33rd Annual Conference of the Canadian Nuclear Society 2011 June 10 – June 13
36th Annual CNS/CNA Student Conference TCU Place, Saskatoon, Saskatchewan

An *Ab Initio* Study of Hydrated Nickel(II) Hydroxy Complexes

Liwei Cheng[1], Jane Ferguson[1] and CoryC. Pye[1]
[1]Saint Mary's University, Nova Scotia, Canada

Abstract

One of the main undesirable processes in SCWR is the possible formation of metal ligandcomplexes from ions present in coolant which is very poorly understood both experimentally and theoretically. As pressurized and heated solutions are difficult to work with, computational methods have now become an important research tool. A series of ab initio calculations of aquanickel(II) and hydroxyaquanickel(II) have been performed at HF, MP2 and B3LYP levels with 6-31G* and 6-31+G* basis sets. A thorough examination of geometries, energies and vibrational frequencies has been carried out for all species up to and including hexacoordinatespecies. The computational results are compared with experimental data where available.

1. Introduction

Supercritical Water-Cooled Reactors (SCWR)are one of the six innovative concepts selected for nuclear reactors based on safety and environmental issues [1]. One of the most undesirable processes is the formation of metal ligands from ions present in the feedwater or released into the coolant by corrosion processes.These corrosion products may then be transported throughout the loop and settle in low-lying areas (i.e. connections between pipes) or reprecipitate in the pumps or valves thereby corroding these areas and altering the water chemistry.Nickel-based alloys have been proposed for Generation IV reactors in-core components [2]. However, certain aggressive anionscan induce passivity breakdown, resulting in various forms of localized corrosion which can result in cracks of the alloy substrate. Therefore, Ni(II) ion could be leached into environment by forming complexes with water molecules and anions such as hydroxides and chlorides. These may lead to deposition of corrosion products on the fuel or turbines and if they become neutron activated in the reactor core, create a radiological harzard[3].

2. Methods

All the calculations were performed using GAUSSIAN-03 program [4]. We had performed HF, MP2 and DFT on $[Ni(OH)_m(H_2O)_n]^{2-m}$ clusters, where m+n was varied up to 6. Geometries at the levels MP2/6-31+G* and B3LYP/6-31+G* were sequentially optimized. We present only the results from the MP2/6-31+G* and B3LYP/6-31+G* as the added polarization and diffuse functions and electron correlations provided satisfactory results.All the calculations were performed at zero kelvin in gas phase. Although the temperature and pressure in SCWR were quite high, it only affected the chemical equilibrium, and it did not affect the structures of molecules. Therefore, ab initio calculations were suitable for supercritical calculations.Our calculations are exact within the constraints of the model. There is no uncertainty really because they are not derived from an experiment.

3. Results

The results obtained for $[Ni(OH)_m(H_2O)_n]^{2-m}$ (where $m \leq 6$, $n \leq 6$, $m+n \leq 6$) at MP2/6-31+G* and B3LYP/6-31+G* were described below. Only the most stable structures were presented as they were most possible to exist in SCWR. The resulting structures optimized were depicted in figures 1-4.

3.1 AquanickelComplexes, $Ni(H_2O)_n^{2+}$

The structures of the aquanickel complexes were given in Figure 1.The monohydrate had C_{2v} symmetry. For the dihydrate, C_2 was proved to be a minimum. For the trihydrate, two D_{3h} structures were tried, and the planar D_{3h} structure had imaginary frequencies at both levels, whereas the other one was stable. A C_3 structure was proved to be the lowest energy. For the tetrahydrate, D_{4h}, C_{4h}, S_4, C_s, C_2 and C_1 structures were sequentially tried, and only C_2 and C_1 structures were stable at both levels and C_1 structure had lowest enery. The pentaaquanickel and hexaaquanickel had C_{2v} and T_h symmetry respectively.

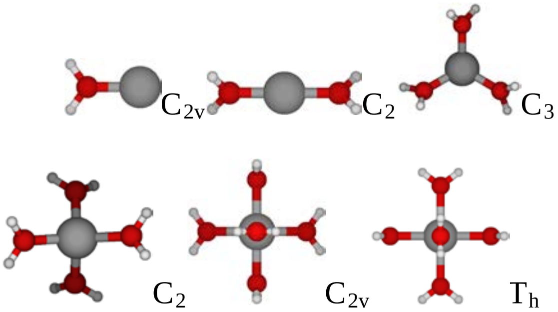

Fig. 1 Structures of aquanickel complexes. (Since the structures optimized at both levels look the same, we only present the pictures at MP2/6-31+G*level for all complexes.)

3.2 HydroxyaquanickelComplexes, Ni(OH)(H_2O)$_n^+$

The structures of monohydroxyaquanickel complexes were given in Fig. 2. Hydroxynickel itself had C_s symmetry. For the monohydrate, two C_s structures were tried, but only the planar C_s was stable. The preferred dihydrate and trihydrate structures were C_1. For the tetrahydrate, C_1 structure was the most stable and possesses no imaginary frequencies. For the pentahydrate,various C_s were tried, but all of them showed imaginary frequencies or dissociation at bothlevels. The preferred structure for the pentahydrate was C_1.

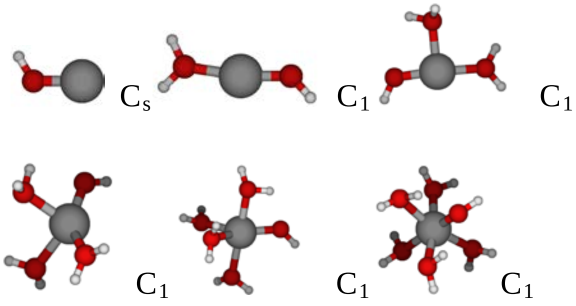

Fig. 2 Structures of monohydroxyaquanickel complexes.

3.3 DihydroxyaquanickelComplexes, Ni(OH)$_2$(H_2O)$_n$

The structures of dihydroxyaquanickel complexes were given in Fig. 3. Two C_{2v} structures were tried for the dihydroxynickel, but only the "W" shaped structurewas stable at both levels. A C_2 structure was proved to be an energy minimum. The preferred monohydrate and dihydrate structures were both C_1. For the trihydrate, C_{2v}, C_2 and C_s were tried, but they all had imaginary frequencies at both levels. The preferred trihydrate structure was C_1. The tetrahydrateaquanickel had C_1 symmetry with one water molecule in the second hydration shell.

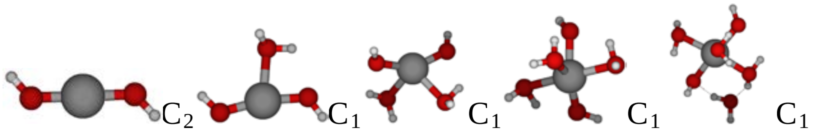

Fig. 3 Structures of dihydroxyaquanickel complexes.

3.4 TrihydroxyaquanickelComplexes, $Ni(OH)_3(H_2O)_n^-$

The structures of trihydroxyaquanickel complexes were given in Fig. 4. The anhydrate had C_3 structure. When a single water added to $Ni(OH)_3^-$, a C_1 structure was formed and the water molecule preferred to stay in the second hydration shell. The dihydrate had C_1 structure with one water molecule migrated to the second hydration shell. Two C_{3v} structures were tried for the trihydrate, and the first one was only stable at MP2/6-31+G* and possessed imaginary frequencies at B3LYP level, whereas the second one was stable at both levels. For the stable trihydrate C_{3V} structure, all the water molecules were in the second hydration shell.

3.5 TetrahydroxyaquanickelComplexes, $Ni(OH)_4(H_2O)_n^{2-}$

The structures of tetrahydroxyaquanickel complexes were given in Fig. 4. The anhydrate itself had C_2 symmetry. When single water added to tetrahydroxynickel, a C_2 structure was formed and the water molecule was in the second hydration shell. Attempt to add two water molecules to $Ni(OH)_4^{2-}$ resulted in the two water molecules hydrogen bonding to the ion to form a C_2 structure. All attempts at creating a penta- or hexahydroxynickel ion resulted in dissociation of hydroxide ions.

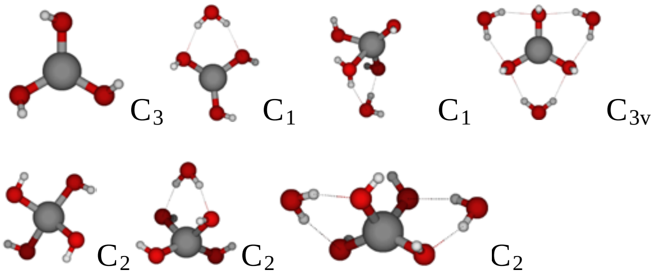

Fig. 4 Structures of trihydroxyaquanickeland tetrahydroxyaquanickelcomplexes.

4. Discussion and Literature Comparison

Previous calculations and experimental data could be compared to our work. The structures they obtained are in good agreement with our results in terms of bond length. Our results of Ni-O bond length of $Ni(OH)^+$is 1.768Å (B3LYP/6-31+G*) and 1.734Å which is slightly longer than

1.712Å which was obtained by Ricca and Bauschlicher[6] using B3LYP and a different basis set ([8s4p3d] contraction of the (14s9p5d) primitive set). Magnusson and Moriarty[7] calculated a Ni-O bond length of 1.767Å which is in very good agreement with our results. Fujii et al[9] calculated the Ni-OH bond length of 2.11 Å – 2.14 Å and Ni-H_2Obond length of 1.944Å for $Ni(OH)(H_2O)_5^+$and Ni-OH bond length of 2.17-2.19 Å and Ni-H_2O bond length of 1.988 Å for $Ni(OH)_2(H_2O)_4$.Our results are slightly shorter than Fujii's values, and this could be explained by our smaller basis set (6-31+G*) than theirs (6-311+G (d, p)). To the best of our knowledge, no literature has been found on any of the other complexes to compare in terms of structure to our results.

5. Conclusions and Future Work

Ab initio calculations on hydroxyl aquanickel complexes are carried out. The lowest energy structures for each complex were shown and bond lengths and vibrational stretching frequency data were compared, where appropriate, with other computational and experimental data found in the literature. These *ab initio* studies will be extended to nickel(II) complexes with mixed ligand combinations including chloride, ammonia, hydroxide and water.

6. References

[1] Torgerson, D., Shalaby, B., Pang, S., "CANDU technology for Generation III+ and IV reactors", *Nucl.Eng. Des.*, Vol. 236, Issue 14-16, **2006**, pp.1565-1572.

[2] Davis, J. R. "ASM specialty handbook: nickel, cobalt, and their alloys". Materials Park, Ohio. **2000**

[3] P. Kritzer."Corrosion in high-temperature and supercriticalwater and aqueous solutions: a review."*J.Supercrit Fluids,* Vol. 29, Issue 1-2, **2004**, pp. 1–29.

[4] Frisch, M. J. et al., Gaussian 03, Gaussian Inc., Wallingford, CT. **2004**.

[6] Ricca, A., Bauschlicher, W. C. "Successive OH binding energies of $M(OH)_n^+$ for n=1-3 and M = Sc, Ti, V, Co, Ni and Cu". *J. Phys. Chem. A.* Vol 101, **1997**, pp. 8949-8955

[7] Magnusson, E., Moriarty, N. W. "Binding patterns in single-ligand complexes of NH_3, H_2O, OH^-, and F^- with first series transition metals". *Inorg. Chem*. Vol. 35, **1996**, pp. 5711-5719

[9] Fujii, T., Moynier, F., Dauphas, N., Abe, M. "Theoretical and experimental investigation of nickel isotopic fractionation in species relevant to modern and ancient oceans". *Geochim.Cosmochim.Acta*. Vol. 75, **2011**, pp. 469-482.

[10] Shankar, J. and De Souza, B.C., "Hydrolysis of $Co^{2+}_{(aq)}$ and $Ni^{2+}_{(aq)}$ ions", *Aust. J. Chem.*, Vol. 16,**1963**, pp.1119-1122.

[11] Palmer, D. A., Benezeth, P., Xiao, C., Wesolowski, D. J., Anovitz, L. M. “Solubility measurements of crystalline NiO in aqueous solution as a function of temperature and PH”. *J. Solution. Chem*. Vol. 40, **2011**, pp. 680-702.