
Simulations of a neutral complex (OH^- , H_3O^+)

Abstract

Using molecular dynamics, we studied the temporal evolution of the molecular system (OH^- , H_3O^+). We simulated a new model (Model 1) of atomic force fields, which we compared to others (TIP3P, COSMO, SPC/E) with fixed charges.

We found that the diffusion of hydroxide (OH^-) is primarily vehicular, and that of hydronium (H_3O^+) is structural.

Keywords: Water; the hydrogen bond; TIP3P; SPC / E; molecular dynamics.

1. Introduction

Water has varied physical properties due to the formation of three-dimensional hydrogen bond networks [1].

This research is based on establishing an equilibrium concentration distribution (OH^-) and (H_3O^+), which is an important factor in creating materials with specific properties for various applications such as filtration, water purification, gas separation, and more. These membranes can be made from organic or inorganic materials, including solids like metals, ceramics, homogeneous films, polymers, or liquids.

A new model (Model 1) is suggested and compared with other references (TIP3P, COSOM, and SPC/E). The system is stable at room temperature. The Nosé-Hoover solid chain thermostat is an algorithm used in molecular dynamics simulations to control the temperature of the system (OH^- , H_3O^+) and is monitored by a canonical dynamics (NVT) process from 0 to 1000 ps. Dispersion forces were accounted for using the DCACP (Dispersion-Corrected Atomic Nucleus Pseudopotential) scheme. The B-LYP+DCACP method is used in previous studies because it provides good results for interactions [2,3].

The study of the complex ($\text{HO}^- \dots \text{H}_3\text{O}^+$) in a water box with counterions (H_3O^+), corresponding to a concentration of 0.01 mol/l. This research addresses two main areas:

- 1- The effect of concentration
- 2- The choice of the appropriate model based on the models (TIP3P, COSOM, SPC/E)

2. Methodology

The system simulated by molecular dynamics “MD” using the modified AMBER.10 software [4] in which the potential energy U is described empirically by a sum of the bond, angle and dihedral strain energies and one additive per pair 1-6-12 (electrostatic + van der Waals) interactions between unbound atoms.

$$U = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_{\Theta} (\Theta - \Theta_{\text{eq}})^2 + \sum_{\text{dihedrals}} \sum_n V_n (1 + \cos n\phi) + \sum_{i < j} 4\epsilon_{ij} \left(\left(\frac{R_{ij}^0}{R_{ij}} \right)^{12} - \left(\frac{R_{ij}^0}{R_{ij}} \right)^6 \right) + \sum_n q_i q_j / R_{ij} - C / R_{ij}^6$$

The terms representing the interaction between two or more van der Waals variables were constructed according to the Lorentz-Berthelot rules. The parameters of the H_3O^+ and HO^- ions are taken from references [5].

The H_3O^+ electric charges were modified or positioned to correspond to specific electric potentials (DFT-B3LYP / 6-31G ** calculations). for water [6,7].

Periodic boundary conditions allow the simulation of systems repeated indefinitely in space, at 300 K in a cubic box of 5 Å on each side. Each box contains 256 water molecules.

The systems were first minimized by the conjugate gradient energy minimization method. Then, the system temperature is gradually increased until reaching the room temperature plateau of 300 K. The simulation is performed at constant pressure ($P = 1$ atm) on an isothermal-isobaric (NPT) ensemble. NPT equilibration at 300 K for 10 ns is performed for the system. Langevin dynamics is a tool for modeling the dynamics of molecular systems, particularly for controlling temperature, (thermostat.). Langevin Nose-Hoover dynamics is not directly a means of controlling pressure, but can be used to simulate a system where pressure is controlled by external forces. Cell volume variations occurred uniformly in all directions during this period. At the end, the system volumes reached stable values with cell edge lengths of 39.68, 39.48, and 39.65 Å.

In simulation, the units used to represent the model are fixed, while maintaining constant temperature (300 K), volume (NVT ensemble) after 10 ns, and an MD time step of 1 fs. The Leapfrog algorithm was used to integrate the equations of motion, and trajectories were stored every 1000 fs.

3. Results

3.1. Temperature and energy

Temperature measurements were performed on all four models (TIP3P, COSMO, SPC/E, and Model 1). It is clear that both temperature and energy values fluctuate during the equilibrium period and during the production cycle. The energy of the systems also reaches a near-steady state, indicating a good equilibrium.

3.2. (OH^- , H_3O^+) (H_2O)₂₅₆ Structure

The radial distribution function, which describes the probability of finding an oxygen atom within a certain distance of another oxygen atom in a system (OH^- , H_3O^+). These values are used to analyze the structure of condensed systems such as liquids and solids, and to understand the interactions between atoms. These are calculated for the three models (TIP3P, SPC/E, and Model 1), and the results are compared with data from previous work.

The calculations are performed by taking the average of all the oxygen atoms of the ions, and the results are presented in Figure (1). We did not consider the COSOM model, because it has a 20% larger O-O volume than the TIP3P model, according to the literature.

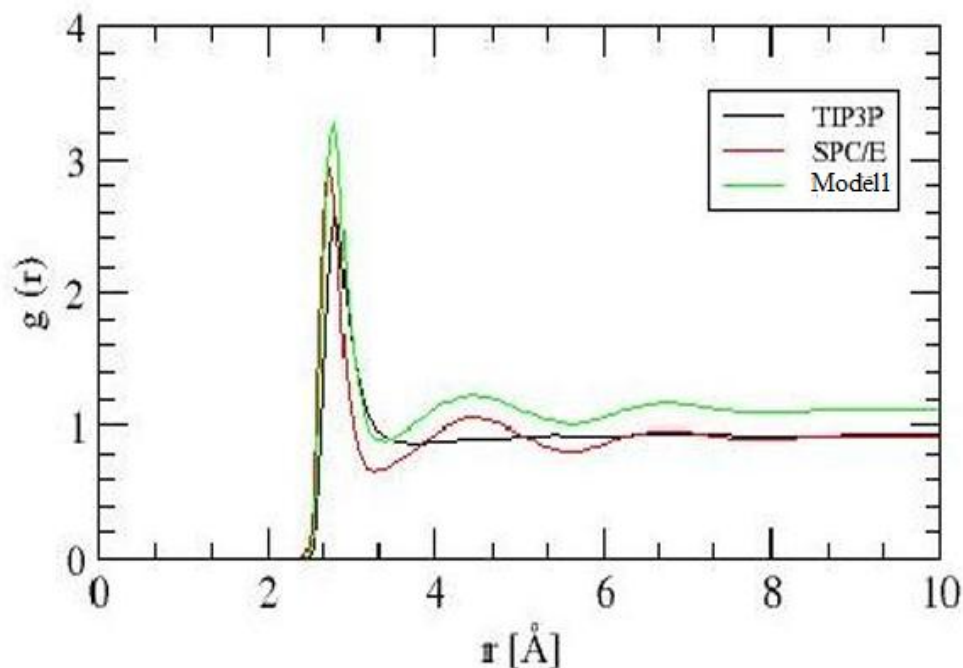


Figure 1. Pairwise correlation function, $g(r)$, of ions for all three models.

For all three models, a first peak is observed for TIP3P, SPC/E and model 1 at about 2.8 Å, 2.7 Å and 2.6 Å, respectively. The description refers to the distribution of ions in a solvent model. A first peak, which represents the ionic structure, is followed by a second at about 4.6 Å in model 1 and SPC/E. Beyond this second peak, the ionic structure attenuates considerably, except in model 1 where it persists more.

a difference in water structuring between three models (Model 1, TIP3P and SPC/E). Model 1 shows a more pronounced structuring, as evidenced by its first intense peak, unlike TIP3P and SPC/E whose peaks are less pronounced. Model 1 has a greater amount of hydrogen bonds between water molecules, compared to the TIP3P and SPC/E models, and these values are listed in Table (1). Hydrogen bonds are important intermolecular forces that influence the properties of water.

TABLE 1: Parameters of TIP3P, SPC/E, COSOM and Model1 (OH^- , H_3O^+)

Parameters	TIP3P	SPC/E	COSOM	Model 1
$r_{\text{OO}} (\text{Å}^\circ)$	2.805	2.805	2.085	2.085
$\sigma_{\text{OO}} (\text{Å}^\circ)$	5	5	5	5
$r_{\text{OH}} (\text{Å}^\circ)$	0.98	0.98	0.98	0.98
HOH angle	110.025	110.025	110.025	110.025
$q_{i(e)}$	-0.8340	-0.8340	-0.8340	-0.8340
$q_{j(e)}$	0.417	0.417	0.417	0.417
C_{ij}				8210.2

3.3. Mouvement translationnel

Le mouvement translationnel des ions est étudié à l'aide de trajectoires simulées en calculant les déplacements quadratiques moyens (DMS) $\langle \Delta r^2 \rangle$ des ions. Le DMS peut être défini comme suit :

$$\langle \Delta r^2 \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle$$

où $r_i(t)$ et $r_i(0)$ sont les vecteurs de position de l'atome d'oxygène de la i ème molécule d'ion à l'instant t et à $t = 0$, respectivement.

La moyenne est calculée sur tous les ions-waters à différents instants. Les calculs sont effectués pour les quatre modèles. Les valeurs sont présentées dans le tableau II.

TABLE 2. Self-Diffusion co-efficient, D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$) values of TIP3P, SPC/E, MOSOM and model1. The experimental D value for ion-water has also been included in the table for comparison.

Systems	Self diffusion co-efficients (D)water	Self diffusion co-efficients (D) H_3O^+	Self diffusion co-efficients (D) OH^-
TIP4P	3.8	-	-
SPC/E	2.8	-	-
MOSOM	2.5	0.09	0.35
Model 1	2.7	0.070	0.13
OH^- [32]	0.17	-	0.45
Water (experiment) ^{33,34}	2.3	-	-

Comparing the values with the available experimental data, we find that among the four models (TIP3P, SPC/E, MOSOM and model 1), the value of the self-diffusion coefficient for COSOM water ions and model 1 is well correlated with the experimental value.

4. Discussion

The hydroxide ion is surrounded by water molecules. This aquatic environment forms a layer of water called "solvation sphere" where water molecules interact with the hydroxide ion, mainly by hydrogen bonds at 2.7 Å , these results are confirmed by the sources mentioned in reference [11, 12, 13, 14, 15, 16, 17, 18, 19] which contains two water oxygens and one hydronium ion (H_3O^+) (instead of three).

The second solvation shell is located about 4 (Å) from the central ion. This result is consistent with the data found in references [11, 12, 13, 14, 15, 16, 17, 18, 19]) contains eight oxygens. It is well known that the diffusion mechanism of hydroxide ions (-OH) is strongly influenced by the structure of the (-OH) solution [11, 12, 13, 14, 15, 16, 17, 18, 19].

These ions (-OH) are generated by the dissociation of a base in water and increase the pH of the solution. the hydroxide (-OH) ion and the two water molecules continue to diffuse by vehicle diffusion to the neighboring cation until the hydroxide (-OH) ion forms the stable triple “resting” structure again near the next cation.

The first solvation shell of the hydronium ion (H₃O⁺) is located at 2.6 Å. To better understand Under the diffusion conditions of hydronium ions (H₃O⁺), the first peak, located at approximately 4.2 Å, corresponds to H.. -OH, in which an H₃O⁺ has transferred a proton to an HO⁻, The second peak is at 3.7 Å. The values for the first and second solution layers are 2.7 and 4.2 Å, respectively. the reaction:

$\text{OH}^- + \text{H}_3\text{O}^+ \leftrightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$, the complex has a neutral charge To verify this, we calculate the percentage of time that the hydronium ions (H₃O⁺) spend in the form of HO⁻ and H₂O.

which proves that the hydronium ion (H₃O⁺) appears in the form of H₂O for 48.78% of the simulation time.

The protonation state of the system (-OH, H₃O⁺) is an important factor in the diffusion mechanism of hydronium ions (H₃O⁺).

Model 1 and MOSOM simulations were used to obtain an in-depth atomistic perspective of two models, SPC/E and idealized in confined geometries under hydration conditions ($\lambda = 10$ and 1000). It is observed that the distribution of water in the simulation cell is not uniform, which concludes that the effect on hydroxide (-OH) and hydronium (H₃O⁺) ions is fundamentally different. Hydroxide ions generally have a first layer, where solvent molecules interact directly with the ion, and a second layer, which is less strongly bound.

The diffusion mechanism is mainly vehicular [20]. Whereas, the diffusion of hydronium ions (H₃O⁺) is structural rather than vehicular, with the participation of anions according to the reaction: $\text{OH}^- + \text{H}_3\text{O}^+ \leftrightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$ (see Figure 2).

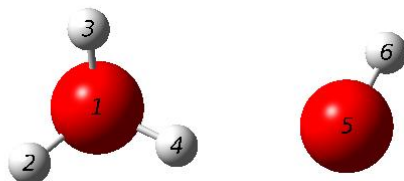


Figure 2. the structure (OH^- , H_3O^+).

Comparing water diffusion, it is found that for model 1, The diffusion coefficient of hydroxide ions is considerably higher than that of water molecules, partly due to the water-specific proton transport mechanism., because the vehicle The diffusion is synchronized between the two species. However, for the TIP3P and SPC/E models, water molecules diffuse much more slowly than hydronium ions (H_3O^+), Structural diffusion of hydronium ions (H_3O^+) is a complex process where the mobility of individual water molecules is not necessary, but the structure of water plays a crucial role.

In this work, the study focuses on the detailed atomistic mechanisms of transport of the hydroxide ion (OH^-) and the hydronium ion (H_3O^+). This atomistic approach makes it possible to identify the fundamental steps that govern the migration of these ions in a medium, particularly focusing on interactions with environmental molecules. It was found that the diffusion of hydroxide (OH^-) is vehicular, and that of hydronium (H_3O^+) is structural

The results presented show that (OH^-) ions diffuse only when they possess a second solvation shell containing at least one water oxygen. This second solvation shell provides the hydration required for (OH^-)

we observe that the second solvation layer favors vehicular diffusion.

Molecular simulation allowed us to understand the phenomenon of hydration in a clean ionic complex (OH^- , H_3O^+).

5. Conclusion

In this research, we determined a new model that represents well the diffusion of ionic ions. Compared with other similar models, TIP3P and SPC/E, we concluded that the diffusion of hydroxide (OH^-) is mainly vehicular, while that of hydronium (H_3O^+) is structural.

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