MD Simulation of NaCl & NaBr Salts in Water at 298.15 K

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ABSTRACT The molecular dynamic simulation of $Na^+ + Cl^- + H_2O$ and $Na^+ + Br^- + H_2O$ systems were carried out using 72 and 8 molecules of water and Na+ and Cl^- (or Br^-) ions respectively at 298.15K. It is reported that in case of $Na^+ + Br^- + H_2O$ system shows higher aggregation as compared to the $Na^+ + Cl^- + H_2O$ which may be due to the higher ionic radii and atomic weight of Br^- ions.

***Key words*:** NaCl, NaBr, MD Simulation

Introduction

The Molecular dynamic simulation, a theoretical technique, provides valuable information about the system. It also helps in predicting the number of physical properties and hence helps in understanding the various types of forces involved in the system [*Alder and Wainwright, 1959*]. The process of simulation activates by assigning the number of selected molecules in an ensemble. Atoms or molecules in a system are allowed for interaction in fix time scale to evaluate dynamic state of the system. With evolution of time, the trajectories are determined using the Newton's equation of motion [*Rahman,1964*]. The interaction between the molecules and their potential and kinetic energies are calculated using inter-atomic potentials [Rahmanand Stillinger, 1971].

MD simulation helps in providing the valuable information on radial distribution function, molecular level kinetics, total energy and potential energy at particular temperature. It can be designed to calculate the density, viscosity and other valuable physical parameters of the system [Tuckerman *et.al*., 1991].

Material and Method

The simulation procedure is initially standardized with 375 water molecules using TIP4P force field. The obtained results were compared with the literature values [Vega et.al, 2007 and 2009]. It is reported that our method provides the results as per the literature values.

In present study we have simulated the $Na^+ + Cl^- + H_2O$, and $Na^+ + Br^- + H_2O$ systems around 298.15 K with the fixed number of molecules. All the MD simulations were executed using *LAMMPS* [LAMMPS Manual,2014 and Plimpton, 1995] and *Molden* [Schaftenaar and Noordik, 2000] software. The basic MD simulations were performed in *Molden* software. To evaluate the values of Radial distribution function (RDF) among various ions, *LAMMPS* used with Optimized Potentials for Liquid Simulations (OPLS) force field [*Jorgensen et. al. 1988* and 1996]. Before simulation three files were created viz. Data file having molecular arrangement description, Force-Field file and Input file having the basic simulation commands. After simulation the results are stored in *logfile*. The simulation in *LAMMPS* and *Molden* performed with same data file and basic simulation input parameters.

Table 1. Input Parameters for simulation of salts in water

S. No.	Parameter	Value
1	Temperature	298.15K
2	Time Step	0.5 S
3	Number of Steps	50000
4	Cut-Off Radius (A)	7
5	Ensemble	Constant Volume and Shape
6	Thermostat	Nose-Hoover
7	Energy Minimization Tolerance	1.00E-04 Kcal/Mol.
8	Preliminary Equilibrium Step	5000
9	Data output step	10
10	Force Field	Optimized Potentials for Liquid Simulations (OPLS)
11	Total Water Molecules	72
12	Total Cations (Na+)	8
13	Total Anions (Cl- or Br-)	8
14	Ensemble Volume:	8000 A^3
15	Density (as per ensemble volume)	0.912119 gm/cm^3
16	Total Mass	4394.23447265 amu

Table 1

$Na^+ + Cl^- + H_2O$, and $Na^+ + Br^- + H_2O$ systems simulated separately with same number of water, cations, anions and water molecules. The initial positions of cations (Na^+) and anions (Cl^- or Br^-) were random.

The simulation process initiated with energy minimization for 5000 steps with acceptable tolerance of 1.00E-04 kcal/mol. The obtained potential for $Na^+ + Cl^- + H_2O$ and $Na^+ + Br^- + H_2O$ are plotted against iteration (simulation steps) and shown in the figure 1 and 2 respectively.

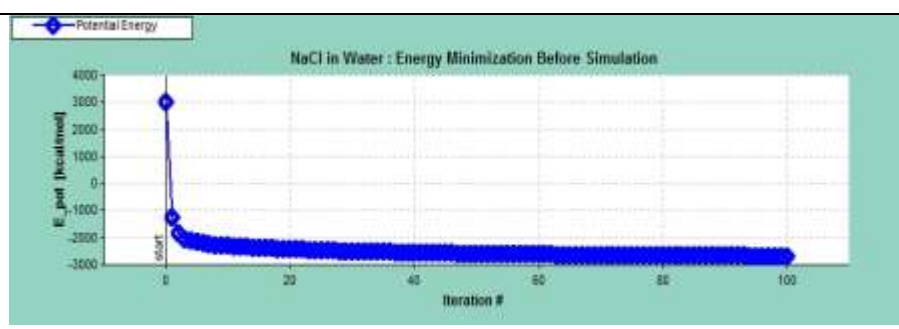

Figure 1. Energy minimization curve before simulation of Na+ + Cl- + H2O at 298.15 K

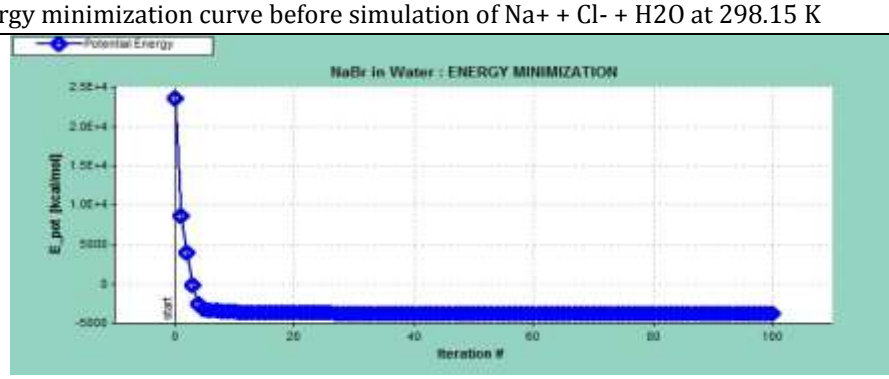

Figure 2. Energy minimization before simulation of Na+ + Br- + H2O in Water at 298.15 K

Figure 1 & 2

Once energy minimization achieved, simulation carried out for equilibrium. In both the cases it was achieved within 5000 steps. The equilibrate system simulated for next 50000 steps to observe the variation of kinetic energy, potential energy and total energy. Figure 3 and 4 show the variation of kinetic energy, potential energy and total energy profile for $Na^+ + Cl^- + H_2O$ and $Na^+ + Br^- + H_2O$ respectively.

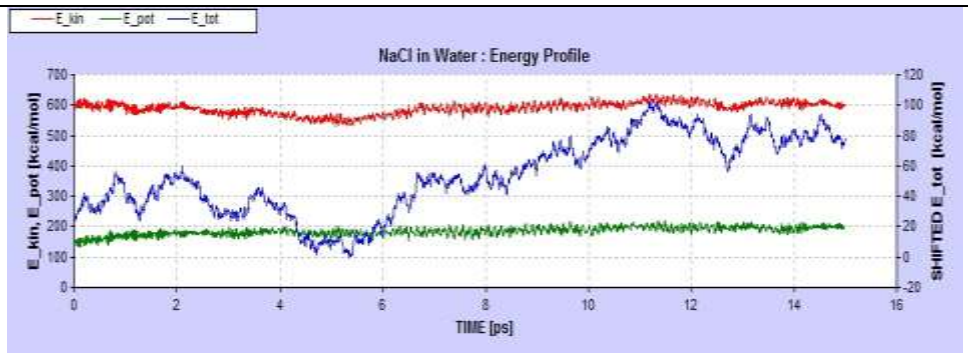

Figure 3. Energy profile of Na+ + Cl- + H2O system: Kinetic energy, total energy and potential energy curves in simulation progress at 298.15 K

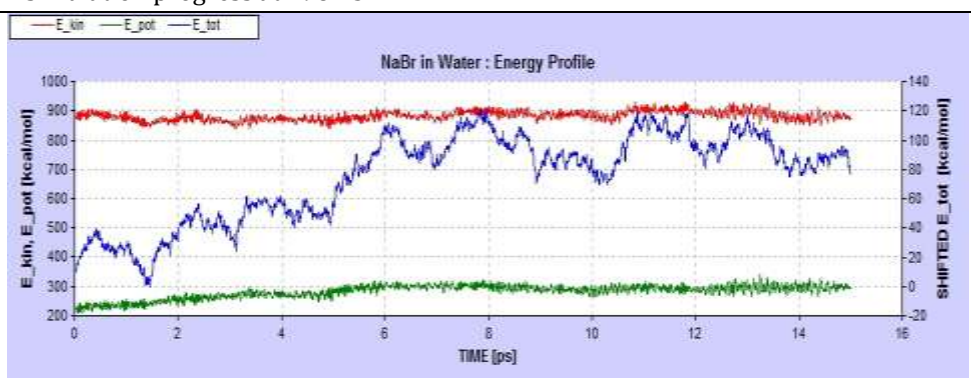

Figure 4. Energy profile of Na+ + Br- + H2O system: Kinetic energy, total energy and potential energy in simulation progress at 298.15 K

Figure 3 and 4

The simulation performed with 298.15 K temperature scale. However, the obtained temperature profile with simulation time for $Na^+ + Cl^- + H_2O$ and $Na^+ + Br^- + H_2O$ are shown in figure 5 and 6 respectively, which is around 298.15 K (± 0.5 K).

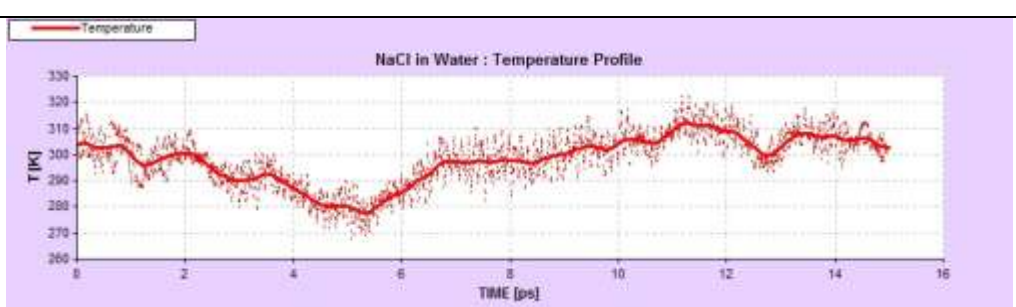

Figure 5. Temperature profile Na+ + Cl- + H2O at 298.15 K

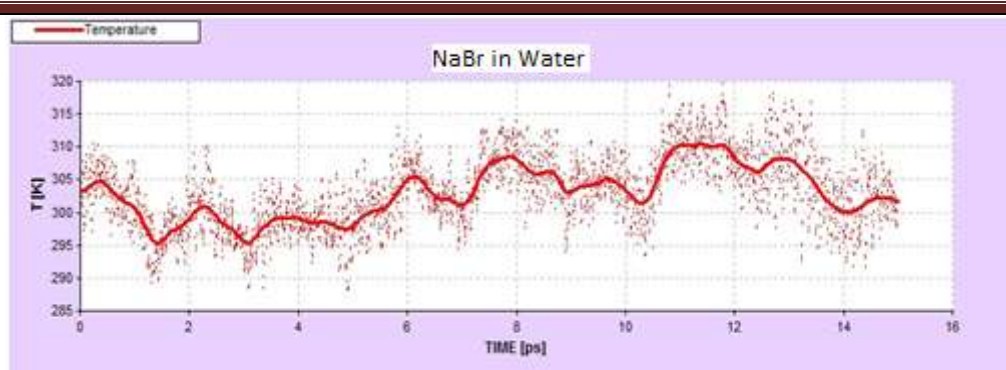

Figure 6. Temperature profile Na+ + Br- + H2O at 298.15 K

Figure 5 and 6

Results

In case of $Na^+ + Cl^- + H_2O$ and $Na^+ + Br^- + H_2O$ the energy minimization are reported to be less than -3000 kcal/mol and -5000 kcal/mol respectively. System after this had very little change and that too within the 1.00E-4 Kcal/mol.

In both the cases the temperature scale was near to 298.15 K and variation of the temperatures was -20.0K but the average temperature was within the allowable standard deviation of ±3.0K. The total energy of $Na^+ + Cl^- + H_2O$ decreases initially, then slowly increases to 600 kcal/mol. at the end of simulation. In case of $Na^+ + Br^- + H_2O$ total energy initially increases and then maintains nearly constant values around 800 kcal/mol.

Figure 7 and 8 shows the obtained radial density profile for $Na^+ + Cl^- + H_2O$ and $Na^+ + Br^- + H_2O$ systems respectively. The number density profile of $Na^+ + Cl^- + H_2O$ system indicates the minimum density of 2 at the distance of 2A° whereas in case of $Na^+ + Br^- + H_2O$ it is reported to be 19 at around 2A°. On increasing the distance the radial density function decreases as expected in both the cases. In case of $Na^+ + Cl^- + H_2O$ this decrease is not uniform.

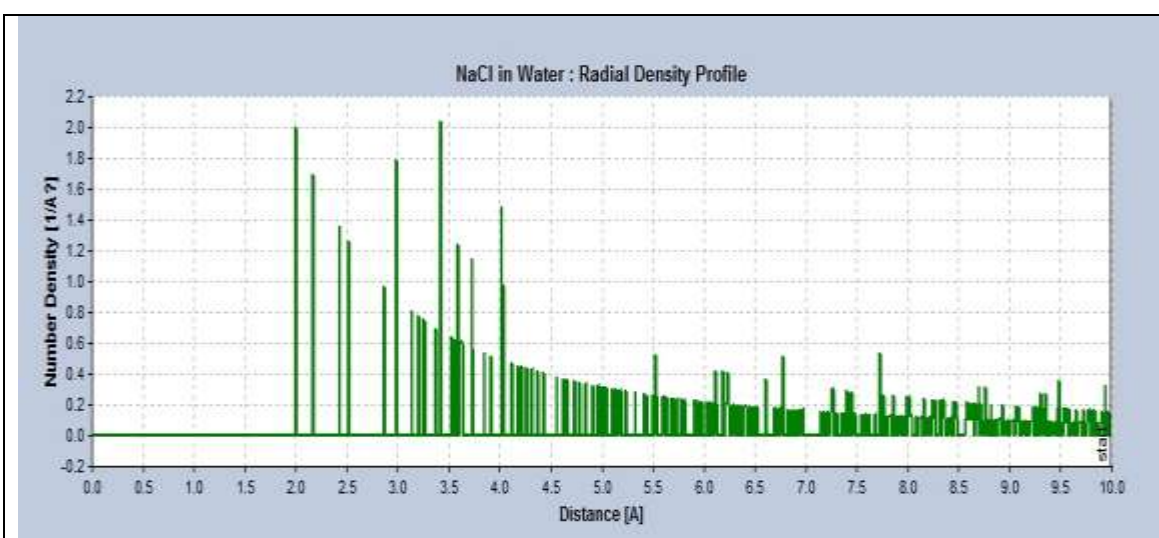

Figure 7. Radial density profile of $Na^+ + Cl^- + H_2O$

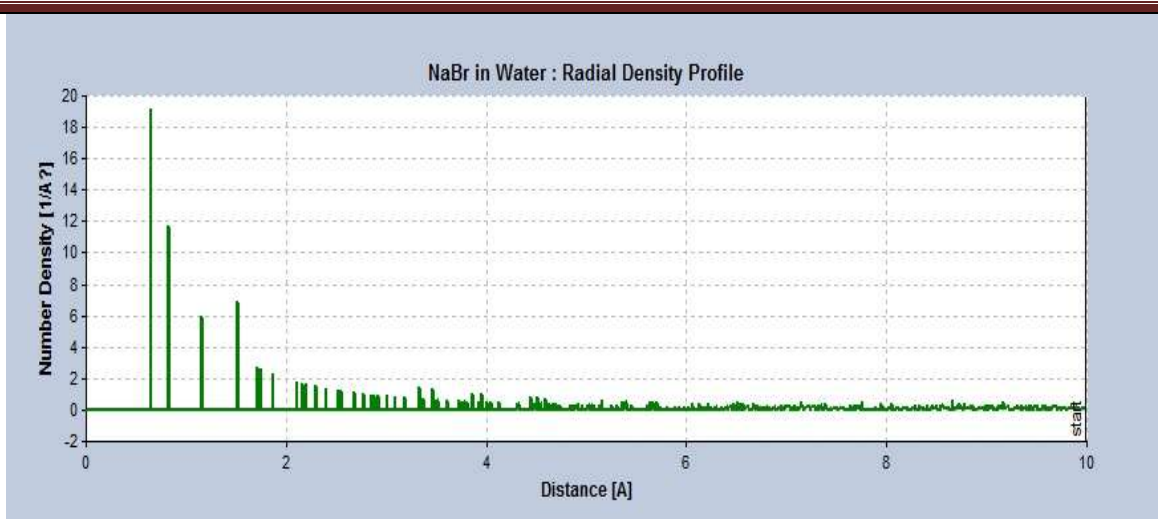

Figure 8. Radial density profile of $Na^+ + Br^- + H_2O$

Figure 7 and 8

Conclusion

$Na^+ + Cl^- + H_2O$ system provide higher degree of interaction with solute-solute interaction as compared with $Na^+ + Br^- + H_2O$. In studied system there is only the difference of Br^- ions into the system. Br^- is bulkier than Cl^- . This may be the reason that system shows more aggregation in case of $Na^+ + Br^- + H_2O$. In both the case, same amount of time provide for simulation, it is reported that $Na^+ + Cl^- + H_2O$ system was more dynamic than $Na^+ + Br^- + H_2O$. This may be due to the difference in anions in these systems. The known ionic size of Cl^- and Br^- is 167 and 182 pm respectively. The effective ionic raidii of Cl^- and Br^- are 181 and 196 pm respectively [Shannon, 1976]. The aggression in case of $Na^+ + Br^- + H_2O$ may be due to the slightly higher ionic size of Br^- and less effective charge as compared with ionic size of Cl^- in $Na^+ + Cl^- + H_2O$.

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Simplicity is the key to brilliance.
~ Bruce Lee