A HYBRID QM/MM MD SIMULATION FOR Y^{2+} ION IN WATER

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Structural study on solvation of Y^{2+} ion in liquid ammonia and water has been done by using a hybrid QM/MM MD simulation. Fitting of energy to analytical functions using Lavenberg algorithm was done at level of UHF (Unrestricted Hartree-Fock) using DZVP (DFT Orbital) basis sets for Y and SV(P) for O, N and H (water and ammonia), respectively. Simulation box was divided into two part (the QM and MM regions, whereas for the transition region was used Smoothing function). Solvation structure properties of Y^{2+} ion in water was characterized using RDF, CND, and ADF data obtained from trajectory files (configuration coordinate every simulation step). Y^{2+} ion in water was solvated to give a flexible complex structure with 7.3 and 15.9 coordination numbers at first and second shell respectively, Y^{2+}-O distances of 2.45 Å and 4.33 Å at first and second shell respectively and Y^{2+}-H distances of 3.13 Å and 5.50 Å at first and second shell respectively.

Key words : QM/MM MD, solvation, Y^{2+}, flexible

INTRODUCTION

In general, the liquid system in nature is in a mixed state (solution system). In the solution system there is an interaction between the solute molecules and the solvent molecules. The interaction in this system is known as solvation. Solvation are caused by electrostatic interactions, hydrogen bonding, or Van der Waals interactions between molecules of solutes and solvent molecules. Solvation of an ion in a solvent is found in many natural processes, for example in the metabolic processes of living things. Generally these solvations occur before and during metabolic processes involving water or non aqueous solvents. If an ion is in the body of a living thing there will be an interaction between ions with other components in the body such as water, fats, carbohydrates, proteins, nucleic acids and enzymes. Therefore, the study of solvation of an ion in a solvent becomes important to do. One of the elements of the IIIB that is interesting to study is yttrium because about 31 ppm of the earth’s crust is yttrium, so this element ranks 28 of the abundance of elements in the earth’s crust and 400 times more than silver. In the human body there are about 0.5 mg yttrium, however biological effects to date have not been widely known. Meanwhile, the system in the living body is dominated by water and biomolecule compounds such as protein, so the interaction between yttrium with water and amine groups of protein is possible. This indicates that both theoretical and experimental studies of yttrium ions in water are important.

Yttrium is a transition metal that has symbol Y and atomic number 39. The physical properties of yttrium are: soft, silvery-metallic, bright and highly crystalline transition metal in group 3, atomic weight 88.90585 g/mol and solid at room temperature. It has a boiling point (3336 °C), melting point (1526°C), heat of fusion (11.42 kJ/mol), heat of vaporization (365 kJ/mol), specific heat capacity (25°C) 26.53 J/mol.K, density (near room temperature) 4.472 g/cm^3, electronegatifity 1.22 (Pauling scale), ionization energies: (1st) 600 kJ/mol, (2nd) 1180 kJ/mol, (3rd) 1980 kJ/mol, atomic radius (180 pm) and covalent radius (162 pm). The common oxidation state of yttrium is +3. As a trivalent transition metal, yttrium forms various inorganic compounds generally in the oxidation state of +3, by giving up all three of its valence electrons, such as YCl_3, YBr_3, YH_3, Y_2O_3 and Y_2S_3, in the oxidation state of +2 has been observed in YH_2 and YC_2. Organoyttrium compounds have yttrium in the oxidation state 0, +1, +2 (Bayse, 2002).

Water is a molecule with a distorted tetrahedral shape, with an H-O-H bond angle of 104.5°. Between water molecules interact using a dipole-dipole interaction, called a hydrogen bond. The length of the OH…O bond in the hydrogen bond between the water molecules is 1,97 Å, while the OH…O bond energy is 21 kj/mol (usually at a temperature of 298 K). The classical energy present in N-rigid water molecules is the kinetic energy for translation and rotation with intermolecular potential. Each water molecule is represented by 6 coordinates, each of which 3 is at the center of mass and 3 on the part that fills the spatial orientation around the center of mass (Hinchliffe, 2003).

Solvation, commonly called dissolution is the process of attraction and association of molecules of a solvent with molecules or ions of a solute). Ions of a solute will distribute and then surrounded by solvent molecules. By an IUPAC definition, solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution. In the solvated state, an ion in a solution is surrounded or complexed by solvent molecules.

Combined Quantum Mechanics (QM)/Molecuar Mechanics (MM) methods based on molecular dynamics (MD) or QM/MM MD is used in this research (Armunanto, 2004), with two-body potential. The structure properties and dynamics of the system of ion solvation can be determined by experimental method and computer simulation. The Spectroscopy and X-Ray Diffraction methods are often used to experimental study. The most common spectroscopy method is EXAFS (Extended X-ray Absorption Fine Structure) and NMR (Armunanto et al., 2004). Molecular simulation is a computational experiment related to a molecular model, as for the molecular dynamics simulations can provide information about the structure and dynamics of the system. Molecular dynamics simulations study of ion solvation are determined by computational method molecular mechanics (MM), and assumed that many body term contribution was so small, that it can be ignored. MM method is well known quite inexpensive in computation time, used to calculate all molecules on simulation systems, then analyzed the result. Limits of the MM method are related to the energy estimates obtained are not very accurate. The Quantum mechanics (QM) is a method with greater accuracy, however it is computationally expensive, so that combined quantum mechanics/molecular mechanics (QM/MM) methods was selected in the research. In a principle QM/MM MD simulation, the system is partitioned into two regions, a QM region and a MM region. QM calculations method is applied into QM region, to the molecules close to the central ion within a certain radius including the central ion. If analogous to the shell phenomenon, a QM region is the central ion and first solvation shell. The second solvation shell to the solvent phase was calculated by MM calculation method. The problem of boundary area of QM/MM is solved by using an algorithm that allows flexibility of particle/molecular migration from the QM to MM region or otherwise.

2. EXPERIMENTAL

2.1. Potential CouplingFunction

The computation of potential coupling function for molecular mechanical interaction Y^{2+}- H_2O and H_2O–H_2O was done at level of UHF (Unrestricted Hartree Fock) using DZVP (DFT Orbital) basis sets (Godbout, 1992) for Y and Def2- SV(P) (Kaupp, 1991) for O and H (water). The energy fittings performed on 4445 interaction points of Y^{2+} - H_2O using the least squares method of Lavenberg-Marguart. The solvent system coordinates need to maintain a rigid structure (fixed bond angle and bond length), based on the experimental data in the gas phase where the O–H distance is 0.9601 Å and the H-O-H bond angle is 104.47◦ (Armunanto, 2004). Simulation of Y^2+ ions in water was carried out at a temperature of 298.16 K, a density of 0.99072 g/cm^3 and a dielectric constant of 78.5. The Potential function of Y^{2+}-OH_2 is defined as:

$$\Delta E^{2bd}(r) = E_{AB}^{ab}(r) - E_A^a - E_B^b \tag{1}$$

where ab is ab initio, E_{AB}^{ab} is Y^{2+}-OH_2 interaction energy terms, r is radial distance of Y^{2+}- OH_2, E_A is energy of the Y^{2+} ion , calculated using Y function and E_B is ligand-water energy, calculated using OH_2 function. Minimum energy configuration for Y^{2+}-OH_2 interaction is -65,43 kcal/mol (2,30 Å). The Fitting energy of two body is defined as:

$$\Delta E_{Fit}^{2bd} = \sum_{i=1}^{4} \frac{q_M qi}{r_{Mi}} + \frac{A_i}{r_{Mi}{}^5} + \frac{B_i}{r_{Mi}{}^7} + \frac{C_i}{r_{Mi}{}^9} + \frac{D_i}{r_{Mi}{}^{12}} \tag{2}$$

where M and i are respectively, Y^{2+} ion and oxygen or hydrogen-atom; A, B, C and D are the optimize parameter; q is partial charge (a charge of -0.65980 to oxygen and 0.32990 to hydrogen). Table 2.1 showed the optimization parameter of potential coupling function.

Table 2.1. The optimization parameter of potential coupling function Y^{2+}–H_2O

Interval	**A** **($\text{kcal.mol}^{-1}.\text{Å}^{5}$)**	**A** **($\text{kcal.mol}^{-1}.\text{Å}^{7}$)**	**A** **($\text{kcal.mol}^{-1}.\text{Å}^{9}$)**	**A** **($\text{kcal.mol}^{-1}.\text{Å}^{12}$)**
Y – O	-12491.92	83158,51	-144051.78	103519.74
Y – H	-257.33	5994.97	-15581.71	15461.70

There is an Y^{2+} ion and hundreds of solvent molecules in the simulation box, interaction occurs between particles involving many-body potential. In the many body potential system, potential energy is expressed by Murrell-Mottram potential (Lloyd, 1998) :

$$V = V^{(1)} + V^{(2)} + V^{(3)} + \cdots + V^{(N)} \tag{3}$$

where $V^{(2)}$ is two-body potential energy, $V^{(3)}$ is three-body potential energy and $V^{(N)}$ is N-body potential energy. Molecular dynamics simulation related to many body usually performed by potential (2+3)-body, influence of many body potential (N>3) is so small that it can be ignored. Actually, the simulation by potential (2+3)-body need to many times and high computational cost. The simulation by potential 2-body becomes one option to overcome the problem and to ensure that it can avoid error, thus need to be validated by some calculation method which has meticulous calculation quality such MP2 (Möller-Plesset Perturbation Theory) and CC (Coupled Cluster) method. Level accuracy in simulation results by potential 2-body, can be compared with the available research results. The simulation box is partitioned into two regions, a QM region and a MM region, whereas for the transition region was used smoothing function. The force system is defined as:

$$F_{Sistem} = F_{MM} + S\left(F_{MK} - F_{MK/MM}\right)(r) \tag{4}$$

where F_{MM} is force of MM for full system, F_{MK} is force QM in QM region, $F_{MK/MM}$ is force MM in QM region and S is smoothing function.

$$S_m(r) = 1 \qquad r \leq r_1$$

$$S_m(r) = \frac{({r_0}^2 - r^2)({r_0}^2 + 2r^2 - 3{r_1}^2)}{({r_0}^2 - r^2)^3} \qquad r_1 < r \leq r_0$$

(5)

$$S_m(r) = 0 \qquad r \geq r_1$$

The migration of ligands between QM region and MM region were allowed to spread freely in this approach (Armunanto, 2004). The illustration of simulation box by using a hybrid QM/MM is shown in Fig 2.1.

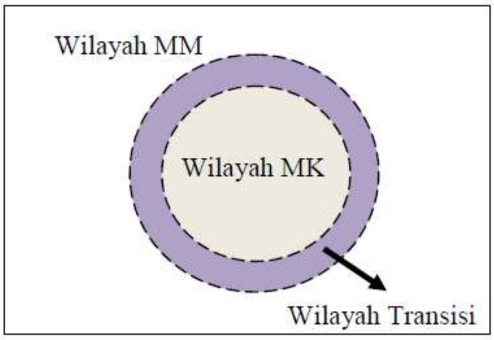


Fig. 2.1. The illustration of simulation box (Armunanto, 2004)

2.2 Structural Analysis

Structural analysis on solvation of Y^{2+} ion in solvent was done to identify a characteristic complex structure included the radial of ion-ligand, the coordination number and the bond angle of ligand-ion-ligand. Solvation structure properties of Y^{2+} ion was characterized using RDF (Radial Distribution Function), CND (Coordination Number Distribution) and ADF (Angular Distribution Function). The radial distribution function or the coupling distribution function or the coupling correlation function g(r) is the probability of finding an atomic within shell (dr) at distance (r) from selected atomic point. Radial Distribution Function system on solvation of α ion in solvent β, $g_{\alpha\beta}$ (r) is defined as :

$$g\alpha\beta = \frac{N_{\alpha\beta}(r)}{4\pi r^2 \Delta c_\beta} \tag{6}$$

where $c_\beta = \frac{N_\beta}{V}$, N_β is number of β species in volume (V). When α species is an ion and β species is a ligand, then coordination number is determined by :

$$n_{ion}^{\beta}(r) = 4\pi c_{\beta} \int_{r_1}^{r_2} g_{ion,\beta}(r) r^2 dr \qquad (7)$$

where n_{ion}^{β} is average number of β species in spherical shell (r1-r2) in certain time.

2.3. Simulation Protocol

QM/MM MD simulation was done by one Y^{2+} ion in 199 of water molecules. The condition system was kept at 298.16 K, density (0.99072 g/cm3), cut off Y^{2+} - H_2O interaction is 12.0 Å and cut off *non-Coulombic* Y-O and Y-H interaction respectively are 5.0 and 3.0 Å.

The simulation was done by dividing into two parts, Y^{2+} ion and all solvent molecules in the first solvation shell was calculated by the concepts of Quantum Mechanics and the entire contents of simulation box was calculated by the concepts of Molecular Mechanics (firstly done a classical MD simulation using only the coupling potential and then performed a simulation using a potential function for QM/MM simulation), while for the transition area between QM and MM used smoothing function. The force on the system was determined by equation (4) and in the state of transition was determined by equation (5).

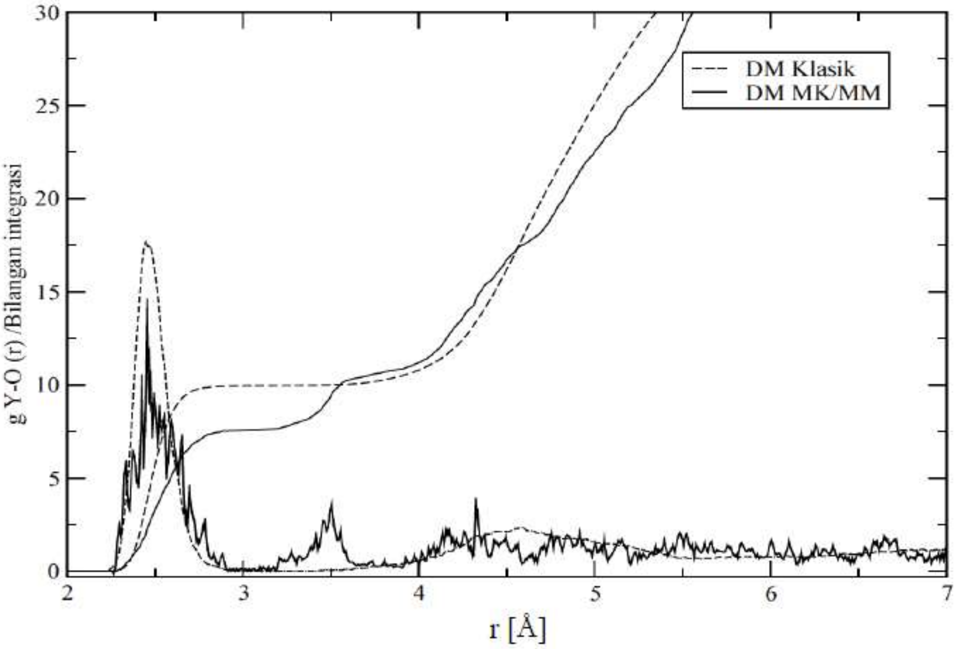
2.4. Analysis of the characteristics properties of the solvation structure

The characteristics properties of the solvation structure was analyzed by using RDF (Radial Distribution Function), CND (Coordination Number Distribution) and ADF (Angular Distribution Function) data obtained from trajectory files (configuration coordinate every simulation step). RDF analysis is used to determine the closest distance, the furthest distance and the mean distance between the ion and the solvent molecule, both in the first and second shell solvation. CND analysis is used to determine the coordination number of solvent molecule located on the first and second shell. ADF analysis is used to determine the solvent-ion-the solvent bonding angle in the structure of the solvation complex geometry on the first shell. RDF, CND and ADF analyzes were performed using FORTRAN 95 software and visualized in graphical form using XMGRACE software. The geometry of the solvation structure on the first shell visualized using RASMOL software.

3. RESULTS AND DISCUSSION

3.1 RDF Analysis

According to both the QM/MM MD and classical MD results, Fig. 3.1 and Table 3.1 displayed respectively, the radial distribution functions for Y^{2+}–O and Y^{2+}–H interaction; and structure properties on solvation of Y^{2+} ion at first and second shell.



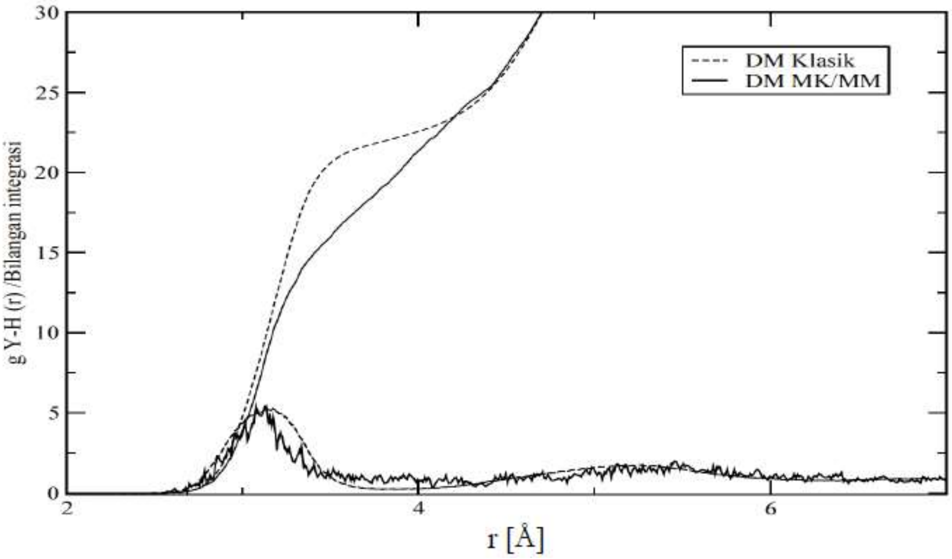


Fig. 3.1. The radial distribution function for Y^{2+}-O and Y^{2+} - H

Table 3.1. The RDF $g_{\alpha\beta}(r)$ characteristic of Y^{2+} in water by QM/MM MD simulation

α	β	r_{M1}	r_{m1}	Nαβ (m_1)	r_{M2}	r_{m2}	Nαβ (m_1)
Y	O	2,45	2,73	7,3	4,33	5,93	20,8
Y	H	3,13	3,68	18,0	5,50	6,19	57,2

According to QM/MM MD simulation, Y^{2+}-O distances of 2.28-2.73 Å at first shell with the highest distance of 2.45 Å. This solvation was flexible and its coordination number of 7.3. The flexible properties was shown by Y^{2+}-O RDF data that never reaches zero. The solvation at second shell was commonly found of 4.33 Å and its average coordination number of 20.8.

By a classical molecular dynamics simulation, oxygen atoms of the water molecule was distributed of 2.21-3.68 Å with the highest of 2,44 Å and its coordination number of 10.0. The abundance of oxygen at second shell was commonly found of 4.55 Å. According to simulation results, either QM/MM MD or classical molecular dynamics, it is observed that Y^{2+} ion in water was solvated to give a flexible complex structure.

According to the result of QM/MM DM simulation, hydrogen atoms of the water molecule was distributed of 2.56 – 3.68 Å, with the highest of 3.13 Å. The abundance of hydrogen at second shell was commonly found of 5.50 Å with the highest of 6.19 Å. Interaction energy of Y^{2+}-H_2O at the furthest point (-11.6 kcal/mol) is stronger than hydrogen bond with a hydrogen on another water molecule (-5.1 kcal/mol). In fact, this result is similar to the classical molecular dynamics. The value of the large interaction energy to the furthest point of the ligands allows for the formation of a relatively stable solvation structure.

3.2 CND Analysis

The coordination number distribution on solvation of Y^{2+} ion in water by using a hybrid QM/MM MD simulation is shown in Fig 3.2.

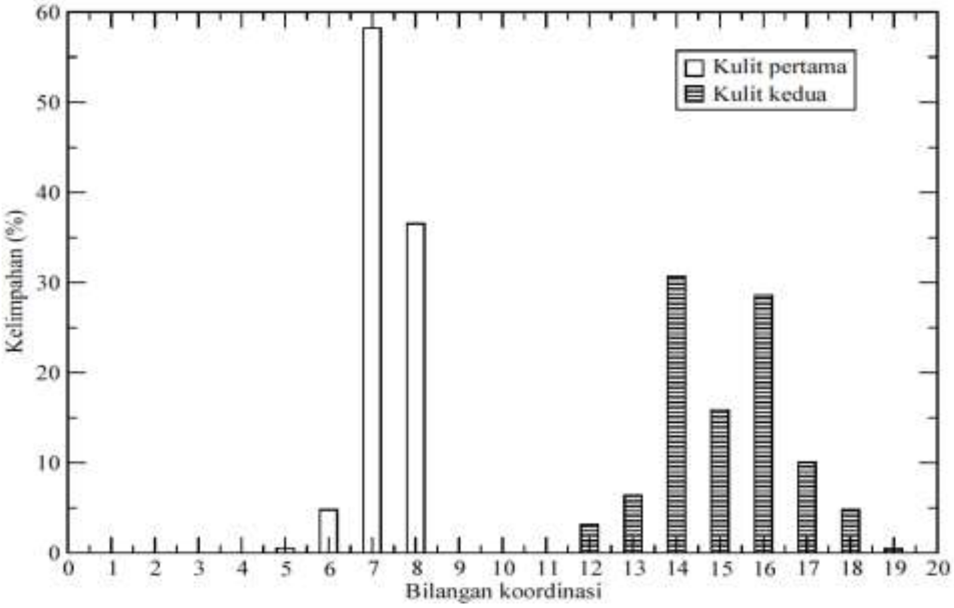


Fig. 3.2. The Coordination number distributions on solvation of Y^{2+} ion in water: QM/MM MD simulation

According to CND analysis by using QM/MM MD simulation, 5-8 coordinated water molecules on the first solvation shell with the greatest abundance in coordination number 7 (58.20%), whereas on the second solvation shell water molecules are coordinated 12-19 with the greatest abundance in coordination number 14 (30.68%) and 16 (28.57%). The presence of large amounts of hydrogen atoms (about 69) observed on the second shell indicates that the solvation on the second shell more flexible than the first shell.

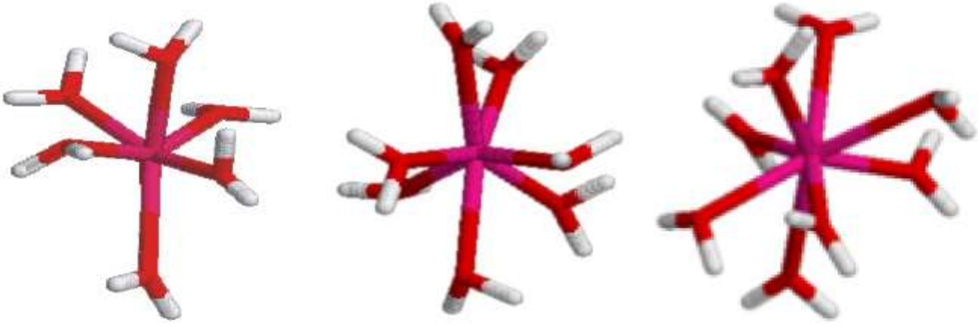

(a) (b) (c)

Fig. 3.3. Structure of Yttrium(II) ion in water on the first solvation shell QM MM/MD: (a) coordination number of 6 (4.76%); (b) coordination number of 7 (58.2%) and (c) coordination number of 8 (36.51%).

The result of this study when compared with the previous research, as depicted in Table- 3.2.

Table 3.2. Comparison of solvation structure of Y^{2+} ions in water with various previous research

System	Y-O (Å)	CN*)	Method	Refferences
1 Y^{2+} ion in 199 of water molecules	2.28-2.73	7.3	QM/MM MD	This research
1 Ag^{+} ion in 499 of water molecules	2.60	5.4	QM/MM MD	Armunanto(2004)
1 Au^{+} ion in 499 of water molecules	2.45	4.7	QM/MM MD	Armunanto(2004)
1 Co^{++} ion in 499 of water molecules	2.17	6.0	QM/MM MD	Armunanto(2003)
$YCl_{3\,(aq)}$ 2.1-0.6 M	2.33 ±0.02	8	EXAFS	Marques (2003)
$YBr_{3\,(aq)}$ 2.1-0.6 M	2.34 ±0.02	8	EXAFS	
$YCl_{3\,(aq)}$ 3.5 M	2.28	8	XRD	Ramos (2001)
$YCl_{3\,(aq)}$ 2.3 M	2.34	8	XRD	
1 Y^{3+} ion in 55.5 of water molecules	2.33-2.39	7.4	NS & EXAFS	Bowron (2007)

The results of this study, in which 1 Y^{2+} ion in 199 of water molecules, was solvated with the average coordination number of 7.3 and the distance Y-O 2.28-

2.73 Ǻ with the highest radial distribution of 2.45 Ǻ is logical when compared with previous research. The difference in distance and coordiantion number between ion and solvent may be influenced by :

a. Size and charge of ions. The smaller the size of the ion and the greater the charge, the greater the coordination number and the ligand-ion distance closer and the more exothermic energy.
b. The concentration of the solution. The greater the ratio of solvent to the ion, the ion-ligand distance closer.

3.3 ADF Analysis

The angle distribution of O-Y^{2+}-O in the structure system of Y^{2+} ion solvation complex geometry in the water of classical MD and QM/MM MD simulation as depicted in Fig. 3.4:

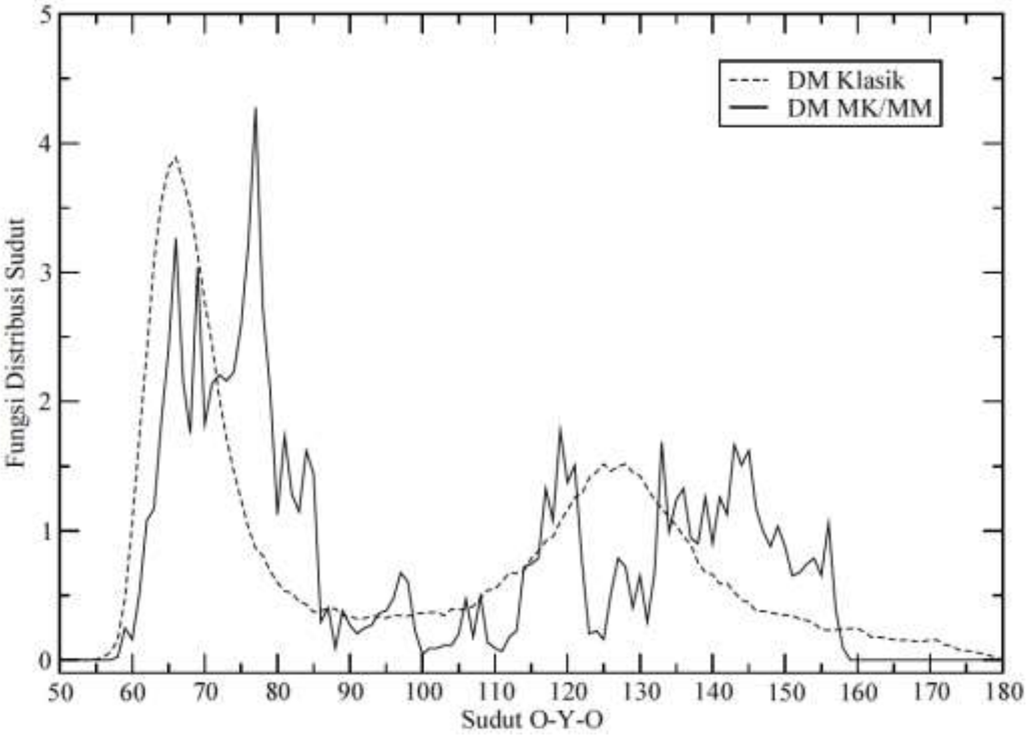


Fig. 3.4. O-Y-O angular distribution in the first solvation shell $[Y(H_2O)_n]^{2+}$

In the complex structure of Y^{2+} ion solvation in water, the O-Y^{2+}-O angle distribution of the dominant QM/MM MD simulation is 66°, 77°, 121°, 143° and 156°. Visualization using rasmol software to complex coordinate 7 (Fig. 3.3(b)) shows that the angle distribution of O-Y^{2+}-O is 92°, 63°, 73°, 80°, 148°, 60° and 65°. This can occur because migrating one ligand from and into complex structure will change the complex shape so the angle of O-Y^{2+}-O is more varied. The number of angle variations of O-Y^{2+}-O simulated results of QM/MM MD indicates that the solvation structure of the first shell is very dynamic in forming structures with coordination of 5, 6, 7 and 8 alternately.

4. CONCLUSION AND SUGGESTION

4.1 Conclusion

It has been shown that Y^{2+} ion in water was solvated to give a flexible complex structure with 7.3 and 15.9 coordination numbers at first and second shell respectively, the average Y-O distances of 2.45 Å, and the O-Y^{2+}-O angle is dominant at 92°, 63°, 73°, 80°, 148°, 60° and 65°.

4.2 Suggestions

For more accurate results, the results achieved in this study need to be improved by using three-body potential correction and a variety of methods.

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