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Hydration Structures and Dynamics of In³⁺ Ion based on Classical Molecular Dynamics Simulation

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Article Info	ABSTRACT
	The hydration structures and dynamics of In³⁺ ion have been studied using classical Molecular Dinamics (MD) simulation. The best basis sets were optimized to construct the 2-bodies, 3-bodies correction equations, and analysis of the trajectory file of the simulation results in the form of the parameter of a solvation structure such as RDF, CND, ADF, and dynamic properties, namely the migration of water ligands between the hydration shells. The results showed that the hydration structure of the In³⁺ ion is $In(H_2O)_9^{3+}$ and $In(H_2O)_6^{3+}$, respectively. The geometric arrangement of In³⁺ hydration obtained through the simulation of classical Molecular Dynamics 2-bd MM 2-bd corrected 3-bd effect is octahedral, which agrees with experimental data and shows the importance of 3-bd correction. The exchange of H_2O ligands between the first and second shell or vice versa was not observed during the classical Molecular Dynamics simulation process (2-body + 3-body potential). The hydration structure of In³⁺ in the first shell was relatively stable. *Keyword: simulation, 2-body potential, 3-body potential, ion In³⁺, water*

1. INTRODUCTION

Indium is known as a group IIIA metal element, has an atomic number of 49, and symbolized as 'In' in the periodic table. Indium was discovered and identified spectroscopically as a minor component in zinc ores and isolated in 1863 by Ferdinand Reich and Theodore Richter. Characteristics of Indium is a shiny metal that has a very soft structure and silvery white color and has stable properties in air and water, but Indium is soluble in acids. Indium in the compound is more in the III oxidation state. It is named Indium because when heated above its melting point, it burns with a non-luminous blue-red flame to produce Indium Oxide (In2O3). Indium is widely used in high-tech fields. In particular nearly 70% of indium has been applied to produce Indium Tin Oxide (ITO) films which are In-Sn alloys consisting of indium oxide (In_2O_3) and tin oxide (SnO_2) at an approximate mass ratio of 9:1 (Nakashima and Kumahara, 2002).

Indium can be used to synthesize a variety of compounds with favorable semiconductive or optoelectronic performance (Li et al., 2011). The main application of indium today is to produce films. Indium Tin Oxide (ITO) is used as a transparent conductor layer which is widely used in plasma screens, liquid crystal displays, touch screens, and antistatic applications. The use of ITO in some

electronic devices can be engraved through air and water thus indium species easily explode into the environment (Y.S. Zimmermann, 2012). Transparent ITO film is an important raw material that acts as an electrode in Liquid Crystal Display (LCD) used for computers, laptops, cell phones, and televisions (Chou and Huang, 2009).

The interaction between the solvent and the solute is called solvation. Solvation involving water as a solvent is called hydration. The interaction between hydrated metal ions causes hydrogen bonds between water molecules to break forming electrostatic associations with metal ions (Mahler and Persson, 2012). Computer simulation can be done in two ways, namely Monte Carlo (MC) and Molecular Dynamics (MD) simulation. The structure and dynamics of ion solvation can be determined through 2 methods, namely classical DM simulation and MK/MM DM simulation. The classical DM simulation method gives less accurate simulation results than the MK/MM DM simulation. The classical DM simulation method in the calculation or simulation process for the required time is relatively faster than the MK/MM DM simulation.

Ion determination in this study uses In3+ ions, which have not yet been studied and identified regarding the structure and dynamics of hydration. The purpose of this study was to determine the structure and properties of the hydration dynamics of the In^{3+} ion based on classical 2-body MM molecular dynamics simulation with 3-body correction. The simulation method that will be carried out in this study is a classical Molecular Dynamics (DM) simulation because the results obtained have a high level of accuracy, the time required for the simulation process is relatively faster, and does not require high computer specifications.

2. RESEARCH METHOD

Instrumentation

The instruments used in this research are a computer with Linux Opensuse 13.2 Operating System dan Windows 10 Pro 64 bit, Processor Intel® Core™ i5-8250U CPU @3,00 GHz, Memory 8192 MB *RAM*, VGA NVIDIA MX150, dan *Har Disk* 1 TB, while the specific software used are Gauss View 5.0, Gaussian09W, Turbomole v5.10, Program khusus simulasi DM versi 1,6, Tmolex19, XMGRACE, dan Mdtools (RDF, CND, ADF, dan Discalc).

Determination of In^{3+}-H_2O coordinates

The initial geometry of In^{3+} in H_2O is written in 3-dimensional Cartesian coordinates with the help of Gauss View to adjust the angles and distances between atoms which is then generated in the form of a structure in the In^{3+}-H_2O coordinate system. The geometry of the H-O-H angle based on experimental data is 104.5o and the O-H bond length based on the experiment is 0.9601 (Armunanto, 2004).

Basis Set Optimazion

A good base set will not cause a significant change in charge of the In^{3+} ion and has a bond energy curve profile with respect to the In^{3+}-O and In^{3+}-H distances according to the profile of the Lennard-Jones potential curve. The selection of an appropriate basis set must also consider the relatively small value of the Basis Sets Supesposition Error (BSSE). The selected base set will be used to determine the 2-body and 3-body potentials.

Construction of 2b and 3b correction potentials

The arrangement of the potential pairing functions that will be determined in this study is the In^{3+}-H_2O pair potential. The ab initio method at the Restricted Hartree-Fock (RHF) level with a base set corresponding to In^{3+}-H_2O was used to calculate the function of the In^{3+}-H_2O pair potential. The calculation of the 2-body potential varies with geometric parameters at various theta (θ) and phi (ϕ) angles as well as variations in the distance of cations and ligands. Theta angle (θ) varies from 0o to 180o

with intervals (0°, 30°, 50°, 70°, 120°, 150°, 180°), while the pi angle (ϕ) is fixed at 0°. Cation and ligand distances are set from 1.4 to 15. These energy points are used to construct the pair potential function.

Energy points data that have been obtained from various theta (θ) and phi (ϕ) angles and distances are then processed through 2-body fittings. This energy fitting is carried out with the aim of obtaining a form of a mathematical equation function that represents the energy with an algorithm. The algorithm used in the preparation of the potential function analytically with the least squares method based on Lavenberg-Marquart. The form of the 2-body potential equation of the In^{3+}–H_2O ion is as follows:

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

a, b, c, d, A_i, B_i, C_i, and D_i are fitting parameters, r_{Mi} i atomic distance from In^{3+} ion and H_2O, q_i dan q_M are charge of In^{3+} dan H_2O respectivelly.

In the arrangement of the 2-body potential of the In^{3+}-H_2O ion and the arrangement of the 3-body potential of the In^{3+}-H_2O ion, basically using the DZP base set for the O and H atoms and the modified SBKJC-VDZ for the In^{3+} ion. The H_2O-In^{3+}-H_2O configuration is indicated by the 3-body correction function. The form of the 3-body correction function equation is as follows:

$$\Delta E_{corr}^{3bd} = (E_{WMW}^{ab} - E_M^{ab} - E_W^{ab}) - \Delta E_{MW}^{2bd}(r_1) - \Delta E_{MW}^{2bd}(r_2) - \Delta E_{WW}^{2bd}(r_3)$$

with *ab* is *ab initio*, *2bd* is pair potential, *MW* and *WMW* is ion-water and water-water interaction, r_1, r_2, and r_3 is distance of ion-water1, ion-water2, and water1-water2.

Molecular Dynamic Simulation

Prior to the classical MD simulation, several good conditions are needed, namely the hydration of In^{3+} ions is carried out in a hydration box with a side length of 24.751 which contains one In^{3+} atom and 499 H_2O molecules, a constant temperature of 298.16 K, the density of the system is considered to be the same as the density. pure water is 0.99702 g cm^{-3}, the cutoff limit for non-Coulomb interactions is set at 5 for O-H and 3 for H-H, and the radial cutoff limit for Columbic interactions is 12 or half the length of the simulation box (Fatmi, et al.., 2005). The first step in the classical MD simulation of hydration of In^{3+} ions is a simulation using a 2-body potential, then after a balanced system configuration is achieved, it is followed by a 2-body classical MD simulation with 3-body correction. In the final configuration stage the results of the 2-body classical MD simulation were then set as a reference for the initial configuration of the 2-body classical MD simulation with 3-body correction. The results in the form of trajectory files are then analyzed.

The results of the data obtained in the classical molecular dynamics simulation are in the form of a trajectory file. The trajectory file is processed to obtain information on structural properties and hydration dynamics between In3+ ions and water including Radial Distribution Function (RDF), Coordination Number Distribution (CND), and Angular Distribution Function (ADF) and includes dynamic properties in the form of ligand exchange in the hydration shell.

3. RESULTS AND DISCUSSION

According to the calculation of the In^{3+}-H_2O energy using the SBKJC-VDZ base set for the In^{3+} atom and the DZP dunning set for the H and O atoms, the BSSE value is relatively small, so that the base set can be used for calculating energy points and simulations at the RHF level.

Radial Distribution Function (RDF)

The RDF of classical MD simulation result with and without 3-body correction potential are shown in Figure 1 and Figure 2. Figure 1 showed the In^{3+} ion hydration RDF graph data obtained from the calculation results of the classical MD simulation with pair potential only. There is an In^{3+}-O RDF for the first hydrated skin which is indicated by the curve starting to rise at a distance of 1.96 to 2.65

and reaching a sharp peak at a distance of 2.16 while the In^{3+}-O RDF for the second hydrated skin is shown with the curve starting to rise at a distance of 3.11 to 5.37 and reaching a sharp peak at a distance of 4.15. The integration number showed a number of 9 for the O atom, mean there are 9 O atoms in the first hydration shell. RDF In^{3+}-H for the first hydration skin which is indicated by the curve starts to rise at a distance of 2.47 to 3.56 and reaches a sharp peak at a distance of 2.92 while the In3+-H RDF for the second hydration skin which is indicated by the curve starts to rise at a distance of 3.80 to 5.94 and reaches a sharp peak at a distance of 4.92. In the graph it is also known that the integration number for the H atom showed the number of 18. This shows that in the first hydration shell there are 18 H atoms.
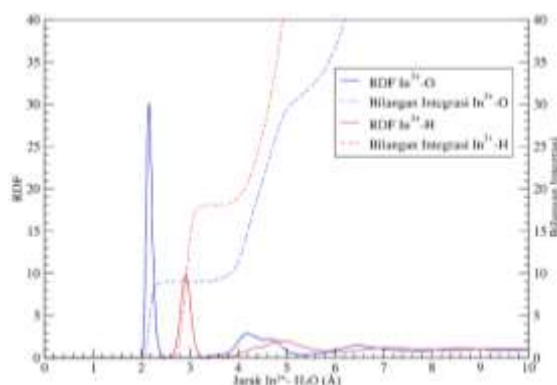

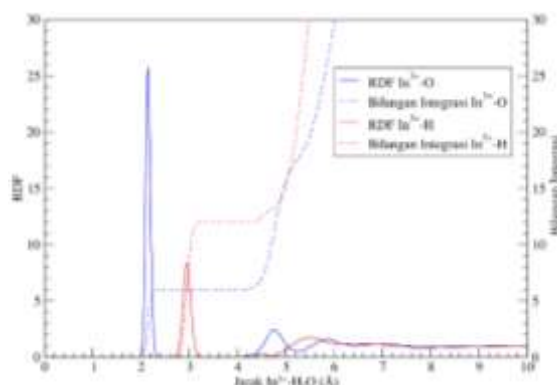**Figure 1.** Radial Distribution Function (RDF) of classical MD with pair potential only

Figure 2. Radial Distribution Function (RDF) of classical MD with 3-body potential

Figure 1 showed the In^{3+} ion hydration RDF graph data obtained from the calculation results of the classical MD simulation with pair potential only. There is an In^{3+}-O RDF for the first hydrated skin which is indicated by the curve starting to rise at a distance of 1.96 to 2.65 and reaching a sharp peak at a distance of 2.16 while the In^{3+}-O RDF for the second hydrated skin is shown with the curve starting to rise at a distance of 3.11 to 5.37 and reaching a sharp peak at a distance of 4.15. The integration number showed a number of 9 for the O atom, mean there are 9 O atoms in the first hydration shell. RDF In^{3+}-H for the first hydration skin which is indicated by the curve starts to rise at a distance of 2.47 to 3.56 and reaches a sharp peak at a distance of 2.92 while the In3+-H RDF for the second hydration skin which is indicated by the curve starts to rise at a distance of 3.80 to 5.94 and reaches a sharp peak at a distance of 4.92. In the graph it is also known that the integration number for the H atom showed the number of 18. This shows that in the first hydration shell there are 18 H atoms.

Figure 2 shows the RDF data for hydration of the In^{3+} ion obtained from the calculation results of the classic 2-body MD simulation with 3-body correction. Based on the figure, there is an In^{3+}-O RDF for the first hydrated skin which is indicated by the curve starting to rise at a distance of 1.96 to 2.42 and reaching a sharp peak at a distance of 2.14 while the In3+-O RDF for the second hydrated skin is

shown with the curve starting to rise at a distance of 3.85 to 5.24 and reaching a sharp peak at a distance of 4.77. In the graph it is also known that the integration number for the O atom shows the number 6. This shows that in the first hydration shell there are 6 O atoms. RDF In^{3+}-H for the first hydration shell which is indicated by the curve starts to increase at a distance of 2.58 to 3.33 and reached a sharp peak at a distance of 2.95 while RDF In3+-H for the second hydration skin as indicated by the curve started to rise at a distance of 4.10 to 4.66 and reached a sharp peak at a distance of 4.52. In the graph it is also known that the integration number for the H atom shows the number 12. This shows that in the first hydration shell there are 12 H atoms.

The two In^{3+} ion hydration RDF graphs obtained from the simulation results of classical 2-body DM and classic 2-body DM simulation with 3-body correction can see data on the distance of In^{3+}-H_2O in the first and second shells, peaks between RDF In^{3+}-O and In^{3+}- H does not experience overlapping because the atomic distance between H and In^{3+} is greater than the distance between O and In^{3+}, and indicates that there is no ligand exchange process between shells during the simulation process.

Coordination Number Distribution (CND)

The CND of classical MD simulation result with and without 3-body correction potential are shown in Figure 3 and Figure 4.
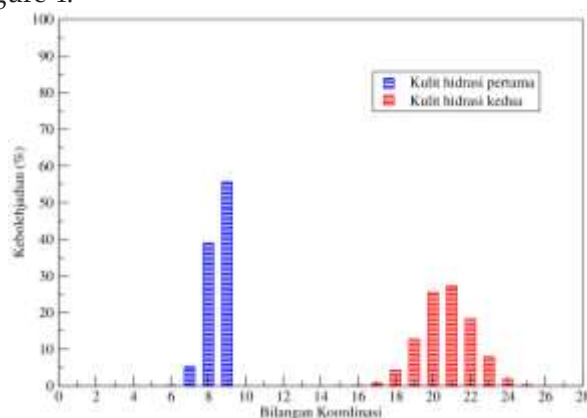

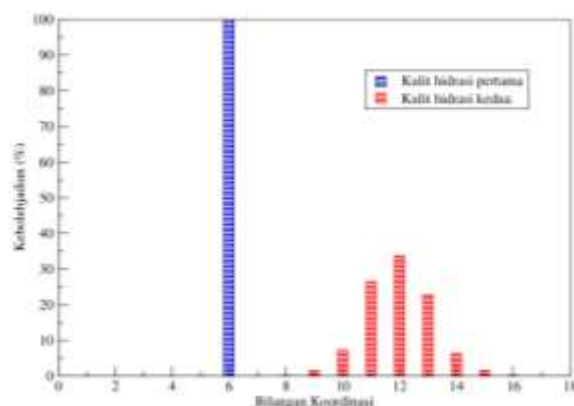**Figure 3.** Coordination Number Distribution (CND) of classical MD with pair potential only

Figure 4. Coordination Number Distribution (CND) of classical MD with 3-body potential

Figure 3 showed the CND graph data of In3+ ion hydration resulting from the classic 2-body MM DM simulation. The CND graph shows that the coordination number in the first hydration skin is 9 with a probability of 55.6%; coordination number 6 with a probability of 0.1%; coordination number 7 with a probability rate of 5.3%; and coordination number 8 with a probability of 39%. In the second hydration skin, different coordination numbers were obtained from 15 to 26 with different probability levels. This shows that the ligands in the first shell and the second shell from the simulation results of

classic 2-body MM DM are still not stable and it is necessary to simulate 2-body classic MD with 3-body correction to get more accurate results.

Figure 4 shows CND graph data of In3+ ion hydration resulting from the classic 2-body MM DM simulation with 3-body correction. The CND graph shows that the coordination number in the first hydration skin is 6 with a probability of 100%. In the second hydration skin, different coordination numbers were obtained from 8 to 16 with different probability levels.

The two CND graphs of hydration of the In^{3+}-H_2O ion obtained from the simulation results of classic 2-body MM DM and 2-body classic DM simulation with 3-body correction show that the second hydration shell has unstable properties because the coordination number and level of hydration are unstable. This is due to the exchange of ligands from the bulk phase to the second shell and vice versa. The simulation results of classic 2-body MM DM show that the first hydration skin is less stable, while the simulation results of classic 2-body MM DM with 3-body correction show that the first hydration skin has stable properties.

Angular Distributin Function (ADF)

The ADF of classical MD simulation result with pair potential including 3-body correction potential are shown in Figure 5.
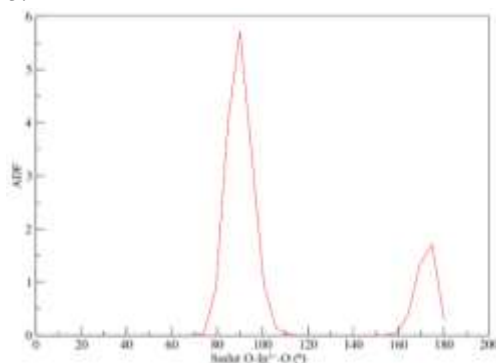

Figure 5. Angular Distributin Function (ADF) of classical MD simulation with pair potential including 3-body potential

Figure 5 showed the ADF graphic data of In^{3+} ion hydration resulting from the classic 2-body MM DM simulation with 3-body correction, data in the form of the O-In^{3+}-O angle can be obtained. The hydration structure of In3+ ions in the first shell with an angle of O-In3+-O forms an angle range of 74^0 to 117^0 with a sharp peak occurring at an angle of 90^0 then forming an angle range of 154° to 180° with a sharp peak occurring at an angle of 175o. This shows that the hydration structure of the In^{3+} ion forms an octahedral geometry with the molecular formula $[In(H_2O)_6]^{3+}$.

Molecul Geometry of In^{3+} hydration structure

After simulating the classic 2-body MD with 3-body correction, the results obtained are Radial Distribution Function (RDF), Coordination Number Distribution (CND), and Angular Distribution Function (ADF). To find out the shape of the hydration structure of the In^{3+} ion, it can be identified using the TMOLEX application, which requires the hotspot_coords geometry file (x, y, and z coordinates) for the first shell and the second shell that is entered into the TMOLEX application. The hydration structure of the In3+ ion simulation results from classic 2-body MM DM with 3-body correction is shown in Figure 6.

(a)   **(b)**

Figure 6. Snapshot of hydration structure of In^{3+} ion a) first hydration shell and b) first and second hydration shell
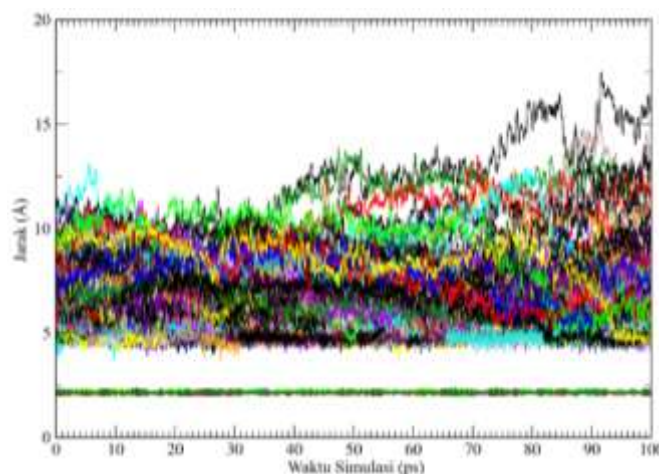

Figure 7. Variation of In^{3+}-H_2O Distance During 2-body MM Classic DM Simulation with 3-body Correction with Simulation Time of 100 ps Indicating No Ligand Exchange Occurred

Figure 7. shows the graphical data of In3+ ion hydration ligand exchange resulting from the classic 2-body MM DM simulation with 3-body correction. This simulation displays a graph in the form of a flow of distance against time. The simulation time used is 100 ps. Based on the graph on the first hydration skin, it can be seen that the water ligands during the simulation process did not exchange with the second hydration skin. This shows that the In^{3+} ion with the H_2O ligand in the first hydration shell has stable properties. But in the second hydration skin, ligand exchange occurs with the bulk phase or vice versa. This shows that the number of ligands or coordination number in the first hydration skin has stable properties.

4.   CONCLUSION

Based on the hydration structure of the In^{3+} ion, the results from the classic 2-body MD simulation with 3-body correction, which shows the results in the first hydration skin are obtained at the In^{3+}-O distance, which is 2.14 , the coordination number is 6 with a probability level of 100%. , and the angle between O-In^{3+}-O is 90^0 and 175^0. The hydration structure of the In3+ ion forms an octahedral geometry with the form of a complex compound, namely $[In(H_2O)_6]^{3+}$. Based on the hydration dynamics of the In3+ ion, the results of the classic 2-body MM DM simulation with 3-body correction showed that there was no ligand exchange in the first hydration shell. This shows that the structure of the first hydration skin has relatively stable properties

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