MONTE CARLO SIMULATION OF I⁻, Br⁻, AND Cl⁻ IN WATER USING AB INITIO PAIR POTENSIAL FUNCTIONS

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ABSTRACT

Monte Carlo simulations were performed for I⁻, Br⁻ and Cl⁻, in water using ab initio pair potential. The systems consisting of one anion in 215 solvent molecules have been simulated at 298 K. Anion-water pair potentials have been newly developed based on ab initio calculations of split valence basis set plus polarization quality. The structure of the solvated ion is discussed in terms of radial distribution functions, coordination number and pair potential distribution. Structural properties were investigated by means of radial distribution functions and their running integration numbers, leading for the first solvation shell to an average 12.60 H_2O around I⁻ with I⁻-O distance of 3.74 Å and I⁻-H distance of 2.86 Å, 11.84 H_2O around Br⁻ with Br⁻-O distance of 3.40 Å and Br⁻-H distance of 2.42 Å, and 10.68 H_2O around Cl⁻ with Cl⁻-O distance of 3.20 Å and Cl⁻-H distance of 2.24 Å, respectively. The structure of the water-anion complexes are agreed with dipole orientation. Pair energy distribution of hydrated anions showed that the pair interaction energy are increase from I⁻, Cl⁻, to Br⁻, namely, -6.28, -9.98 and -13.67 kcal/mol, respectively. The coordination number distribution analysis for the first solvation shell of the all hydrated anions indicated a high exchange rate for the first solvation shell ligands.

Keywords: Monte Carlo simulation, halogen anion, ab initio

INTRODUCTION

The process of solvation is of central importance in chemistry and has been the subject of numerous experimental and theoretical studies. The presence of a solvent influences the outcome of a chemical reaction through the interaction of the local environment with the individual species undergoing the reactions. The solvent, on one level, provides an energy bath for the stabilization of energetic products formed during reactions and provides physical barriers to the motion of the reactive species. Solvation has been shown to be of fundamental importance in such diverse areas as biological activity and atmospheric processes [1].

The phenomenon of ion solvation in water clusters has received considerable attention in recent years for several reasons. First, the size of clusters can be gradually increased to the point where they exhibit many properties of the bulk while still containing a relatively small number of particles. The limited number of degrees of freedom in clusters opens up the possibility for high resolution experiments and accurate theoretical calculations. The recent development of new spectroscopic techniques for charged clusters has renewed interest in the fundamental aspects of the structure and dynamics of the ion-water hydrogen bond [2-4]. Moreover, because of their large surface to interior ratio, clusters are useful models for investigating ion solvation at interfaces of aqueous solutions.

Hydrated halide anions (up to n = 10 for some cases) have been studied by high-pressure mass spectrometry, and the thermochemical parameters are believed to be reasonably well known. The experimental data show no clear indication of a first solvation shell for the different halide ions [5]. A more definite evidence for a shell-solvation structure was obtained from photodetachment experiments of I⁻ $(H_2O)n$, n = 1–15, with a clear indication that the energy of association levels off after six water molecules [6]. These hydrated anions are of particular interest to understand how information obtained in the gas-phase can be extrapolated to aqueous solutions, and to verify to what extent the energetic and dynamics of gas-phase solvated ions can serve as a model for ions solvated in bulk.

The competition between solvent-solvent structure and ion-solvent structure as a cluster grows in size can be understood in terms of the strength of ion-solvent interactions vs solvent-solvent interactions, of which it is well-known that a primary factor is ion size relative to the solvent. Iodide-water interactions are about the same magnitude as water-water interactions, so small water clusters gain the most stability by engaging a large iodide ion without breaking the solvent-solvent hydrogen bonds in aqueous iodide clusters there is a gradual progression from surface states at small cluster size to internal states at large cluster size with the intervening region exhibiting an intermediate degree of surface character [7].

Quantitative theoretical description of halogen ion solvation in water clusters is demanding both on the quality of the interaction potential and on the sampling of the accessible phase space. It has been shown that, for example, including a many-body polarization term in

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an empirical force field notably moves the anion from the interior towards the surface of the cluster. Advanced *ab initio* methods provide, at least for small clusters, a sufficiently accurate interaction model. However, since quantum chemical methods directly provide results relevant to 0 K, sampling of the phase space of these non-rigid clusters with many local minima and low-lying barriers is likely to be insufficient. The advent of the Car-Parrinello *ab initio* molecular dynamics approach permits phase space sampling of non-rigid systems with non-empirical potentials. With this technique it is presently feasible to simulate clusters with tens of heavy atoms for several picoseconds [5-8].

Eighteen water molecules are required to form a complete solvation shell around a chlorine anion. Although fewer water molecules may surround the chlorine anion, these exist as high-energy species. Calculations on the fluorine anion show that fifteen water molecules are required for a complete solvation shell. These results are in good agreement with relative energies predicted by *ab initio* energy calculations which are current in progress [9-11].

Dynamical properties of F$^-$–water and Cl$^-$–water hydrogen bonds in aqueous solution have been studied by ab initio QM/MM molecular dynamics simulations, in which the whole first hydration sphere of the anion was treated at Hartree–Fock level using D95V+, 6-31+G and D95V++ basis sets for F$^-$, Cl$^-$ and water, respectively [12-13]. The arrangement of water molecules around F$^-$ and Cl$^-$ reveals clear differences between the two anions. Within the hydration sphere of F$^-$, most neighboring water molecules donate one of their hydrogen atoms in a linear hydrogen bond to the ion, while water molecules in the hydration shell of Cl$^-$ show a combination between water orientations pointing with only one or both hydrogen atoms towards the ion.

In the present work, the solvation of iodine, bromine and chlorine anions has been studied using *ab initio* quantum mechanics. In particular, we have investigated the number of water molecules required to fully surround each anion. Monte Carlo calculations have been employed in an attempt to find the solvated system with the lowest energy. The results are reported and discussed in terms of structural properties and compared with other theoretical and experimental investigations.

EXPERIMENTAL

Pair Potential of X$^-$-H$_2$O

The X-H$_2$O, where X is Cl, Br, and I pair potentials were constructed using the same procedure as previously done for Cu$^+$-H$_2$O [14]. The basis set proposed by Schäfer et al. [15] was used for halogen anions. The double-ζ plus polarization (DZP) basis set of Dunning [16] corresponding to D95V* in the Gaussian 98 program were used for water. The experimental

geometry of water [17] was kept rigid as well, with O-H distance of 0.9601 Å and H-O-H angle of 104.47°.

To construct the X$^-$-H$_2$O pair potentials, the water molecule was fixed in the origin of the coordinate system and X$^-$ was moved in configuration sphere varying geometrical parameters within 1.5 Å ≤ $r_{Cl\text{-water}}$ ≤ 15.0 Å, 0° ≤ θ ≤ 180° and 0° ≤ ϕ ≤ 60°. The interaction energies, ΔE_{2b}, between X$^-$-H$_2$O were computed by subtracting the *ab initio* energies of the isolated species E_X and E_{water} from those of the monosolvates $E_{X\text{-water}}$. All pair potentials were developed from more than 1500 SCF energy points for X$^-$-water.

The fitting process to an analytical potential function was performed by the least-squares method with Levenberg-Marquart algorithm, with various potential types. The best analytical potential function form describing all electronic and van der Waals interactions resulted as

$$\Delta E_{2b} = \sum_{i=1}^{3} A_{iM} r_{iM}^{-7} + B_{iM} r_{iM}^{-8} + C_{iM} r_{iM}^{-9} + D_{iM} r_{iM}^{-10} + q_i q_M r_{iM}^{-1}$$

for Cl-H$_2$O pair potential,

$$\Delta E_{2b} = \sum_{i=1}^{3} A_{iM} r_{iM}^{-6} + B_{iM} r_{iM}^{-11} + C_{iM} x \exp(-D_{iM} r_{iM}) + q_i q_M r_{iM}^{-1}$$

for Br-H$_2$O pair potential, and

$$\Delta E_{2b} = \sum_{i=1}^{3} A_{iM} r_{iM}^{-7} + B_{iM} r_{iM}^{-8} + C_{iM} r_{iM}^{-9} + D_{iM} r_{iM}^{-10} + q_i q_M r_{iM}^{-1}$$

for I-H$_2$O pair potential.

where A_{iM}, B_{iM}, and C_{iM} denote the fitting parameters, r_{iM} are distances between the *i*th atom of H$_2$O and X$^-$, q_i are the atomic net charges of the *i*th atom of H$_2$O taken from Mulliken population analysis, and q_M is the charge of X$^-$. The charge for O and H is -0.6598 and 0.3299, respectively. Configurations with energies above +30 kcal mol^{-1} were excluded and weighting was performed with respect to the absolute and low-lying energy local minima. Identical coefficients were used for equivalent hydrogen atoms. The final parameters of the function are given in Table 1. The standard deviation of the fitted values from SCF data was ± 1.57 kcal mol^{-1} for the whole region. Figure 1 shows the comparison of the energies obtained from the SCF calculations, ΔE_{SCF}, and from the potential function, ΔE_{FIT}, for (a) Cl$^-$-H$_2$O, (b) Br$^-$-H$_2$O, and (c) I$^-$-H$_2$O system using the final values of the fitting parameters as given in Table 1 for some configurations [14].

Monte Carlo Simulation

Monte Carlo simulations were performed for a system consisting of one X$^-$ and 215 waters using the newly developed two-body function at a temperature of 298 K. The edge length of this box is 18.7170, 18.7429,

and 18.8168 Å for X = Cl, Br, and I, respectively, corresponding to the density of pure water (0.997 g cm^{-3}). For water-water interactions, the CF2 potential proposed by Jancso and Heinzinger [18] was used. Periodic boundary condition and cut-off of exponential terms at half of the box lengths were applied in all simulations [19]. After generating a starting configuration randomly, the systems had reached energetic equilibrium after 3 million configurations, setting an acceptance ratio of 1:3. For the evaluation of structural data a further 3 million configurations were sampled.

RESULT AND DISCUSSION

The dynamics of hydrogen bonds in aqueous electrolyte solutions of charged particles, in particular anions, has been an important subject of both experimental and computational studies. In general, the interactions of anion with water are relatively weak and dominated by ionic hydrogen bonding. These interactions are, in several cases, even energetically comparable with the water-water interactions in pure water, implying that the dynamical properties of such weakly hydrated anions can be very sensitive to the relative strength of anion-water and water-water interactions.

Fig 2 show the structure of the hydrated halogen anion. The global minimum of the interaction energy of -19.832, -14.766, -10.794 kcal mol^{-1} were found for X$^-$-H$_2$O adduct at X$^-$-O distance of 3.13, 3.39 and 3.74 Å, for X = Cl, Br, and I, respectively. The distance of X-H for X$^-$-H$_2$O adduct is 2.20, 2.51, 2.93 Å for X = Cl, Br, and I, respectively. Increasing distance between the negative ion and the water molecule is agreed with decrease of binding energy between anion-water.

Table 1. Final optimized parameters for the interactions of O and H atoms of water with X$^-$, where X = Cl, Br, and I. The atomic net charges are given in a.u., interaction energies and distances in kcal mol^{-1} and Å, respectively.

System	A	B	C	D
Cl- H$_2$O	-317397.1009	2167030.4203	-4704753.0374	3379223.3481
	-41047.2250	173003.6269	-270486.0644	133320.1647
Br- H$_2$O	-933.9300	40444.0305	8959.3916	2.2435
	-4968.3668	10671.8909	39065.8617	3.1363
I- H$_2$O	-15958.3227	793240.7037	-3049424.0612	3292324.9248
	-175671.9937	1000234.0640	-1876642.3510	1170560.4055

Table 2. Characteristic values of the radial distributions functions $g_{\alpha\beta}(r)$ for the X$^-$-water;[a]

α	β	r_{M1}	r_{m1}	$n_{\alpha\beta}(m1)$	r_{M2}	r_{m2}	$n_{\alpha\beta}(m2)$
Cl	O	3.20	3.90	10.66	5.78	6.41	39.69
Cl	H	2.24	2.89	9.71	3.54	5.00	42.04
Br	O	3.40	4.21	11.84			
Br	H	2.42	3.20	10.10	3.86	4.40	27.96
I	O	3.74	5.56	13.65	6.42	7.14	49.93
I	H	2.86	3.50	10.89	3.88	4.60	27.72

[a] r_{M1}, r_{M2} and r_{m1}, r_{m2} are the distances in Å, where $g_{\alpha\beta}(r)$ has the first and second maximum and the first and second minimum, respectively. $n_{\alpha\beta}(m1)$ and $n_{\alpha\beta}(m2)$ are the running integration numbers integrated up to r_{m1} and r_{m2}, respectively
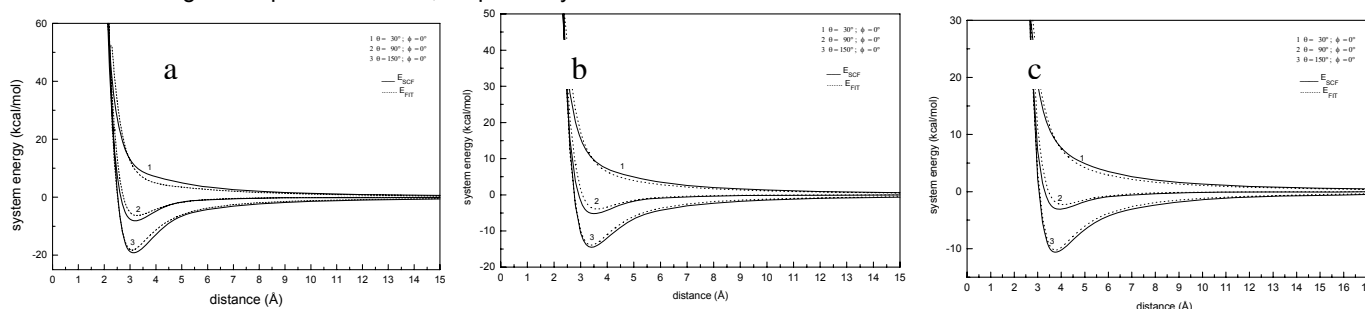

Fig 1. Comparison of the energies obtained from the SCF calculations, ΔE_{SCF}, and from the potential function, ΔE_{FIT}, for (a) Cl$^-$-H$_2$O, (b) Br$^-$-H$_2$O, and (c) I$^-$-H$_2$O system using the final values of the fitting parameters as given in Table 1 for values of θ = 0°, 60° and 150°, and ϕ = 0°

r_{Cl-H} = 2.20 Å; r_{Cl-O} = 3.10 Å
r_{Br-H} = 2.51 Å; r_{Br-O} = 3.40 Å
r_{I-H} = 2.93 Å; r_{I-O} = 3.74 Å

∠ Cl-H-O = 160.82°
∠ Br-H-O = 154.15°
∠ I-H-O = 144.98°

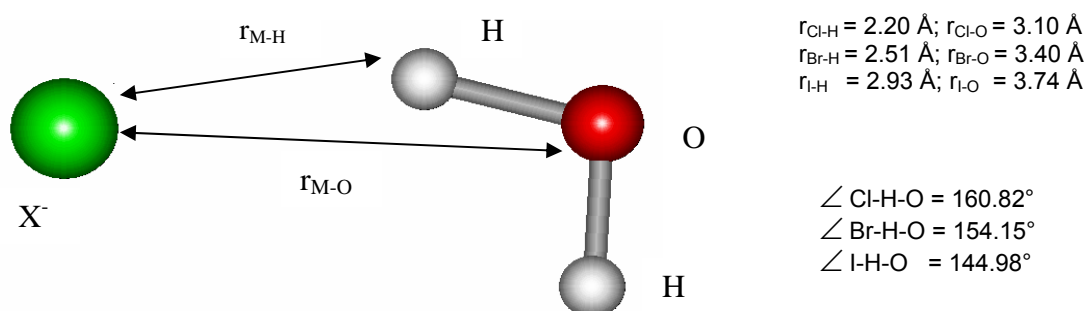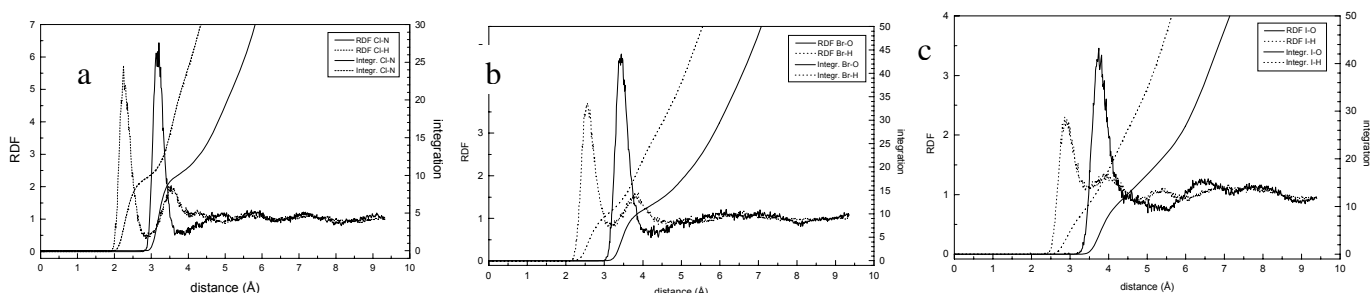**Fig 2.** Characteristic values of structure of hydrated anion from *ab initio* calculations

Fig 3. X-O and X-H radial distribution functions and their running integration numbers of Monte Carlo simulations for hydrated (a) Cl⁻, (b) Br⁻, and (c) I⁻

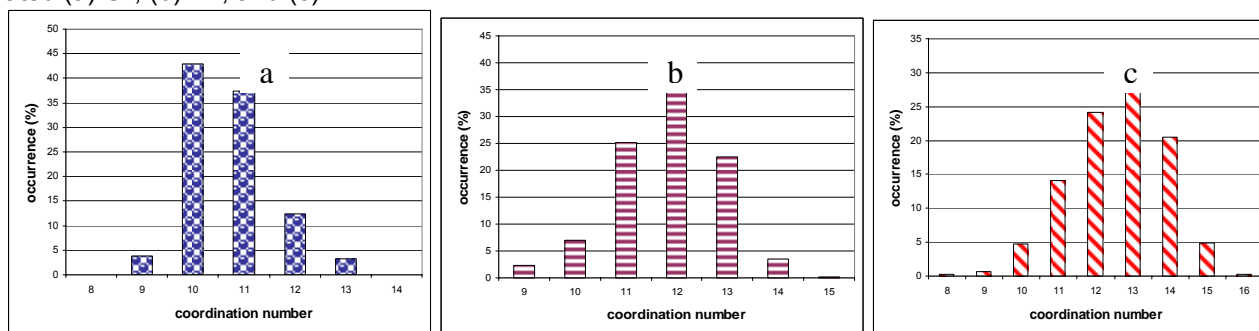**Fig 4.** First coordination number distribution of the hydrated (a) Cl⁻ (b) Br⁻ (c) (a) I⁻

For the halide ions, an asymmetric structure was assumed to be the most likely. This model yields surprisingly good agreement with the experimental values, and the decrease in binding energy in going from Cl⁻ to I⁻ was rationalized by the increasing distance between the negative ion and the water molecule. Although these electrostatic models are useful and physically intuitive, results obtained by *ab initio* calculations are at odds with the above structure. Calculations at the MP2/6–311G(d)//6–31G(d) level [20-21] find that the optimized geometries for F⁻(H₂O) and Cl⁻(H₂O) correspond to asymmetric structures of C_s symmetry. Recent calculations show that adducts retains the asymmetric structure even for the larger halide ions. The QM/MM molecular dynamics of hydrated Cl⁻ also give information that halogen anions have only a minor influence on the O–H bond length of its surrounding water molecules, reflecting the relatively weak ion–water interactions [12]. However, the anion still decreases the average H-O-H angle, partly due to configurations, where one water ligand forms two H-bonds simultaneously. The increase of anion radius implies a loss in linearity, and thus, a weakening of the anion-water hydrogen bonds, resulting in O–H stretching vibrations close to the unperturbed values.

Combariza *et al.* [22] conclude that general theoretical agreement that Cl⁻ and Br⁻ solvate on the surface of the neutral water clusters although the molecular dynamics calculations require careful consideration of the potential and the temperature of the cluster. *Ab initio* calculations of hydrated iodine suggest that a transition from surface to interior solvation may occur at *n* = 6. It is concluded that in aqueous iodine clusters there is a gradual progression from surface states at small cluster size to internal states at large cluster size with the intervening region exhibiting an intermediate degree of surface character.

The radial distribution functions (RDFs) for X-O/X-H in water, where X = Cl, Br, and I together with their corresponding running integration numbers are shown in Fig 3(a), (b), and (c), respectively, and the characteristic values are summarized in Table 2. The water-water RDFs are almost identical to those of pure water [21].

The Cl-O RDF display sharp peaks corresponding to the first solvation shell, and small, broad humps corresponding the second solvation shell. The water molecules in the first solvation shell are typically arranged with one O-H bond pointing toward the ion and one away, as opposed to a symmetrical arrangement with both O-H bonds pointing toward the ion. Thus, the first solvation shell displays two peaks in the Cl-H RDF, at approximately 2.24 Å and 3.54 Å. The first hydration sphere of Cl^- is represented by a sharp peak of the Cl-O RDF, centered at 3.20 Å, 0.1 Å beyond the minimum of the SCF $Cl-H_2O$ potential. The average coordination number for the first solvation shell integrated up to the first minimum of 2.39 Å is 10.66 show that every one Cl^- surrounded by 10.66 water molecule. This value is agreed with the QM/MM molecular dynamics simulation [12]. The fact that the Cl-O RDF comes to zero after its first peak and follow by small and diffuse peak suggests that the first solvation shell is not rigid and ligand exchange with the second shell should be rather fast. The coordination number distribution analysis (Fig 4a) for the first hydration shell of Cl^- leads to 9 (3,73%), 10 (43.02%), 11 (37.4%), 12 (12.43%) and 13 (3.27%) of water molecules around Cl^-. The broad distribution of coordination number agrees with the wider of Cl^--O RDF.

For Br^- in water, a sharp first peak is observed in the Br-O RDF (Fig 3b), located at 3.40 Å. The coordination number distribution analysis (Figure 4b) for the first hydration shell of Br^- leads to 2.27% of 9, 7.03% of 10, 25.2% of 11, 39.3% of 12, 22.5% of 13 and 3,57% of 14 water molecules. The average coordination number of Br^- is 11.4 show that Br^- solvated by more water molecule than on the hydrated Cl^-, because of the differences of size of two anions. The wider range of coordination number distribution of hydrated Br^- compare to Cl^- indicates that ligand exchange should occur somewhat easier in hydrated Br^- compare to Cl^-. The first solvation shell displays two peaks in the Br-H RDF, at approximately 2.42 Å and 3.86 Å. This is reveal that adducts retains the asymmetric structure of water to bind an anion.

RDF of I^--H_2O shows a broad peak centered at 3.74 Å, with corresponding integration number of 12.6 (Figure 3c). The broad peak of the RDF compare to Cl^--H_2O RDF and Br^--H_2O RDF shows that the energy interaction of I^- and water is smallest, namely -6.28 kcal/mol compare to -9.98 for Br^--H_2O, and -13.67 for Cl^--H_2O. Fig 4c shows that coordination number of I^--H_2O dominantly by 13 (30.35%), follow by 12 (24.15%) and 14 (20.45%). The wider of coordination number of I^--
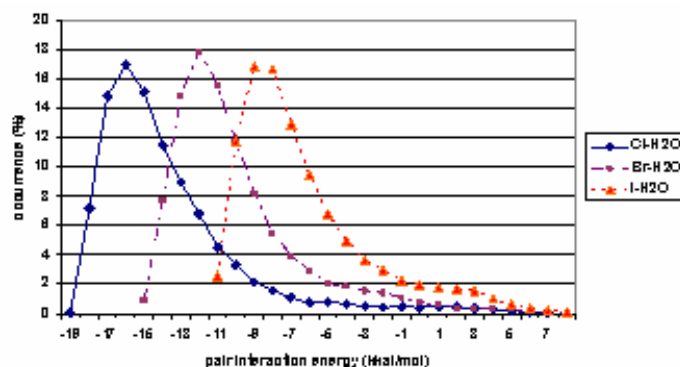

Fig 5. Distribution of X^--H_2O pair interaction energies in the first shell.

H_2O shows the flexibility of ligands in the first solvation shell.

The non-zero first minimum of the RDFs in all anion hydrated systems indicates the lability of water molecules in the first hydration shells of the ions. The X^--water hydrogen bond is relatively weak, leading to a delicate balance between the directional hydrogen bond(s) of each water to the ion and the hydrogen bonding among water molecules, thus producing an asymmetrically solvated X^-. These results are in agreement with some experiment and theoretical calculation [9-12].

The pair energy distributions for $X-H_2O$ are shown in Fig 5. The average pair energy values of -13.67 kcal mol^{-1} for Cl^--H_2O, -9.98 kcal mol^{-1} for Br^--H_2O, and -6.28 kcal mol^{-1} for I^--H_2O system. This value is longer than the global minimum of stabilization energy obtained by calculations, because in the construction of the pair potential, interaction of species in the system are calculated by interactions between one cation and one ligand, neglecting cooperative effects. These results show that the energy hydration of anion halogen is depend on the size of anion. The small anions will easily solvated by water molecule. The energy interaction of anion-water is not larger than the interaction energy of water-water with the result that flexibility of anion around the water solvent.

CONCLUSION

Monte Carlo simulations using *ab initio* pair potential predicted 10.68, 11.84 and 12.60 water molecules in the first solvation shell of Cl^-, Br^- and I^-, respectively. The structure of the water-anion complexes are agreed with dipole orientation. The RDFs, coordination number distributions, and pair interaction energy distribution analyses indicated that ligand exchange reactions take place more easily for the bigger halogen anion because of the lower interaction energy.

159

REFERENCES

1. Hiraoka, K., and Yamabe, S., 1994, Gas-Phase Cluster Ions: Stability, Structure and Solvation. In: *Dynamics of Excited Molecules,* Vol. 82; Kuchitsu, K. Ed.; Elsevier Science: Amsterdam, 399–475.
2. Coe, J.V., 1997, *J.Phys.Chem. A*, 101*,* 2055-2063.
3. Ayotte, P., Bailey, C.G., Weddle, G.H., and Johnson, M.A., 1998, *J.Phys.Chem A*, 102, 3067.
4. Bailey, C.G. Kim, J. Dessent, C.E.H., and Johnson, M.A., 1997, *Chem.Phys.Lett.*, 269, 122.
5. Hiraoka, K., Mizuse, S., and Yamabe, S., 1988, *Chem.Phys.Lett.,* 147, 174.
6. Markovich, G., Pollack, S., Giniger, R., and Cheshnovsky, O.J., 1994, *J.Chem.Phys.,* 101, 9344.
7. Coe, J.V., 1994, *Chem.Phys.Lett*, 229, 161.
8. Tanabe, F.K.J., Morgon, N.H., and Riveros, J.M., 1996, *J.Phys.Chem*, 100, 2862.
9. Xantheas, S.S., 1996, *J.Phys.Chem*, 100, 9703.
10. Xantheas, S.S., and Dang, L.X., 1996, J.Phys.Chem, 100, 3989.
11. Xantheas, S. S. and Dunning, T.H.,Jr., 1994, J.Phys.Chem, 98, 13489.
12. Tongraar, A., and Rode, B.M., 2005, *Chem.Phys.Lett.*, 403, 314.
13. Tongraar, A., Hannongbua, S., and Rode, B. M., 1997, *Chem.Phys.,* 219, 279-290
14. Pranowo, H.D., Setiaji, A.H.B., and Rode, B.M., 1999, *J.Phys.Chem. A*, *103,* 11115
15. Schaefer, A., Horn, H., and Ahlrichs, R., 1992, *J.Chem.Phys.*, *97*, 2571.
16. Dunning, T.H., Jr. 1970, *J.Chem.Phys.*, *53*, 2823.
17. Benedict, W.S. and Plyler, E.K., 1985, *Can.J.Phys.,35*, 890.
18. Jancso, G. and Heinzinger, K.*Z.*, 1985, *Naturforsch.*, *40a*, 1235.
19. Allen, M.P., and Tiedesley, D.J., 1987, *Computer Simulation of Liquids*; Oxford University Press: Oxford, U. K.
20. Gao, J., Garner, D.S., and Jorgensen, W.L., 1986, *J.Am.Chem.Soc.*, 108, 4784.
21. Tanabe, F.K.J., Morgon, N.H. and Riveros, J.M., 1996, *J.Phys.Chem.*, 100, 2862.
22. Combariza, J.E., Kestner, N.R., and Jortner, J., 1993, *Chem.Phys.Lett.,* 203, 423.
23. Pranowo, H.D.,and Rode, B.M., 1999, *J.Phys.Chem. A*, *103*, 4298.

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