



Chemical Engineering Communications

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcec20>

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Accepted author version posted online: 14 Oct 2014.

To cite this article: A. Ansari Dezfoli, M. A. Mehrabian & H. Hashemipour (2014): Molecular Dynamics Simulation of Heavy Metal Ions in Aqueous Solution Using Lennard-Jones 12-6 Potential, Chemical Engineering Communications, DOI: [10.1080/00986445.2014.970251](https://doi.org/10.1080/00986445.2014.970251)

To link to this article: <http://dx.doi.org/10.1080/00986445.2014.970251>

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Molecular Dynamics Simulation of Heavy Metal Ions in Aqueous Solution Using Lennard-Jones 12-6 Potential

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Abstract

The dynamic and structural properties of some heavy metal ions such as Cd^{2+} , Ni^{2+} , and Zn^{2+} solved in water, were studied using Molecular Dynamics (MD) simulation. In this paper the Radial Distribution Function (RDF) and self-diffusion coefficient were determined and compared with the experimental data. The results showed that the surrounding water molecules around the metal ions form a shell-like arrangement. The number of water molecules contributing in this arrangement (N_c) for Ni^{2+} , Cd^{2+} , and Zn^{2+} were respectively 8.8, 7.4, and 6. Noticeable differences between the simulation results and experimental data were observed for the nickel ion structural properties when the MM2 Lennard-Jones parameters were used to predict the interaction of nickel and water molecules. To resolve this problem, the new Ni^{2+} -water Lennard-Jones interaction parameters were used in the MD simulation program to predict the structural properties of Ni^{2+} solution, which gave acceptable results.

KEYWORDS: Separation, Heavy metal ions, Structural properties, Ion water solution

INTRODUCTION

Some heavy metals like iron, cobalt, copper, manganese, and zinc are necessary for living organisms and humans; but exceeding the standard threshold has toxic effects and is dangerous for human health, animals, and plants. Almost all toxic heavy metals are found in aqueous solutions polluted by industrial and mining activities (Wu et al., 2006; Hu et al., 2006; Viral et al., 2004; Xu et al., 2008). It is therefore necessary to remove the toxic heavy metals from wastewater before releasing into the environment. Finding the best operating conditions for removing the heavy metal ions from wastewater requires good knowledge of dynamic and thermodynamic properties of heavy metal solutions.

In recent years, various ion solutions have been studied using MD and Monte Carlo (MC) simulation methods. Lee and Rasaiah (1994) investigated the behavior of alkali metal cation solution in an electric field of 1.0 V/nm and outside the field both at 25°C. They found that some properties of the solution like velocity and force auto-correlation functions are field independent. Their results also show that the surrounding water molecules around the metal ions form a shell-like arrangement named hydration shell. The first hydration shell around the cations moves with ions for a limited time. It was observed that this time for Li^+ , Na^+ , Rb^+ , and Cs^+ was respectively 190 ps, 35 ps, 8 ps, and 11 ps. Kuzminy (1997) adopted x-ray absorption spectroscopy and MD simulation for analyzing the hydration of Zn^{2+} ions in water. They found that the number of water molecules contributing to make the shell-like arrangement for Zn^{2+} is 6, where the inter-atomic distance between oxygen and zinc ions was $2.06 \pm 0.02 \text{ \AA}$.

Inada et al. (2002) used classical MD, classical MC, and combined Quantum Mechanical/Molecular Mechanical (QM/MM) simulations to study the structural properties of Ni^{2+} aqueous solution. They showed that Ni-O distance for the first hydration shell was 2.14-2.25 Å. They also observed a 6-8 coordinate hydration number. Bastug and Kuyucak (2005) investigated the effect of temperature changes on the transport properties (conductivity and diffusion coefficient) of ions in common salt solutions like NaCl, KCl, and CaCl_2 . They observed that by increasing the temperature, the ion transport coefficients are increased. Holovko et al. (2005) studied the effect of ion charge on dynamic and structure of ion in the aqueous solution. The results demonstrated that the average distance between the oxygen in the first hydration shell and M^{Z+} ion increases from 1.63 Å for $Z=6$ to 2.33 Å for $Z=1$. They also showed that the self-diffusion coefficient for mono-valent cation is almost half of that for di-valent cation. An extremely long MD simulation time was employed by Chillemi et al. (2005) to find the structural properties of first coordination shell of water molecules around Cd^{2+} ion. They found the $\text{Cd}^{2+}\text{-(H}_2\text{O)}_6$, $\text{Cd}^{2+}\text{-(H}_2\text{O)}_7$, and $\text{Cd}^{2+}\text{-(H}_2\text{O)}_8$ clusters respectively after 65.97, 34.90, and 0.13 ns. The N_c and $\text{Cd}^{2+}\text{-O}$ distance were respectively 8-6.3 and 2.22-2.33 Å. Mohammed et al. (2005) applied constructed ab initio two-body potentials and a three-body correction function to study the structural data and dynamic properties of Zn^{2+} in aqueous solutions. The results showed 2.16-2.23 Å distance between Zn^{2+} ion and oxygen in the first hydration shell. The results also predicted that the Zn-water cluster is present in the form of $\text{Zn}^{2+}\text{-(H}_2\text{O)}_6$ at the simulation time. Johnson et al. (2006) derived solvation energy for Cd and Pb using MD simulation. They considered a periodic water

box consisting of one cation and 216 water molecules. They obtained the solvation energy for Cd and Pb respectively as -373.4 and -325.3kcal/mol.

A system consisting of one Pb (II) and 499 water molecules was simulated to study the hydration structure of Pb^{2+} by Ali Shah et al. (2006). They found that the first peak of Pb^{2+} -O RDF is located at a distance of 2.07 Å from the ion center. The properties of cadmium ion in water were also investigated by D' Angelo et al. (2008); using a coupled MD method and XANES data analysis. For simulation of water molecules, they employed the SPC/E and TIP5P models. The theoretical diffusion coefficients they calculated for cadmium ion were respectively 0.68 and 0.73 for SPC/E and TIP5P models. They also found that the cadmium-water clusters in $\text{Cd}(\text{H}_2\text{O})_6$, $\text{Cd}(\text{H}_2\text{O})_7$, and $\text{Cd}(\text{H}_2\text{O})_8$ forms exist in different times. The hydration free energy, structure, and dynamics of the zinc cation solved in water were studied by Wu et al. (2010). They found that the number of water molecules contributing to make the shell-like arrangement is 6 for zinc. It was also found that the residence time of the water molecules in the shell around the zinc ion is 2.2×10^{-9} s.

The aim of this study is to provide full investigation on the dynamic and structural properties of heavy metal ion solutions such as RDF, and self-diffusion coefficient using MD simulation. Cadmium, nickel, and zinc were chosen for this investigation, because of their toxic properties and widespread presence in wastewater (Wu et al., 2006; Hu et al., 2006; Viral et al., 2004; Xu et al., 2008; Ruparelia et al., 2008). To examine the reliability of data, they were compared with experimental and other theoretical results.

POTENTIAL MODELS

It is difficult to detect the structure and properties of different systems in nano-scale.

Therefore, computational methods, such as MD simulation, have been widely used as the alternative approaches to determine the mechanisms of solutions and characteristics of different systems in molecular scale. In addition, water molecules are precisely modeled in MD using different models like SPC (Berendsen et al., 1981), SPC/E (Berendsen et al., 1987), and TIP4P (Jorgensen et al., 1983). The investigations show that the SPC/E model can reproduce the properties of water such as potential energy, specific heat, self-diffusion coefficient, and RDF (Berendsen et al., 1987). The SPC/E model is expressed as follows:

$$U_{Total} = U_{bond} + U_{angle} + U_{vdw} + U_{coulomb} \quad (1)$$

Where U_{bond} , and U_{angle} are respectively the bond strength and angle bending energy.

They are defined as

$$U_{bond} = \sum_{bond} k^{bond} (r_{O-H} - r_{O-H}^{eq})^2 \quad (2)$$

$$U_{angle} = \sum_{angle} k^{angle} (\theta_{H-O-H} - \theta_{H-O-H}^{eq})^2 \quad (3)$$

Where, k^{bond} and k^{angle} are force constants, r_{O-H} the bond length, r_{O-H}^{eq} the equilibrium bond length, θ_{H-O-H} the angle between H-O-H, and θ_{H-O-H}^{eq} the equilibrium angle between H-O-H. The last two terms in Equation 1 describe respectively the van der Waals (vdW) and electrostatic non-bonded interactions:

$$U_{vdw} = \sum_i \sum_{j>i} \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (4)$$

$$U_{coulomb} = \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (5)$$

In this paper a simple Lennard-Jones 12-6 potential form is used for simulation of vdW interaction. ϵ and σ are the well-depth and diameter of the potential (D' Angelo et al., 2008). q_i and q_j are the charges of atoms i and j , and are located at the center of atoms. The vdW and electrostatic non-bonded interactions between ion and water molecules were simulated. For computation of ϵ and σ between unlike atoms (O-ion interaction) the Lorentz-Berthelot mixing rule can be use (Allen and Tildesley, 1987):

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (6)$$

The cutoff radius is selected 9 Å for each molecule. The Lennard-Jones parameters, the bond strength parameters, the angle bending parameters, and the partial charges used in the present SPC/E water model are listed in Table 1. The Lennard-Jones and electrostatic parameters for heavy metal ions are listed in Table 2.

SIMULATION METHOD

The heavy metal ions/water system is modeled using an in-house computer program written in FORTRAN language. This code supports NVT (Isothermal) ensemble and uses Berendsen thermostat method (Berendsen et al., 1984) to account for the temperature of the system. In Berendsen thermostat method, the particle velocity of system at each step is rescaled by a factor, λ , which is defined as:

$$\lambda = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T}{T_0} - 1 \right) \right]^{\frac{1}{2}} \quad (7)$$

Where τ is the user defined time constant (typically 0.5–5.0 ps), T is the current temperature (298 K), T_0 is the desired temperature and Δt is the time step which was chosen as 0.5 fs. Such a small time step is necessary for adjusting simulation of the bonding and bending of the water molecules.

A periodic water box consisting of 215 water molecules in FCC initial position and one cation in the center was considered. The length of periodic water box is 18.642 Å. In addition, the initial velocities were assigned from uniform velocity distribution [Haile, 1992]. During the simulation, the Rattle algorithm was employed (Allen and Tildesley, 1987; Andersen, 1983). The Rattle algorithm is used for integrating the motion equation of molecular dynamics problem with an internal constrain. In every state, the code runs for 1×10^6 time steps, whereas the last 8×10^5 time steps were used to calculate the results. Information about the potential energy and solvation energy of solutions from the MD simulation are given in Table 3. The solvation energy is calculated by subtracting the potential energy of ion/water system from the potential energy of water system (Johnson et al., 2006).

RESULTS

Figure 1 shows the vdW, the electrostatic, and the total interaction energies between the heavy metal ion and oxygen. The total energy is defined as the sum of the vdW energy and the electrostatic energy. In distances larger than σ , both vdW interaction, and

electrostatic energy cause attractive forces, but in distances shorter than σ , the vdW interaction energy causes repulsive forces, while the electrostatic energy causes attractive forces. Thus, the total energy curves can be divided into two separate components: attractive and repulsive. The distance at which the total energy becomes a minimum is the equilibrium distance between the metal ion and oxygen. In the equilibrium distance, the repulsive and attractive forces are equal. The equilibrium distance for Ni^{2+} , Cd^{2+} and Zn^{2+} are respectively 2.73, 2.34, and 1.83 Å.

Figure 2 shows the ion-oxygen and ion-hydrogen RDF. The RDF curve can explain the atomic density of water molecules around the ions. In this paper RDF is defined as (Kalinichev and Kirkpatricka, 2007):

$$RDF = \lim_{r \rightarrow 0} \frac{p(r)}{4\pi\rho r^2 dr} \quad (8)$$

Where r is the distance from the center of ion, $p(r)$ is the number of oxygen or hydrogen atoms around the ions found at a distance between r and $r+dr$, and ρ is the number density of water molecules in the system. The RDF is zero near the ion center because of the repulsive forces between ions and oxygen that is shown in Figure 1. For all ions, the RDF curve has a peak, where after and before this peak the RDF is zero. This peak shows that the surrounding water molecules around the metal ion form a shell-like arrangement. The presence of a water shell around ions has been confirmed by x-ray diffraction (XRD) and numerical investigation (Lee and Rasaiah, 1994; Kuzmin et al. 1997; Inada et al., 2002; Holovko et al., 2005; Chillemi et al., 2005; Mohammed et al., 2005).

The key feature of Figure 2 is the difference in the location of the RDF peaks for ions.

The shell form of water molecules is located at a distance of 1.97 \AA from the Zn ion center, while it is located at a further distance from other ions. In Figures 1 and 2 one can see that ions with larger equilibrium distances are located further from their peaks. Table 4 gives more detailed comparison among Ni^{2+} , Cd^{2+} , and Zn^{2+} ions. The appearance of peak in Figure 2 is related to equilibrium time, there is a possibility that for longer or shorter equilibrium times the shoulder will be eliminated. The shoulder is most probably because of computational method.

The water molecules around a heavy metal ion are located in five regions:

- Region I: There are no water molecules because of repulsive interaction forces between oxygen and ions. This region is very close to the ions.
- Region II: The first hydration shell of water molecules is formed around an ion (the first RDF peak). The first hydration shell contains 6-9 water molecules that interact directly with the heavy metal ion.
- Region III: The second hydration shell of water molecules is formed around an ion (the second RDF peak). In this region, the water molecules interact with the ion indirectly; they also interact with the first hydration shell.
- Region IV: Disordered region, this region is located between Region III and Region V. In this region the effect of ion is negligible but this small effect can change the bulk water arrangement as indicated in the RDF curves.

- Region V: Bulk water is not affected by the ion. In this region the RDF is reduced to one. In Figure 3 the regions of water molecules around an ion are demonstrated for Zn^{2+} -oxygen RDF.

The number of water molecules contributing to make the shell-like arrangement around the ions can be calculated using RDF (Kalinichev and Kirkpatricka, 2007):

$$N_c = 4\pi\rho \int_{r=0}^{R_{\min}} \text{RDF}(r)r^2 dr \quad (9)$$

Where N_c is the number of water molecules contributing to make the shell-like arrangement around the ions and R_{\min} is the distance between the first zero value after RDF peak and CNT centerline. The number of water molecules contributing to make the shell-like arrangement obtained from Equation 9 is presented in Table 5. It was observed that the ions with large equilibrium distances have enough space to attract more water molecules in the shell arrangement. That is why Ni^{2+} has more water molecules in its shell-like arrangement.

A summary of structural parameters of the first hydration shell around heavy metal ions available in the literature are listed in Table 6.

Table 6 shows that the present results for Zn^{2+} and Cd^{2+} are in good agreement with other simulation results and experimental data. But it is clear that the Lennard-Jones potential using MM2 parameter is unable to simulate the hydration shell for Ni^{2+} correctly.

Curve fitting between 2-body potential and 6-12 Lennard-Jones potential, suggest 30.02 kcal/mol for the well depth ($\epsilon_{\text{O-Ni}^{2+}}$) and 1.73 Å for the diameter ($\sigma_{\text{O-Ni}}$) of the potential. Figure 4 demonstrates the potential using MM2 parameters, 2-body potential and Lennard-Jones with suggested parameters. The structural data of Ni^{2+} -water solution simulated by new Lennard-Jones are listed in Table 7. The new Lennard-Jones parameters can improve the results, because the new structural data are in good agreement with the experimental results for Ni ion.

The ions can be presented as $\text{M}^{2+}-(\text{H}_2\text{O})_6$, $\text{M}^{2+}-(\text{H}_2\text{O})_7$, $\text{M}^{2+}-(\text{H}_2\text{O})_8$, and $\text{M}^{2+}-(\text{H}_2\text{O})_9$ clusters in water. In this investigation the $\text{Ni}^{2+}-(\text{H}_2\text{O})_6$, $\text{Ni}^{2+}-(\text{H}_2\text{O})_7$, $\text{Ni}^{2+}-(\text{H}_2\text{O})_8$, and $\text{Ni}^{2+}-(\text{H}_2\text{O})_9$ are respectively present as 0%, 0%, 21.25%, and 78.75% of the simulation time when using MM2 parameter for Lennard-Jones potential. The higher percentage of Ni^{2+} in the form of $\text{Ni}^{2+}-(\text{H}_2\text{O})_9$ causes to shift its RDF peaks to the left, but for simulation of Ni^{2+} -water solution with new Lennard-Jones parameters, the nickel ion solution is present only in $\text{Ni}^{2+}-(\text{H}_2\text{O})_6$ form, thus its RDF peaks shift to the right. The RDF curve for Ni^{2+} with suggested parameters is shown in Figure 5. More details about heavy metal ions-water cluster are listed in Table 8. Figure 6 illustrates the $\text{Zn}^{2+}-(\text{H}_2\text{O})_6$ and $\text{Cd}^{2+}-(\text{H}_2\text{O})_7$ clusters.

The diffusion coefficient, D, is computed and reported in Table 9. For calculating D, the mean square displacement (MSD) of ions is used which is defined as (Allen and Tildesley, 1987):

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{MSD}{t} = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle [r(t+dt) - r(t)]^2 \rangle}{t} \quad (10)$$

Where r is the ion position and t is the time. The results demonstrate that the self-diffusion coefficient of ions is increased when the ion-water cluster mass is reduced. The average cluster mass of Ni^{2+} , Cd^{2+} , and Zn^{2+} are respectively (215.9-165.7), 245.6, and 173.4 AMU. Note that the force acting on all ions was almost equal.

CONCLUSIONS

In this paper the structural data of Cd^{2+} , Ni^{2+} , and Zn^{2+} ions in water were investigated. The MD simulation demonstrated that the coordinate number and ion-oxygen distance obtained using available 12-6 Lennard-Jones parameters is in good agreement with the experimental data. The coordinate number and ion-oxygen distance observed for nickel ion were respectively 8.8, and 2.64 Å. These values may not be sufficient to describe the nickel solution correctly where experimental data show the coordinate number and ion-oxygen distance observed for Nickel ion are respectively 6, and 2.06 Å. For improving MD simulation results the 12-6 Lennard-Jones potential parameters were reproduced by curve fitting. The new parameters when using 12-6 Lennard-Jones potential, are respectively 30.02 kcal/mol and 1.73 Å for the well depth ($\epsilon_{O-Ni^{2+}}$) and diameter (σ_{O-Ni}) of the potential. The new parameters have been tested and the results are in good agreement with the experimental data. Finally the comparison between the self-diffusion coefficients of all ions demonstrates that the self-diffusion coefficient of ions is increased when the ion-water cluster mass is reduced.

NOMENCLATURE

Abbreviations

AMU	Atomic mass unit
M	Metal ion
MC	Monte Carlo
MD	Molecular Dynamics
MSD	Mean Square Displacement
MM2	MM2 force field
NVT	Number, volume, temperature constant ensemble
QM/MM	Quantum Mechanical/Molecular Mechanical
RDF	Radial distribution function
SPC/E	simple point charge/Edited
TIP/3P	Transferable Intermolecular Potential/ 3 point
XANES	X-ray Absorption Near Edge Structure

English symbol

D	Diffusion coefficient, m^2/s
k^{bond}	Bond force constant, $\text{kcal}/(\text{mol} \cdot \text{\AA}^2)$
k^{angle}	Bond force constant, kcal/mol
N_c	Number of water molecules contributing to make the shell-like arrangement
$p(r)$	Number of oxygen or hydrogen atoms around the ions found at the distance between r and $r+dr$
q	Atom point charge, e

R_{\min}	Distance between the first zero value after RDF peak and CNT centerline, \AA
r	Distance, \AA
r_{O-H}	Bond length, \AA
r_{O-H}^{eq}	Equilibrium bond length, \AA
T	Temperature, K
T_o	Desired temperature, K
t	Time, s
U_{total}	Total potential energy, kcal/mol
U_{bond}	Bond strength energy, kcal/mol
U_{angle}	Angle bending energy, kcal/mol
U_{vdW}	Van der Waals energy, kcal/mol
U_{coulomb}	Electrostatic energy, kcal/mol
Z	Point charge of ion

Greek symbols

\AA	Angstrom, 10^{-10} m
θ_{H-O-H}	Angle between H-O-H, degree
θ_{H-O-H}^{eq}	Equilibrium angle between H-O-H, degree
E	Well-depth of potential, kcal/mol
ϵ_0	Permittivity of free space, $8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
Σ	Diameter of the potential, \AA
ρ	Number density, kg/m^3
T	User defined time constant

Units

E	Electron unit, $1.6 \times 10^{-19} \text{C}$
Fs	Femto second, 10^{-15}s
Ps	Pico second (10^{-12}s)

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Table 1 Parameters used in SPC/E model (Ansari dezfoli et al., 2011)

Symbol	Unit	SPC/E
r_{OH}	[nm]	1.00
θ_{HOH}	[$^{\circ}$]	109.47
ϵ_{OO}	[kcal/mol]	0.15
σ_{OO}	[nm]	0.3166
ϵ_{HH}	[kcal/mol]	0.0
σ_{HH}	[nm]	0.0
q_O	Electron unit	-0.82
q_H	Electron unit	0.41
k^{bond}	[kcal/(mol. \AA^2)]	529.6
k^{angle}	[kcal/mol.rad 2]	34.05

Table 2 Parameters used in the potential function

Heavy metal ion	σ (\AA)	ϵ [kcal/mol]	q [Electron unit]	Atomic weight	Reference
Cd^{2+}	2.76	0.047	+2	112.4	Chillemi et al., 2005
Ni^{2+} (MM2 force field)	3.91	0.02	+2	57.7	Burkert et al., 1982
Zn^{2+} (AMBER force field)	1.96	0.0125	+2	65.4	Weiner et al., 1986

Table 3 Potential and solvation energy values for the cations

System	Total Potential Energy (kcal/mol) This work	Solvation Energy (kcal/mol) This work	Solvation Energy (kcal/mol) Experimental data
water	-1986.0±4	-	-
Ni ²⁺ - water	-2377.3 ±11	-391.3	-
Cd ²⁺ - water	-2345.7±8	-359.7	-436.9 ^(Franks, 1973)
Zn ²⁺ - water	-2450±4	-464.0	-467.7 ^(Marcus, 1994)

Table 4 Peak position of RDF curve for the cations

Cations	Peak in ion-O RDF (Å), this work
Ni ²⁺	2.64
Cd ²⁺	2.37
Zn ²⁺	1.97

Table 5 Number of water molecules contributing in the shell-like arrangement around the cations

cations	N_c
Zn^{2+}	6
Cd^{2+}	7.4
Ni^{2+}	8.8

Table 6 The structural parameters of the first hydration shell

Solution	Method	Potential model	N_c	Peak in ion-O RDF (Å)	Ref
Ni^{2+} - water	MD	Lennard-jones 6- 12	8.8	2.64	This work
Ni^{2+} - water	MD	2 and 3-body interaction	6	2.25	(Inada et al., 2002)
Ni^{2+} - water	MC	-	6	2.21	(Inada et al., 2002)
Ni^{2+} - water	QM/MM- MD	2 and 3-body interaction	6	2.14	(Inada et al., 2002)
Ni^{2+} - water	MD	2and 3-body interaction	8	2.17	(Bounds, 1985)
Ni^{2+} - water	MC	2-body interaction	8	2.09	(Cordeiro et al., 1993)
Ni^{2+} - water	Experimental	-	6	2.06	(Inada et al., 2002)
Cd^{2+} - water	MD	Lennard-Jones 6- 12	7.4	2.37	This work
Cd^{2+} - water	MD	2-body interaction	8	2.33	(Chillemi et al., 2005)
Cd^{2+} - water	MD	2-body interaction	6.3	2.22	(D'Angelo et al., 2008)

Cd^{2+} - water	MD	2-body interaction	7	2.27	(Chillemi et al., 2005)
Zn^{2+} - water	MD	Lennard-Jones 6- 12	6	1.97	This work
Zn^{2+} - water	QM/MM MD	2-body interaction	6	2.16	(Mohammed et al., 2005)
Zn^{2+} - water	MD	2-body interaction	6	2.23	(Mohammed et al., 2005)
Zn^{2+} - water	QM/MM MD	2-body interaction	6	2.06	(Kuzmin et al., 1997)
Zn^{2+} - water	MD	2-body interaction	6	2.08	(Kuzmin et al., 1997)
Zn^{2+} - water	MD	Buffered 14-7	6	1.98	(Wu et al., 2010)
Zn^{2+} - water	Experimental	-	6	2.07	(D'Angelo et al., 2002)

Table 7 The structural data of Ni^{2+} -water solution

Ion	N_c	Peak in ion-O RDF (\AA)
Ni^{2+}	6.02	1.93

Table 8 Percentage of ion-water cluster of the simulation time

Heavy metal ion	$M^{2+}-(H_2O)_6$ cluster	$M^{2+}-(H_2O)_7$ cluster	$M^{2+}-(H_2O)_8$ cluster	$M^{2+}-(H_2O)_9$ cluster
Ni ²⁺ Simulated using MM2 parameters	0	0	21.25	78.75
Ni ²⁺ Simulated using new vdW parameters	100	0	0	0
Cd ²⁺	2.5	57.5	40.0	0
Zn ²⁺	100	0	0	0

Table 9 Diffusion coefficients, D, for heavy metal ions in water

Heavy metal ion	D ($\times 10^{-10} \text{m}^2/\text{s}$)
Ni ²⁺ - Simulated using MM2 parameters	9.61
Ni ²⁺ - Simulated using new Lennard-Jones parameters	9.67
Cd ²⁺	6.78
Zn ²⁺	9.65

Figure 1 vdW, electrostatic and total Interaction energies between metal ion and oxygen

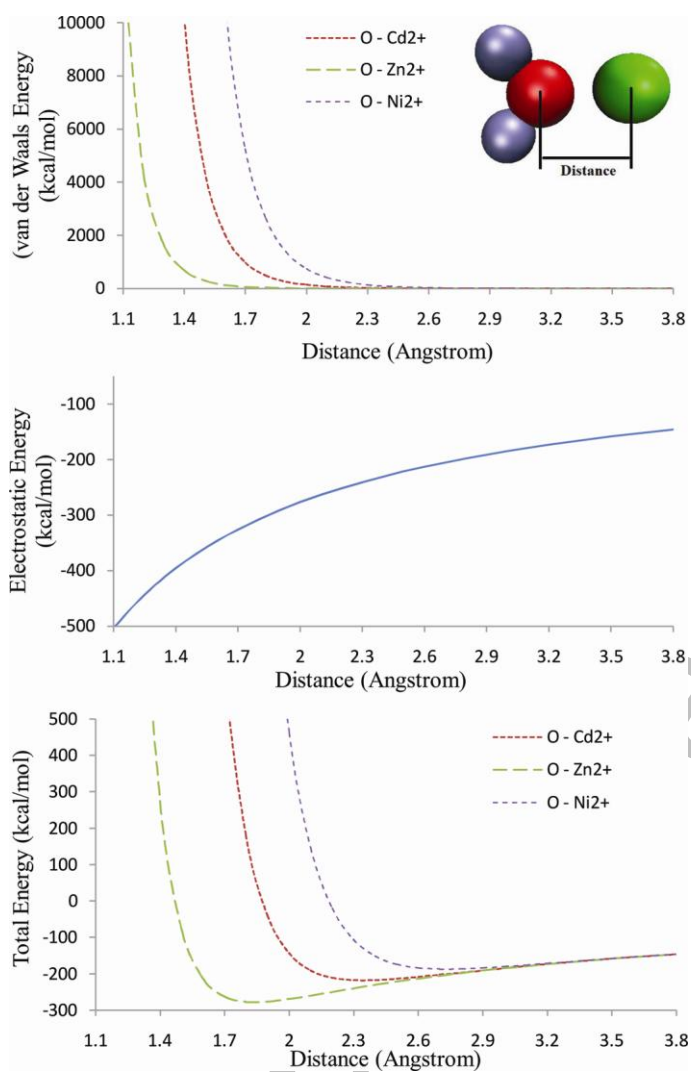


Figure 2 The RDF curve for ion-Oxygen and ion-Hydrogen in water for three cations

Ni^{+2} , Cd^{+2} and Zn^{+2}

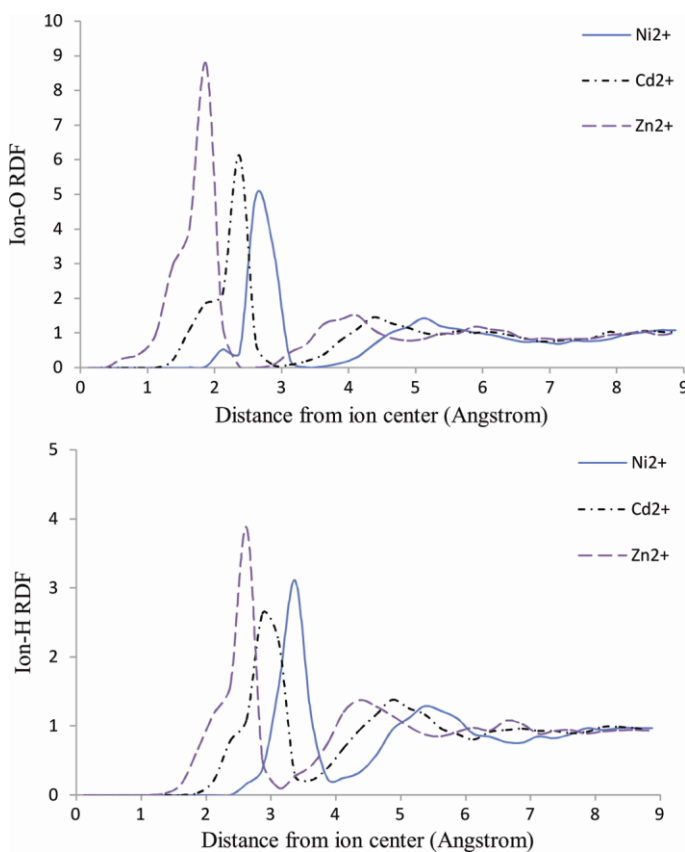


Figure 3 Different water molecules regions around an ion of Zn^{+2}

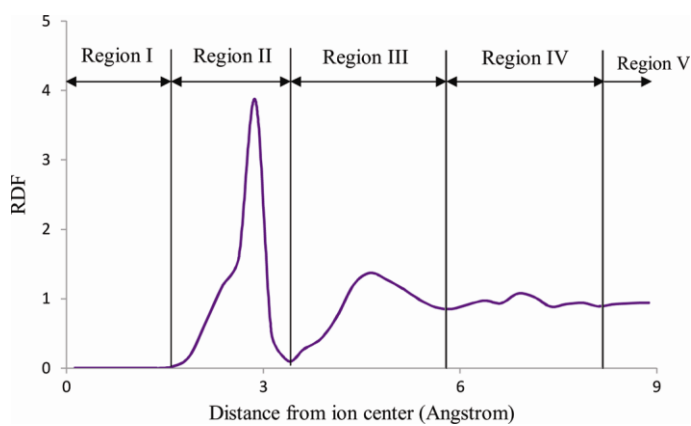


Figure 4 MM2 Lennard-Jones potential, 2-body potential and Lennard-Jones potential with suggested parameter.

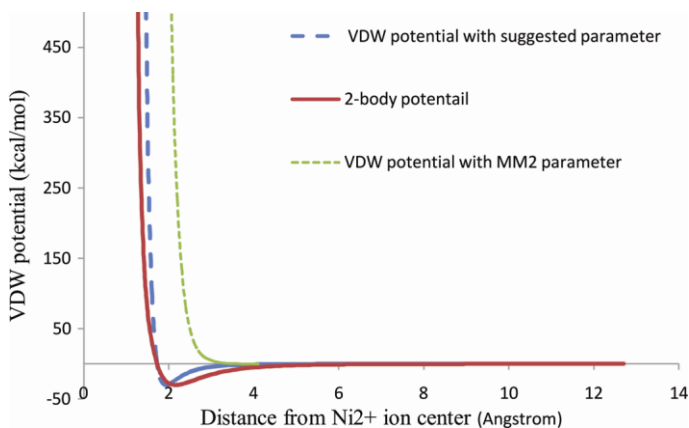


Figure 5 (A) Ni-O and (B) Ni-H radial distribution functions with new Lennard-Jones parameter

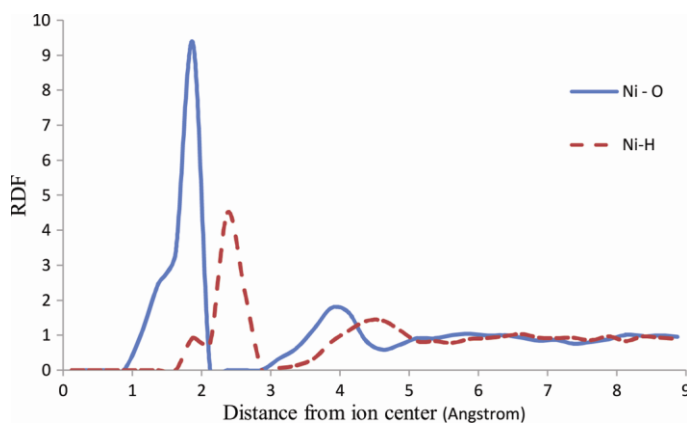


Figure 6 The snapshots of water molecules ion-water cluster $\text{Zn}^{2+}\text{-(H}_2\text{O)}_6$ (b) $\text{Cd}^{2+}\text{-(H}_2\text{O)}_7$ clusters

