



Research Article

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MD simulation of KCl, KBr and KI salts in water at 298.15 K

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ABSTRACT

The molecular dynamic simulation of $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ systems were carried at 298.15K. It is reported that in case of $K^+ + Br^- + H_2O$ system shows higher aggregation as compared to the $K^+ + Cl^- + H_2O$ which may be due to the higher ionic radii and atomic weight of Br^- ions. $K^+ + Cl^- + H_2O$ system provide higher degree of interaction with solute-solute interaction as compared with $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$. It is concluded that system having smaller ions like Cl^- , the orientation of water molecules indicates dominance of electrostatic mechanism, whereas in case of Br^- ions surrounding water, it may be due electrostatic orientation and water-water hydrogen-bonding ordering mechanism of water molecules. In case of I^- anions, which is larger in size, the water molecule orientation may be due to electrostatic tendency to orient dipole with respect to ion and hydrogen-bonding tendency to orient adjacent water molecules as shown by Barbara Hribar in their study.

Keywords: KCl, KBr, KI, MD Simulation

INTRODUCTION

Molecular dynamics is a form of simulations in which atoms and molecules are allowed to interact for a period of time by approximations of known physics giving a view of the motion of the particles.

The use of computers to explore the properties of condensed matter goes back to the decade of 1950's and the first Monte Carlo (MC) and Molecular Dynamics (MD) simulations of model liquids performed by Metropolis et al. [1] and Alder and Wainwright [2], respectively.

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 [2]. 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 [3]. The interaction between the molecules and their potential and kinetic energies are calculated using inter-atomic potentials [4].

MD simulation provides information on kinetic energy, total energy, potential energy. It also provides valuable information like radial distribution function, density, viscosity etc. [5]. Selection of force-field in MD simulation plays a vital role in providing the interactions among molecules. Ideally this can be done from first principles, solving the electronic structure for a particular configuration of the nuclei, and then calculating the resulting forces on each atom [6].

The aim of the present study is to understand the configuration of binary aqueous system. Also to know various energy profiles.

EXPERIMENTAL SECTION

The simulation procedure is initially standardized with 375 water molecules using TIP4P force field. The obtained results were compared with the literature values [7]. The water simulation results are comparable with our previous work and literature.[7,8,9].

The simulation of binary systems activated by selecting correct ensemble, followed by adding water molecules, cations and anions. In present study we have simulated the $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ systems around 298.15 K with the fixed number of molecules. All the MD simulations were executed using LAMMPS [10,11] and Molden software [12].

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 [13,14]. Three files created for simulation process. The 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. The supplied input parameters are listed in table 1.

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 (K^+)	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

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

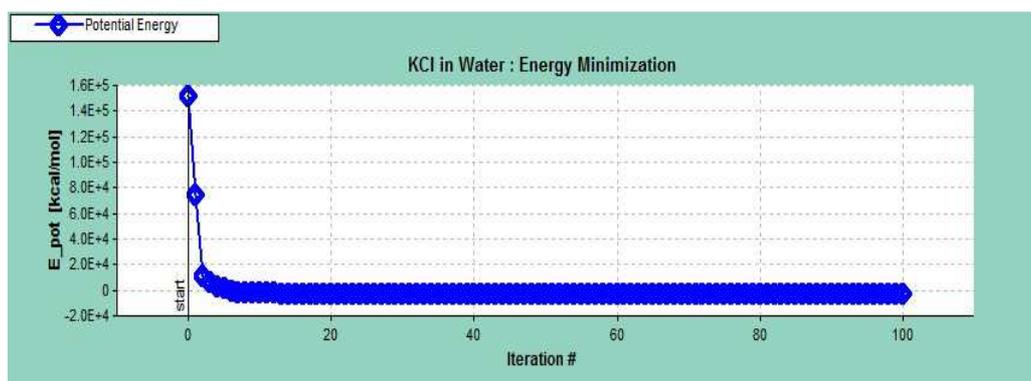


Figure 1. Energy minimization curve before simulation of $K^+ + Cl^- + H_2O$ at 298.15 K

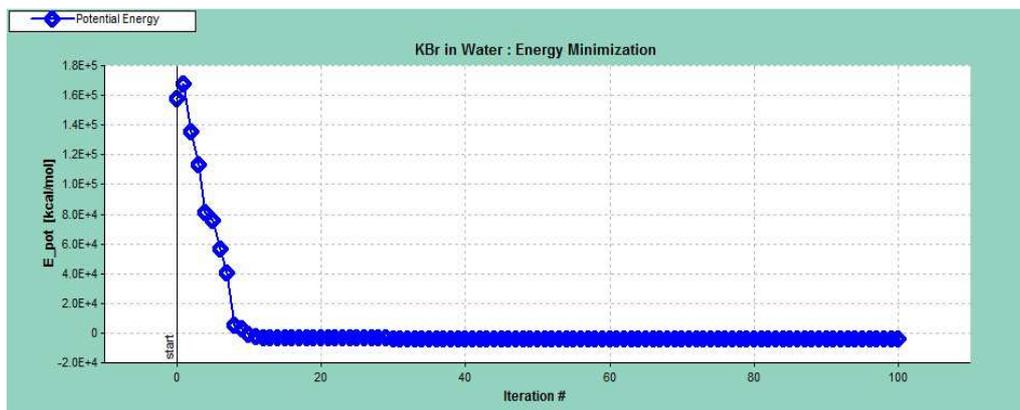


Figure 2. Energy minimization before simulation of $K^+ + Br^- + H_2O$ in Water at 298.15 K

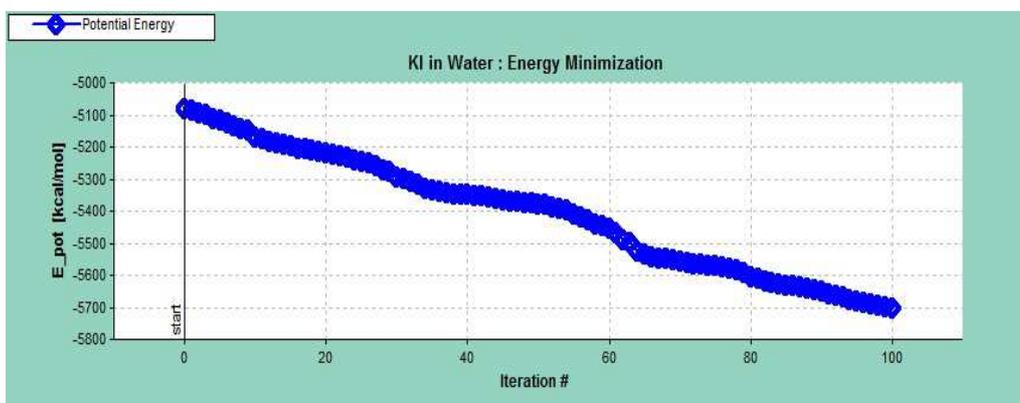


Figure 3. Energy minimization before simulation of $K^+ + I^- + H_2O$ in Water at 298.15 K

The simulation process initiated with energy minimization for 5000 steps with acceptable tolerance of $1.00E-04$ kcal/mol. The obtained potential for $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ are plotted against iteration (simulation steps) and shown in the figure 1, 2 and 3 respectively.

After energy minimization, simulation was continued until equilibrium achieved. It is reported that equilibrium achieved within 5000 iterative steps. Furthermore, the equilibrate system simulated for 50000 steps to observe the variation of total energy, kinetic energy and potential energy. Figure 4, 5 and 6 show the variation of total energy, kinetic energy and potential energy and profiles for $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ respectively.

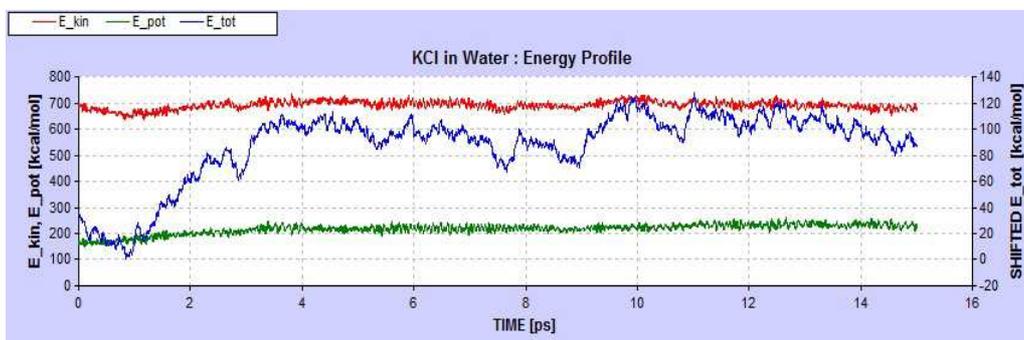


Figure 4. Energy profile of $K^+ + Cl^- + H_2O$ system: Kinetic energy, total energy and potential energy at 298.15 K

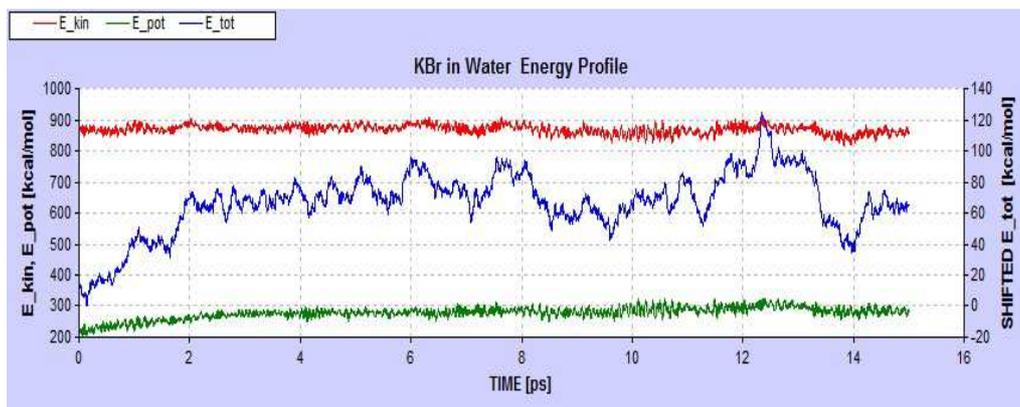


Figure 5. Energy profile of $K^+ + Br^- + H_2O$ system: Kinetic energy, total energy and potential energy at 298.15 K

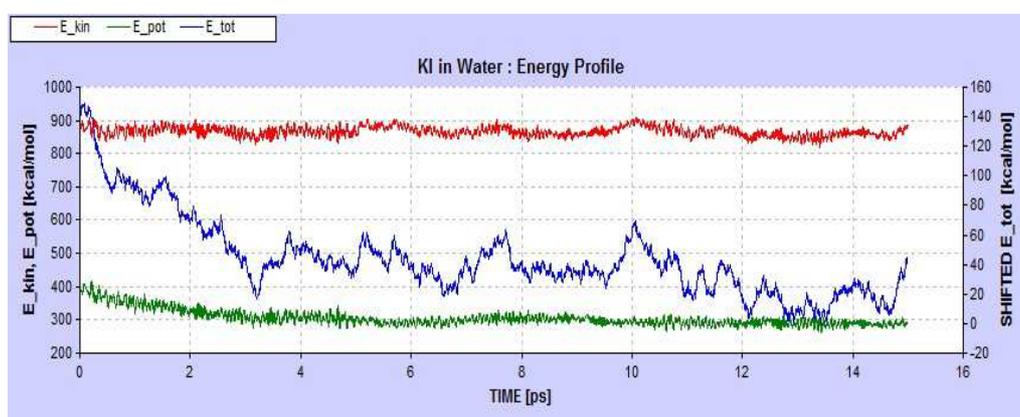


Figure 6. Energy profile of $K^+ + I^- + H_2O$ system: Kinetic energy, total energy and potential at 298.15 K

The simulation performed at around 298.15 K temperature scale. However, the obtained temperature profile with simulation time for $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ are shown in figure 7, 8 and 9 respectively, which is around 298.15 K.

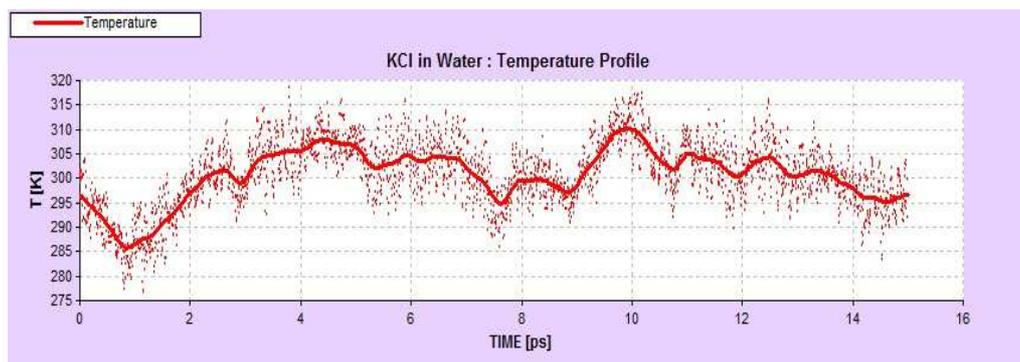


Figure 7. Temperature profile $K^+ + Cl^- + H_2O$ at 298.15 K

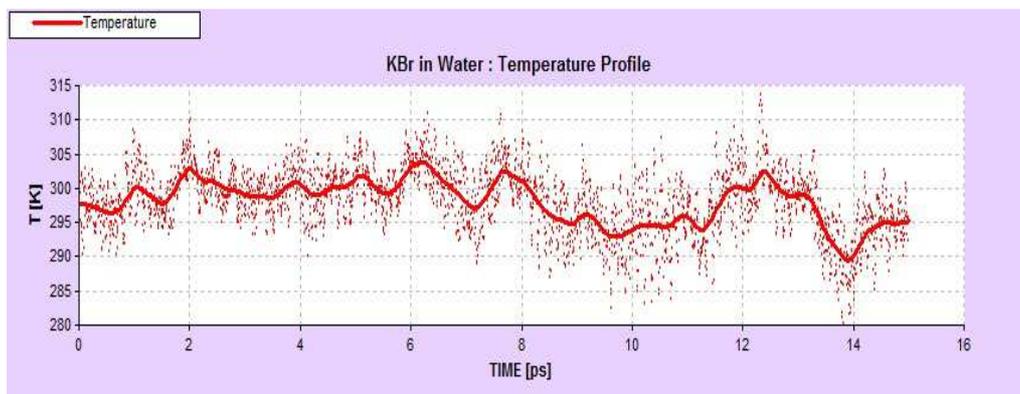


Figure 8. Temperature profile $K^+ + Br^- + H_2O$ at 298.15 K

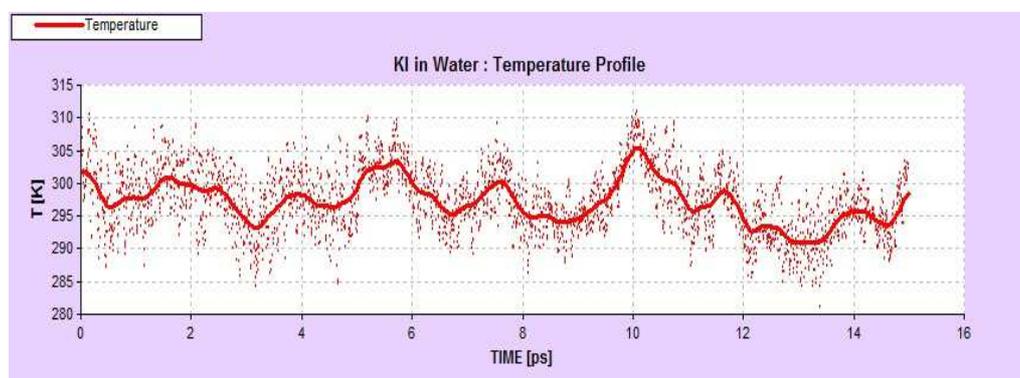


Figure 9. Temperature profile $K^+ + I^- + H_2O$ at 298.15 K

RESULTS

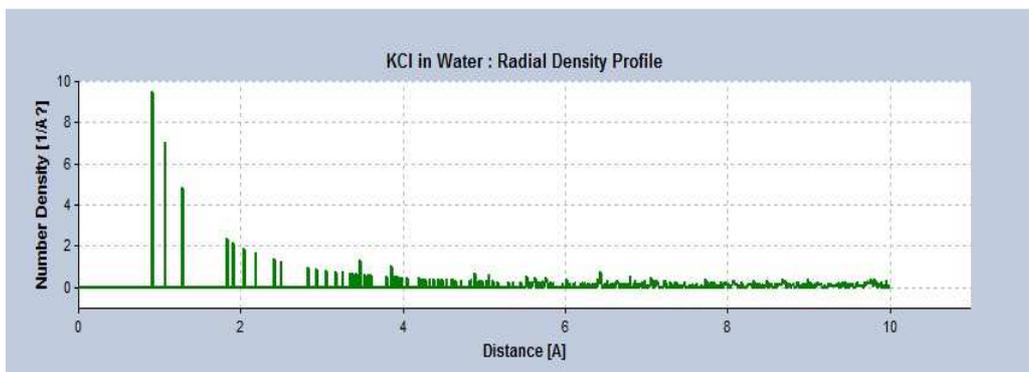
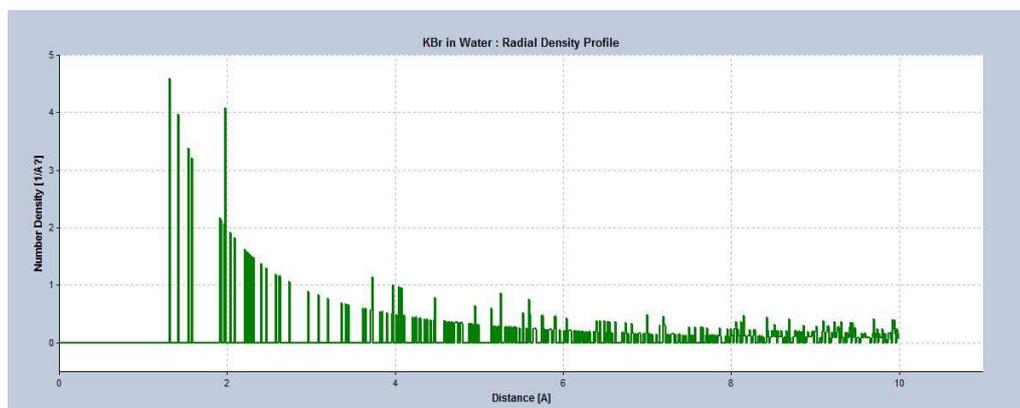
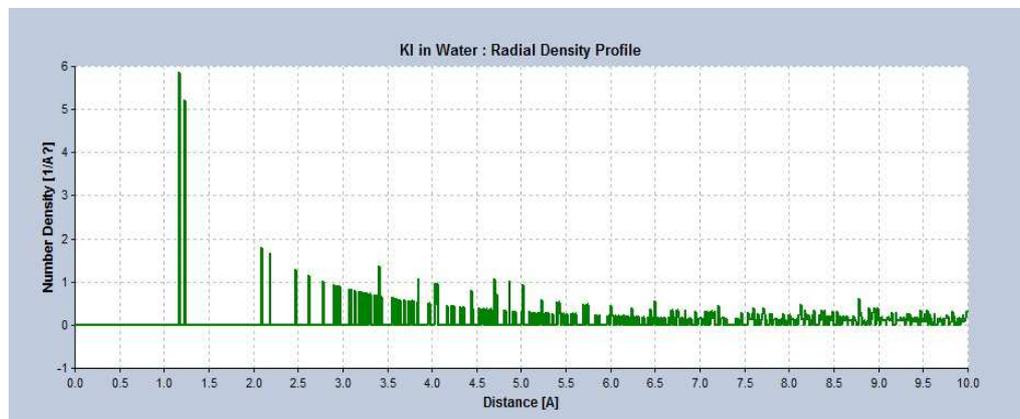
In both systems $K^+ + Cl^- + H_2O$ and $K^+ + Br^- + H_2O$ energy minimization are reported to be less than $-2.0 E^4$ kcal/mol. In case of $K^+ + I^- + H_2O$ the energy minimization is decreased uniformly upto -5700 kcal/mol. The process of energy minimization was fastest for $K^+ + Cl^- + H_2O$ and slowest for $K^+ + I^- + H_2O$. This may be due to difference of ionic size and mass of Cl^- and I^- .

In all simulation the temperature scale was near to 298.15 K and variation of the temperatures was $-18.0K$ with average temperature kept within the allowable standard deviation of $\pm 3.0K$. Figure 7,8 and 9 depicting the temperature variations for $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ systems respectively.

In case of energy profile, the Kinetic energy of $K^+ + Cl^- + H_2O$ decreases initially, then increases slowly to 700 kcal/mol. In case of $K^+ + Br^- + H_2O$ kinetic energy initially increases and then maintains nearly constant values around 900 kcal/mol. However in system $K^+ + I^- + H_2O$ kinetic energy initially increases and then become constant at around 850 kcal/mol.

Figure 10, 11 and 12 shows the obtained radial density profile for $K^+ + Cl^- + H_2O$, $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ systems respectively. The number density profile of $K^+ + Cl^- + H_2O$ system indicates the maximum number density of 9.5 at the distance of $0.8A^0$ whereas in case of $K^+ + Br^- + H_2O$ it is reported to be 4.6 at around $1.3A^0$ and in system $K^+ + I^- + H_2O$ the maximum number density of 5.9 approximately at $1.2 A^0$. On increasing the distance the radial density function decreases as expected in all the cases. In case of $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$ this decrease is not uniform.

The configuration shows that smaller ions bind closer to water molecules as compared to bigger ions like I^- . This is comparable with the work of Barbara Hribar [15].

**Figure 10. Radial density profile of $K^+ + Cl^- + H_2O$** **Figure 11. Radial density profile of $K^+ + Br^- + H_2O$** **Figure 12. Radial Density Profile of $K^+ + I^- + H_2O$**

CONCLUSION

$K^+ + Cl^- + H_2O$ system provide higher degree of interaction with solute-solute interaction as compared with $K^+ + Br^- + H_2O$ and $K^+ + I^- + H_2O$. In studied system, there is only the difference of anions into the system. The effective ionic radii of Cl^- and Br^- and I^- are 181, 196 and 220 pm respectively [16]. In case of anion Cl^- , radial density profile shows the number density decreases with increase in distance. This clearly indicates that the interaction of ions and molecules decreases with distance. The same is reported for the systems having Br^- and I^- anions.

The potential energy profile for $K^+ + Cl^- + H_2O$ and $K^+ + Br^- + H_2O$ increases, whereas for $K^+ + I^- + H_2O$ decreases. This may be due to the effective charge on anions. The I^- is bulkier than Cl^- and Br^- and hence potential energy

decreases as simulation progresses in case of I⁻. Secondly, I⁻ ions are not closely packing the water molecules which reduces the interactions.

In the system having smaller ions like Cl⁻, the orientation of water molecules indicates dominance of electrostatic mechanism, where water molecule try to orient in most comfortable electrostatic orientation with respect to surrounding anion [15]. Whereas in case of Br⁻ ions surrounding water, it may be due electrostatic orientation and water–water hydrogen-bonding ordering mechanism of water molecules.

In case of I⁻ anions, which is larger in size, the water molecule orientation may be due to electrostatic tendency to orient dipole with respect to ion and hydrogen-bonding tendency to orient adjacent water molecules [15].

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