

Hydration Structures and Dynamics of Ga³⁺ Ion Based on Molecular Mechanics Molecular Dynamics Simulation (Classical DM)

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ABSTRACT

The structure and hydration dynamics of Ga³⁺ ion have been studied using classical Molecular Dynamics (MD) simulations. The data collection procedure includes determining the best base set, constructing 2-body and 3-body potential equations, classical molecular dynamics simulations based on 2-body potentials, classical molecular dynamics simulations based on 2-body + 3 potential-body. The trajectory file data analysis was done to obtain structural properties parameters such as RDF, CND, ADF, and dynamic properties, namely the movement of H₂O ligands between hydrations shells. The results of the research indicated that the hydration complex structure of Ga(H₂O)₈³⁺ and Ga(H₂O)₆³⁺ was observed in molecular dynamics simulations (MM-2 body) and (MM-2 body + 3-body), respectively. The movement of H₂O ligands occurs between the first and second shell or vice versa in the MD simulation of MM-2 bodies but does not occur in MD simulations of (MM-2 bodies + MM-3 bodies). Therefore, the water ligands in the first hydrated shell are stable.

Keyword: hydration, simulation, 2-body potential, 3-body potential, 2-bodyMM, 3-bodyMM, ion Ga³⁺

1. INTRODUCTION

Along with the development of science, understanding of chemistry does not only occur because of the results of observations of an experiment in a laboratory, but also the development of quantum mechanical theory, which is to predict the properties of an atom or molecule. And also along with the development of computer science, it can also be resolved and lead to the birth of a new subfield, namely computational chemistry, which studying the relationship between chemical compounds and modeling a compound using a computer that aims to produce physicochemical data from an element or compound, chemical reactions and molecular interactions that are not easy to do with experiments

One of the properties that can be known through computational chemistry is hydration. An example of hydration carried out in this research is the hydration of Ga³⁺ ions. The structure and dynamics of the hydration of Ga³⁺ ions with water (H₂O) ligands are interesting to study. Gallium is a post-transition metal. It is a metallic element that lies between the transition metals and metalloids (nonmetals) on the periodic table. Post-transition metals have some of the properties of transition metals but tend to be softer and behave worse. Gallium is an element that can be found in the body in very small amounts. Some vitamins and commercial drinking water are known to contain very small amounts of gallium at concentrations of less than one part per million. Gallium ion is usually used as a

drug in the form of gallium nitrate, which is a drug to reduce high levels of calcium due to cancer. The growth of cancer cells can cause changes in calcium metabolism and the breakdown of calcium from bones.

Simulations on determining the structure and hydration dynamics of Ga^{3+} ions can be carried out using Monte Carlo (MC) and Molecular Dynamics (DM) simulations (Pranowo and Hetadi, 2011). DM simulation is divided into two, namely classic DM and DM MK/MM. DM MK/MM simulation provides accurate simulation results. However, the DM MK/MM simulation requires a relatively longer time than other methods.

This study uses a classic DM simulation to get accurate results and in accordance with the experiment. Of course, to obtain accurate results, several steps are needed, including: selection of an appropriate base set, arrangement of 2-body potentials, arrangement of 2-body potentials with 3-body correction and DM/MM simulation of ion (Ga^{3+}) and ligand (H_2O) interactions.

2. RESEARCH METHOD

The equipment used in this research is a PC (Personal Computer) with specifications: Linux OS openSUSE 13.2, Intel Core i3 2.1 GHz, 3,76GB effective RAM, 2GB NVIDIA GT GPU, 1TB hard disk. The software used in this study include Gauss View, Gaussian 98W, Turbomole 5.10, DM simulation program, TmoleX, and xmgrace.

2.1. Determination of Ga^{3+} - H_2O coordinate

The initial geometry of Ga^{3+} in H_2O is modeled in three-dimensional Cartesian coordinates by adjusting the angles and distances between atoms in the system. By using the software, namely Gauss View, a structure can be generated in the form of a Ga^{3+} - H_2O coordinate system. With the help of Gauss View, if written in Cartesian coordinates, the initial geometry is Ga^{3+} in H_2O . In addition to the help of Gauss View, the coordinates of Ga^{3+} - H_2O in the Cartesian coordinate system can also be obtained by reading the output data from the Gaussian09W program running the Ga^{3+} - H_2O ion. The geometry of the H-O-H angle based on experimental data is 104.5° and the O-H bond length is 0.9601 (Armunanto, 2004).

2.2. Determination of Proper Basis Set

The basis set selected in this study is a basis set that does not cause a significant change in charge on the Ga^{3+} ion and has a bond energy curve profile with respect to the Ga^{3+} -O and Ga^{3+} -H distances according to the Lennard-Jones potential curve.

2.3. Construction of Pair Potential and 3-body Potential

Ga^{3+} - H_2O pair potential function was calculated using the ab initio method at the Restricted Hartree-Fock (RHF) level. To construct the Ga^{3+} - H_2O pair potential, energy points are needed at various theta (θ) and phi (φ) angles as well as at various cation and ligand distances. Theta (θ) angle varies from 0° to 180° with certain intervals (0, 30, 50, 70, 120, 150, 180), while the phi (φ) angle is zero (0) degrees. Cation and ligand distances are set from 1.0 to 15. These energy points are used to construct the pair potential function. The collection of these energy points is done with the help of the Turbomole program on Linux OS. The pair potential of Ga^{3+} - H_2O was constructed based on equation:

$$\Delta E_{Fit}^{2bd} = \sum_{i=1}^n \frac{q_M q_i}{r_{Mi}} + \frac{A_i}{r_{Mi}^a} + \frac{B_i}{r_{Mi}^b} + \frac{C_i}{r_{Mi}^c} + \frac{D_i}{r_{Mi}^d}$$

a,b,c,d is exponential number while A_i , B_i , C_i and D_i are fitting parameters of ion-O and ion-H, r_{Mi} is atomic distance at-i from Ga^{3+} and H_2O , q_i and q_M are atomic charge of Ga^{3+} and H_2O .

In the Ga^{3+} - H_2O pair potential and 3-body potential construction, it used DZP basis set for O and H and modified Ahlrics TZV for Ga^{3+} . To construct the 3-body potential based on the fitted pair potential, it needs interaction energy points between H_2O - Ga^{3+} - H_2O . Pre-defined H_2O - Ga^{3+} - H_2O configuration parameters are required. The parameters in question are variations in the distance Ga^{3+} -

O, r_1 ($1.6 \leq r_{\text{Ga}^{3+}\text{-O}} \leq 6.0$), r_2 ($1.5 \leq r_{\text{Ga}^{3+}\text{-O}} \leq 7.0$) and r_3 , the distance O-O between two water molecules, and the torsional angles ($\tau = 0^\circ, 30^\circ, 60^\circ, \text{ and } 90^\circ$) between the planes of the two ligands calculated by the ab initio method at the Restricted Hartree-Fock (RHF) level.

The Ga^{3+} ion hydration simulation begins with a classic DM simulation using the MM2bd simulation performed for 100 ps, then continued with the MM2bd simulation with 3-body correction performed for 100 ps. In all interactions at the final configuration stage the results from the MM2bd simulation are used as the initial configuration of the 3-body corrected MM2bd simulation by looking at the RDF graph results derived from the trajectory files analysis.

2.4. Data Analysis

The data obtained in the molecular dynamics simulation of molecular mechanics is in the form of a trajectory file. The file was further analyzed to obtain information on the structural properties and solvation dynamics between Ga^{3+} ions and water. The trajectory file processing is carried out on the structure including the radial distribution function (RDF), the coordination number distribution (CND), and the angle distribution function (ADF) as well as their dynamic properties.

3. RESULTS AND DISCUSSION

The base set used for hydrogen and oxygen atoms is the Dunning DZP base set (Dunning, 1970). For the Ga^{3+} ion, the base set used is the modified Ahlrics TZV. This modification does not cause a significant change in charge of the Ga^{3+} ion and has a curve profile of interaction energy vs. distance with respect to $\text{Ga}^{3+}\text{-O}$ in accordance with the profile of the Lennard-Jones potential curve.

3.1. Radial Distribution Function (RDF)

The radial distribution Function (RDF) of $\text{Ga}^{3+}\text{-O}$ dan $\text{Ga}^{3+}\text{-H}$ with and without 3-body potential are shown in Figure 1 and 2. The RDF graph of the Ga^{3+} hydration using pair potential only (Figure 1) shows that the curve starts to rise at a distance of 1.8 Å with peak between 1.965 Å and 2.3 Å. It indicated that there is an interaction between Ga^{3+} ions and oxygen atoms (O) from water molecules (H_2O) in the first shell layer at a distance of 1.965 Å. The graph also shows the integration number of the O atom showing the number 8. This means that in the first shell layer there are 8 O atoms bonded as ligands by Ga^{3+} at a distance of 4.1 Å. Integration number of H atom was found at 16, means there are 16 hydrogen at the first shell at a distance of 4,8 Å.

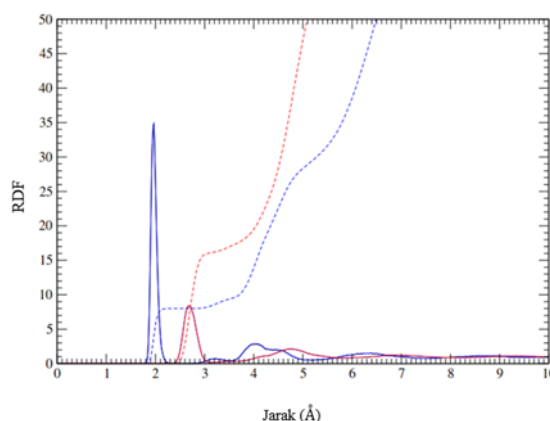


Figure 1. RDF of Ga^{3+} hydration using MM2bd

The RDF graph of the hydration of the Ga^{3+} MM2b+3bd simulation (Figure 2) shows the calculation results of the classical molecular dynamics (MM2b+3bd) simulation of the hydration system of the $\text{Ga}^{3+}\text{-H}_2\text{O}$. Based on the figure, it is found that the curve starts to rise at a distance of 1.8 then reaches a peak at a distance of 1.915 and ends at a distance of 2.1 Å. At a distance of 1.915 Å, the peak point indicates the interaction between the Ga^{3+} ion and the O atom of the water molecule (H_2O) in the first shell layer. In the graph, the integration number of the O atom shows the number 6 which means

that there are 6 O atoms bonded as a ligand by the Ga^{3+} in the first shell. The RDF graphs performed on $\text{Ga}^{3+}\text{-O}$ and $\text{Ga}^{3+}\text{-H}$ both the results from the MM2bd and MM2b+3bd simulations produce almost the same graphs, only the difference lies in the interaction distance between the ions. In the second shell, the distance between oxygen atoms (O) and Ga^{3+} ions is at the peak of 4.4 Å, which indicates the interaction of oxygen atoms (O) with Ga^{3+} .

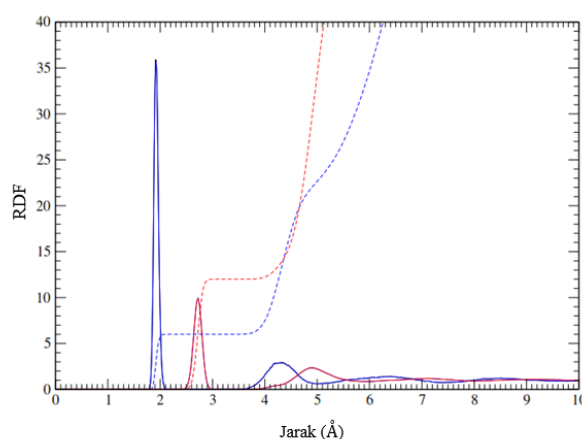


Figure 2. RDF of Ga^{3+} hydration using MM2bd+3b

In addition to the interaction between the central ion Ga^{3+} and the oxygen atom (O), Figure 2 also shows an interaction between the central ion Ga^{3+} and the hydrogen atom (H) of a water molecule (H_2O) at a distance of 2.7 Å and the integration number of the H atom is shown to be at number 12. This distance looks further when compared to the distance between the oxygen atom and the Ga^{3+} ion. This shows that the first peak of the RDF of $\text{Ga}^{3+}\text{-O}$ and $\text{Ga}^{3+}\text{-H}$ does not overlap. In the second shell layer, the distance between hydrogen atoms (H) and Ga^{3+} ions is at a peak of 4.9 Å which indicates the interaction between hydrogen atoms with Ga^{3+} .

3.2. Coordination Number Distribution (CND)

Coordination Number Distribution (CND) serves to determine the coordination number between the central ion and the ligands in the first shell and second shell. Figure 3 shows that the CND value in the first shell is 8 with a 98% probability and the CND value is 7 with a 2% probability. The same thing was found in the second shell. The number of ligands in the second shell varies from 17 to 24 with varying degrees of probability. Based on these data, it shows that the ligands in the second hydration shell are very dynamic and flexible and also the results from the MM2bd simulation are not in accordance with the coordination bond theory of $\text{Ga}^{3+}\text{-H}_2\text{O}$.

The CND graph obtained from the MM2b+3bd simulation (Figure 4) shows different results from the previous graph in the MM2bd simulation. The results of the MM2b+3bd simulation calculation shown in the graph show that in the first shell the coordination number is 6 with a probability level of 100%. It can be said that the ligands in the first shell have stabilized and are in accordance with the coordination bond theory of $\text{Ga}^{3+}\text{-H}_2\text{O}$. Meanwhile, in the second shell, various coordination numbers are obtained, starting from 9 to 17 with varying probabilities. This indicates that the ligands in the second shell are still dynamic and flexible. Based on the results of the two simulations above, the MM2b+3bd simulation produces a coordination number that is more accurate than the MM2bd simulation. The CND value is in accordance with the coordination number of the Ga atom, which is 6 (Sugiyarto, 2012).

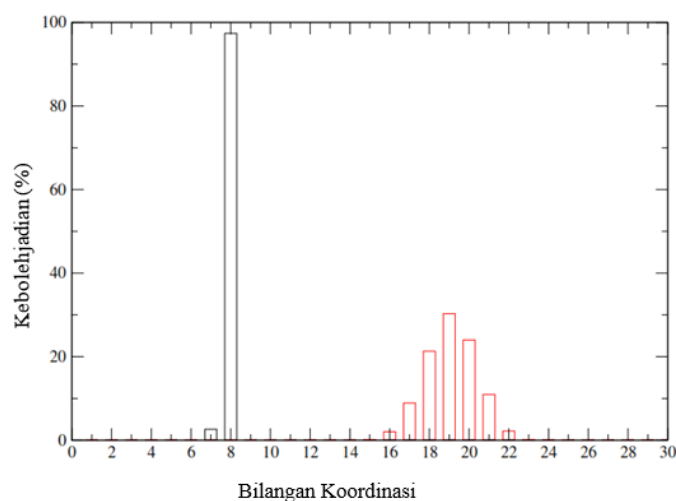


Figure 3. CND of Ga^{3+} hydration using MM2bd

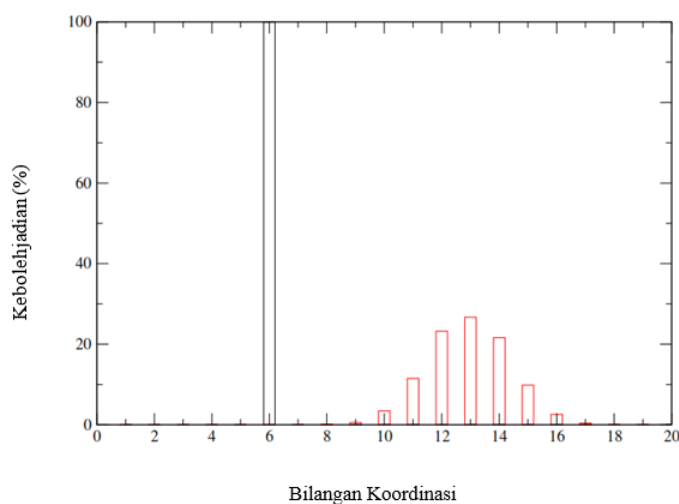


Figure 4. CND of Ga^{3+} hydration using MM2bd+3b

3.3. Angular Distribution Function (ADF)

Angular Distribution Function (ADF) is a function that can describe the distribution of angles with a time span during the molecular dynamics simulation process. It can be used to obtain the distribution of bond angles formed between ligand 1 (O1 atom) – central ion (Ga^{3+}) – ligand 2 (O2 atom). The ADF graphs of the Ga^{3+} hydration of simulation results from MM2bd and MM2b+3bd are presented in Figure 5 and Figure 6.

The ADF graph of the Ga^{3+} ion hydration system from the calculation of the MM2bd simulation above can be obtained data that the O(1)- Ga^{3+} -O(2) atoms form an angle ranging from 65° to 159° . Based on the graph above, there are several angular peaks that are formed, with two main angular peaks and the rest are minor angular peaks that also appear during the simulation process. The peak of the first principal angle occurs at an angle of 75° and the second peak occurs at an angle of 141° . While another small peak occurs at an angle of 117.5° .

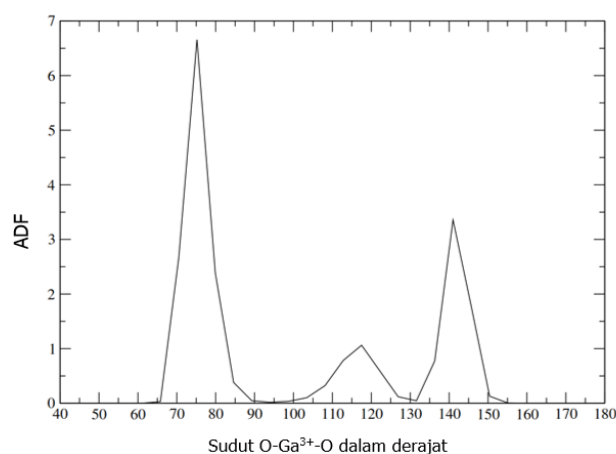


Figure 5. ADF of Ga^{3+} hydration using MM2bd

Figure 6 is an ADF graph of the calculation results of the MM2bd+3bd simulation of the Ga^{3+} ion hydration system. The results obtained indicate that the atoms of $\text{O}(1)\text{-Ga}^{3+}\text{-O}(2)$ are able to form angles with a range of about 78° to 180° . Based on the graph, it can be seen that there are two vertices of the angle formed, with the peak of the first angle occurring at an angle of 88° and the peak of the second angle occurring at an angle of 176° . In the ADF graph from the MM2b+3bd simulation, there is a reduction in the peak angle of the ADF graph from the MM2bd simulation.

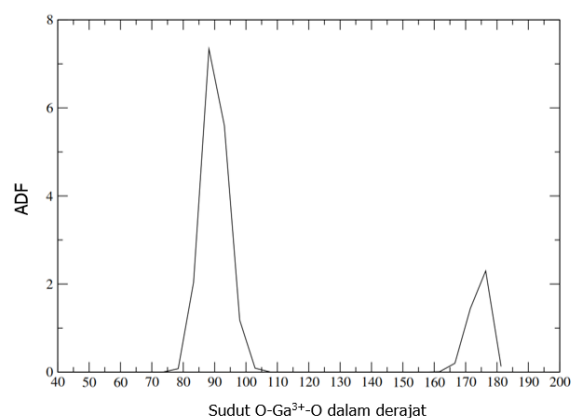


Figure 6. ADF of Ga^{3+} hydration using MM2bd+3b

3.4. Hydration Structure of Ga^{3+}



Figure 7. Hydration structure of Ga^{3+} from MM2b+3bd simulation

The hydration structure of the Ga^{3+} ion can be analyzed using the calculated data from the Radial Distribution Function (RDF), Coordination Number Distribution (CND), and Angular Distribution

Function (ADF) which have been discussed previously. The structure was identified using the TMOLEX 19 application on Linux OS with the result in the form of a snapshot that forms an octahedron geometry.

4. CONCLUSION

Based on RDF, CND, ADF data and a snapshot of the hydration geometry of Ga^{3+} obtained from the MM2-bd and MM2bd+3bd simulations, it can be seen that the hydration structure of the Ga^{3+} is $\text{Ga}(\text{H}_2\text{O})_8^{3+}$ with a Ga^{3+} -O distance in the first hydration shell. of 1,965 Å and O- Ga^{3+} -O angles of 75° and 141°, and $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ with a distance of Ga^{3+} -O in the first hydration shell of 1,915 Å and O- Ga^{3+} -O angles of 88° and 176° and form a geometry octahedral.

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