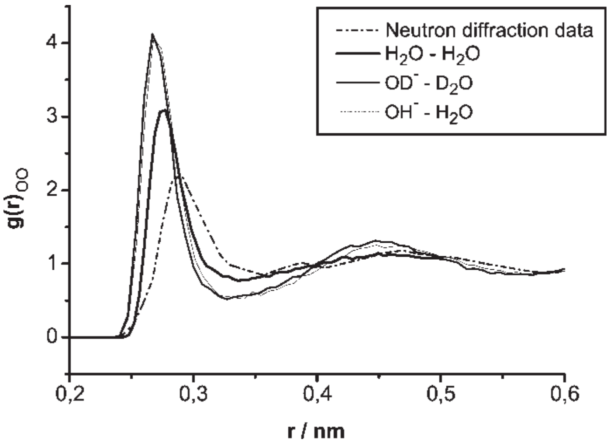

FIGURE 3 Oxygen–oxygen radial distribution functions of different hydration structures and for water (experimental diffraction data from Ref. [13]).

structures studied here, both show a more pronounced peak shifted to shorter distance from the origin, which means there is a more compact structure around the hydroxyl ions as compared with pure water. Moreover, the $g_{OO}(r)$ curve of the OD^- has a more defined second peak. This fact may be interpreted as indicating that the hydration structures around the solutes in heavy water are more compact than in ordinary water.

The radial distribution functions shown are an average of the radial distribution functions corresponding to each hydration structure. An analysis of each structure shows that the first peak position moves away from the origin as solvent molecules are added to the shell. The successive peaks of the radial distribution functions move in the same direction as the first. This displacement takes place in both Systems (Table I).

Angular Distribution Functions

To study the distribution of water and heavy water around the ions we computed the angular distribution function, $P(\cos\phi)$ vs. $\cos\phi$, where ϕ is the angle formed by the atoms H^*—O^*—H, when the atom O^* acts as a proton acceptor (H^*—O^* – – – H—O—H). In an ideal tetrahedral structure this angle would be 109.47°, and $\cos\phi = -1/3$. The results show that in all structures the angle between solvent hydrogen and solute lies in an interval between 80° and 110°. Figure 4 shows the angular distribution function for each of the structures in the System 1.

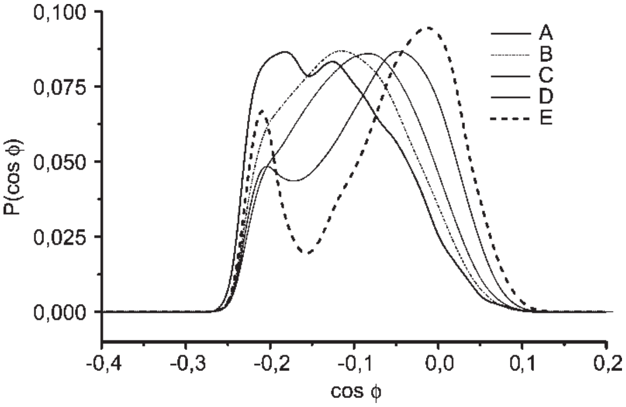

FIGURE 4 Angular distribution functions of the angle ϕ (defined in the text) for the different hydration structures.

In structure A, ϕ is larger than for the other cases, and in this way the structure fits better in the environment. Structures B and C, where the function almost reaches a maximum around 94°, are nearly in a planar configuration. For D and E structures, two maxima appear, one near 90° and another near 100°. In Table II a comparative analysis of the peaks of the functions of angular distribution is presented.

The angular distribution functions of the solute are quite similar in both systems. However, there are significant differences for the solvent. Figure 5 shows angular distribution functions for water and for heavy water, in which we adopted the same definition of angles as above. For these cases we can see that the curves are much broader than for the hydration of solutes, which have more defined structures. The peak in the angular distribution function of SPC/E water is found at 115°, and for HW it is in 109°.

Life Time

Using the trajectories we computed the life time of the hydrogen (deuterium) bond of the structures. The results are shown in Table III.

TABLE I Position of the first, second and third peaks in the $g_{O^*O}(r)$ function in System 1 and 2

	First peak (Å)		*Second peak (Å)*		*Third peak (Å)*	
	System 1	*System 2*	*System 1*	*System 2*	*System 1*	*System 2*
A	2.70	2.70	4.57	4.50	6.87	6.77
B	2.71	2.71	4.59	4.51	6.88	6.77
C	2.72	2.72	4.59	4.51	6.88	6.78
D	2.75	2.75	4.62	4.54	6.91	6.80
E	2.79	2.79	4.65	4.57	6.93	6.81

TABLE II Peaks for the angular distribution functions in the different structures (note that the structures B and C exhibit only one peak)

Structure	*First peak (°)*	*Second Peak (°)*
A	97	100
B	96	–
C	94	–
D	92	101
E	90	102

TABLE III Life time of the hydrogen bonds between water and the different hydration structures and the solvent

	τ, fs (life time)	
Hydration structure	*System 1*	*System 2*
A	14	19
B	21	27
C	32	36
D	42	45
E	28	38
H^*/D^*-O^-	6,7	7,4
H/D_2O	7,7	9,6

We can observe that the life time of bonds in D_2O is larger than in H_2O. The life time of the hydrogen bonds in water formed between H* and the oxygen of the water (H^*-O) is 6.7 fs while the equivalent in heavy water is 7.4 fs. For comparison, the life time of H (D) bonds in water and heavy water (H–O) is 7.7 and 9.6 fs, respectively. We can see that for the water–water association the increase in the life time of bonds of heavy water is around 30%, while for the hydration structures of the ions—which are much larger—the increase is about 10%.

The life times of the water–water structures are around 5 times smaller than the life times of the two more frequent structures ($H_5O_3^-$ and $H_7O_4^-$), in H_2O as well as in D_2O. This clearly identifies a hydration state around the oxygen of the OH^-, where the solvent molecules are strongly bound to the ions (Fig. 6).

Diffusion of OH^- and OD^-

In both System 1 and System 2, we can see that the diffusion coefficient of the solvent is not altered by the presence of the solute, giving a value of $2.7 \times 10^{-3}\,\mathrm{nm^2\,ps^{-1}}$ in the case of H_2O, and of $2.1 10^{-3}\,\mathrm{nm^2\,ps^{-1}}$ for D_2O. This agrees with simulation [11] as well as with experimental values [14] for pure water. We obtain $5.3 \times 10^{-3}\,\mathrm{nm^2\,ps^{-1}}$ as diffusion coefficient for OH^- in H_2O in coincidence with experimental values [15]. The diffusion coefficient for OD^- in D_2O is significantly smaller at $3.2\,\mathrm{nm^2\,ps^{-1}}$.

CONCLUSIONS

Through classical molecular dynamics, we have studied the solvation and diffusion of the OH^- and OD^- ions. We may conclude that the presented models of OH^- and OD^- reproduce convincingly the dynamic properties of these ions, and they are adequate for computer simulation.

Comparing the results of both systems we have found several similarities. From the five different hydration structures of the O–H (O–D) ion that we have observed we have seen that those with hydration number 2 and 3 (called B and C) are the most abundant. The residence times of the structures follow the order $\tau_A < \tau_B < \tau_C < \tau_D$, suggesting that the stability of the structures increases with

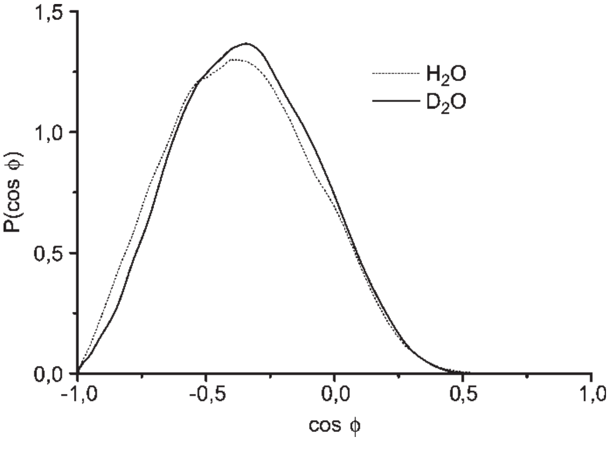

FIGURE 5 The angular distribution functions of ϕ, as in Fig. 4, for water and heavy water.

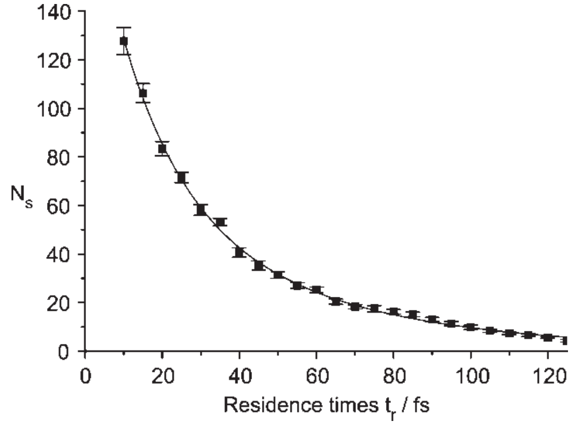

FIGURE 6 Decaying process of residence time of the structure $H_7O_4^-$. The full line corresponds to the exponential fitting curve for water. The error bars are shown.

the hydration numbers. However, this rule is not satisfied for the structures of type E, where $\tau_E \approx \tau_C$, seemingly indicating that four hydration water molecules with an orientation angle $H---O^*H^*$ $(D---O^*D^*)$ around 90° is the most favourable structure in terms of stability.

There are, however, some differences. For the heavy water system the residence time of the hydration structures is around 30% larger with smaller diffusion coefficients, and better-defined first and second peaks in the radial distribution functions of the water oxygen atoms around oxygen atoms belonging to the ions. These properties are in agreement with the structural and dynamic properties of heavy water as compared with regular water.

Some of the hydration structures we observe were also detected by Tuckerman *et al*. The $H_9O_5^-$ structure found by Tuckerman *et al.* has a planar configuration, does not diffuse structurally, and has a $g_{O^*O}(r)$ function with first peak at 2.7 Å. We also find this structure, with the links of hydrogen atoms located around the angles 92° and 101°, and a $g_{O^*O}(r)$ function with first peak 2.7 Å. However, we do observe structural diffusion. Tuckerman *et al.* also describe a tetrahedral $H_7O_4^-$ structure with structural diffusion and a first peak of the $g_{O^*O}(r)$ function at 2.6 Å. In contrast, we find that $H_7O_4^-$ has a planar structure, with structural diffusion and a first peak of $g_{O^*O}(r)$ at the same distance. Both simulations find that the O^*–O distance increases when solvent molecules are added to the hydration sphere.

As regards the only hydration structure found by Hashimoto and Hiwatari, the $H_9O_5^-$, our findings are in agreement as far as the position of the first peak of $g_{O^*O}(r)$ and planar structure are concerned.

The reliability of the present results is supported by the agreement with previous experimental results, such as the diffusion coefficients of the solutes and the solvent. Our results indicate that substituting deuterium for hydrogen (as done in previous works) introduces significant changes in many properties.

Acknowledgements

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