Dynamics and structure of iron hydroxide in high temperature and supercritical water

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Summary

In order to model the behaviour of neutral and ionic species in pressurized water reactor (PWR) and supercritical water reactor (SCWR) heat transport system, the dynamics and structure of iron hydroxide under sub and supercritical conditions are examined by using molecular dynamic (MD) simulation. Radial distribution functions (RDF), diffusion coefficients of Fe^{2+} are investigated; binding energy and IR spectra for different size clusters are also given.

1. Introduction:

With the world's increasing future energy demand, Generation IV CANDU supercritical water cooled reactor (SCWR) becomes one of the selected novel designs. By utilizing supercritical water both as a coolant and as a working fluid, SCWR takes advantage of both simplicity and energy efficiency. However, while SCWR is expected to boost thermal efficiency of current designs from 33% to about 44% [1] it may have a potential disadvantage that the transport of radiation products including containments from condenser leaks, activated corrosion products, fission products and products of radiolysis may lead to high radiation fields, since the reactor will have supercritical water flowing through the reactor core and directly into turbines. Therefore the long-term viability of the SCWR depends on the ability of designers to predict and control water chemistry, in order to minimize corrosion and radionuclide transport associated [2]. Iron hydroxide known as the "green rust" is the transient compounds between metallic iron and final corrosion products and therefore may govern the mechanism and kinetics of corrosion. Generally speaking, the need for understanding dynamics and structure of iron hydroxide under supercritical water reactor condition becomes very crucial.

Computer simulation has become an essential part of modern physical chemistry. Molecular simulation methods provide information about the thermodynamic, transport and structural properties of a model system [3]. In our case it requires an understanding of molecular interactions and phase behaviour of aqueous electrolyte solutions in extreme conditions. Computer simulation not only takes the advantage of its ability to gain insight into the microscopic molecular-level origin of the macroscopic phenomena but it is also valuable for the examination of system properties under extreme conditions, where physical experiments are difficult or impossible to perform.

In this research, MD simulations of ionic solution in the temperature range from 298K to 673K are performed, along the coexistence curve and in the supercritical region, the radial distribution functions and diffusion coefficients of iron species in water are obtained. We have also performed the simulation of nano-iron hydroxide clusters formed at hydrothermal conditions, these hydrothermally produced clusters are isolated and examined under conditions which imitate an argon bath.

2. Radial distribution function and diffusion coefficient of Fe^{2+} in water:

In this work, parallel molecular dynamics code for an arbitrary molecular mixture (M.DynaMix) has been employed and modified to perform molecular dynamic (MD) simulation of iron-water system which includes 1 Fe^{2+} and 342 simple point charged /expended (SPC/E) water [4] molecules. The simulated state points are shown in Table 1.

Table 1. Simulation detail of Fe^{2+} in SPC/E water.

Temperature K	298	373	473	573	673
Density g/cm^3	0.998	0.947	0.833	0.652	0.304

The radial distribution function (RDF) describes how on average atoms are radially packed around each other. The integration of the RDF yields the coordination number that gives the average number of neighbours that are within a certain radial distance. RDFs of iron and oxygen atoms at ambient, high temperature and supercritical conditions are illustrated in Figure 1. The coordination numbers derived from RDF are given in Table 2.

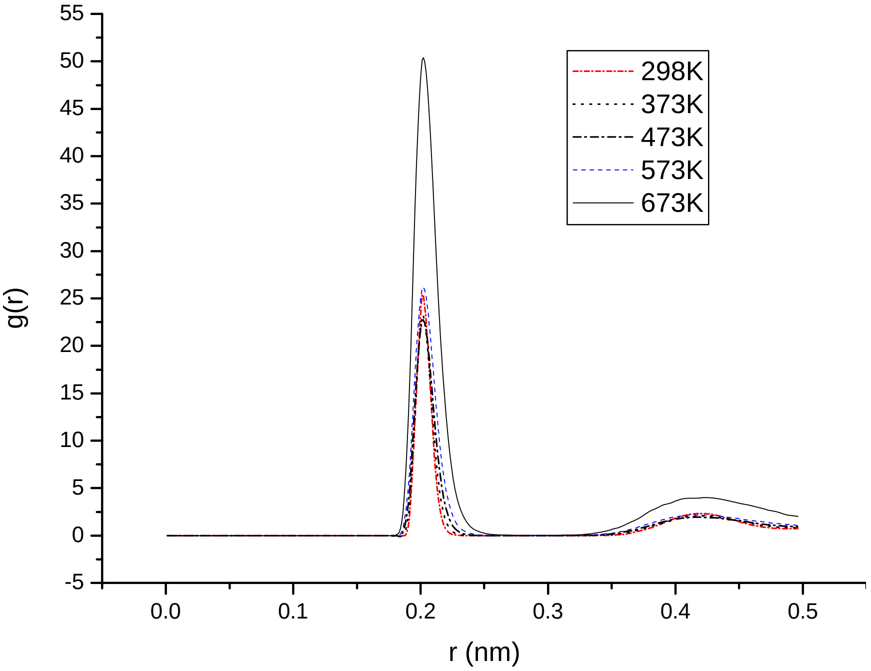

Figure 1. Radial distribution function of Fe^{2+} - O (water) pairs at different conditions.

Table 2. Coordination number of iron in water at different conditions.

Temperature K	298	373	473	573	673
Density g/cm^3	0.998	0.947	0.833	0.652	0.304
Coordination Number	6.0004	6.0045	6.0229	6.0190	6.0205

The fluid transport properties are represented by diffusion coefficients. The diffusion coefficient of Fe^{2+} is presented in Figure 2. It has been found that diffusion coefficient gradually increases from 0.5572×10^{-9} m^2/s to 8.775×10^{-9} m^2/s at subcritical conditions. When the temperature reaches 673K, the diffusion coefficient of Fe^{2+} goes up to 15.12×10^{-9} m^2/s. We also compare our MD data with theoretical predictions obtained through the Stokes-Einstein relation in Figure 2 [5].

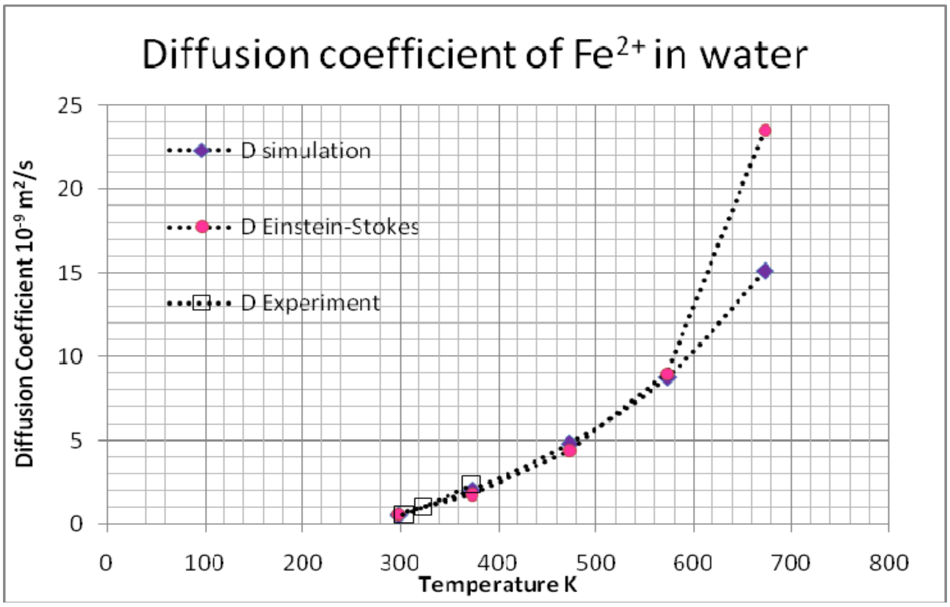

Figure2. Diffusion coefficient of Fe^{2+} in water at different temperatures [5].

3. Binding energy and spectrum of iron hydroxide clusters:

We were also investigated the iron hydroxide clusters formed under supercritical conditions by using MD simulation, the binding energy of different size clusters are shown in Table 3.

Table 3. Binding energy of clusters formed in high temperature water.

Cluster Size	$Fe(OH)_2$	$Fe_2(OH)_4$	$Fe_3(OH)_6$	$Fe_4(OH)_8$	Bulk Crystal
$U_{binding}$ 10^5 J/mol	8.88742	9.58991	9.6648	9.87364	11.0333
Cluster Size	$Fe(OH)_3^-$	$Fe2(OH5)^-$	$Fe_2(OH)_6^{2-}$	$Fe_3(OH)_7^-$	$Fe_3(OH)_8^{2-}$
$U_{binding}$ 10^5 J/mol	8.0187	9.09932	8.16015	9.52	8.8292

The spectrum of dimer is illustrated in Figure 3. The first group of peaks appears around 220 cm^{-1} to 300 cm^{-1}. This may be attributed to the Fe-Fe vibrations where the second group of peak shows up in the range from 300 cm^{-1} to 1000 cm^{-1}, they belong to libration of OH. It is worth mentioning that the experimental spectrum literature indicates that $Fe(OH)_2$ solid has its peaks of lattice vibration at 260 cm^{-1} and 407 cm^{-1} [6].

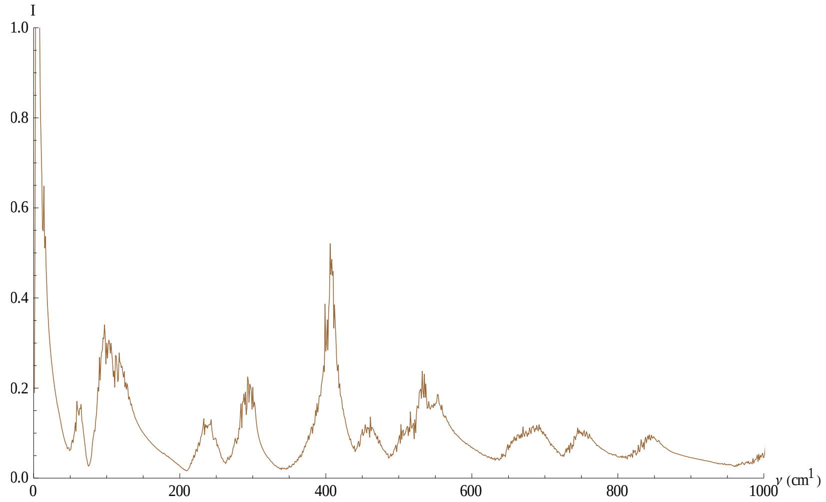

Figure 3. Simulation spectrum of $Fe_2(OH)_4$ dimer cluster.

4. Conclusion:

In this research, dynamics and structure of iron hydroxide under high temperature and supercritical water conditions are examined. Radial distribution function of iron in water is computed which gives iron-water coordination number around 6. The diffusion coefficient of iron species in water ranges from 0.5572×10^{-9} m^2/s to 8.775×10^{-9} m^2/s at subcritical conditions and rises up to 15.12×10^{-9} m^2/s at supercritical point. The potential binding energies of hydrothermally produced iron hydroxide clusters are calculated as well as the vibrational spectra.

5. References

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