Large Scale Molecular Dynamics Simulation of Aqueous NaCl Solutions

Takahiro Koishi[1*], Shigeru Tamaki[2] and Toshikazu Ebisuzaki[1]

[1]Computational Astrophysics Laboratory, RIKEN (The Institute of Physical and Chemical Research),
Hirosawa 2-1, Wako, Saitama 351-0198, Japan
[*]E-mail: t-koishi@riken.jp
[2]Department of Physics, Faculty of Science, Niigata University, Niigata 950-2181, Japan

We performed molecular dynamics simulations at low concentrations; 0.05 mol% (0.028M), 0.10 mol% (0.055M) and 0.50 mol% (0.276M), of aqueous NaCl solution. The radial distribution function, the coordination number, the life time of Na^+-Cl^- pair and the self-diffusion constants are estimated. We employed two types of potentials for Na^+-Cl^- interaction and compare the results of both potentials.

1. Introduction

The understanding of aqueous solution properties is recognized as being important in many areas of physical chemistry and molecular biophysics. Computer simulation has become an important tool in understanding the structure and dynamics of aqueous electrolyte solutions at the atomic or molecular level. Many works of molecular dynamics (MD) simulations have been carried out to investigate hydration structure and dynamic properties of aqueous solutions [1–4].

We carried out large scale molecular dynamics simulations to investigate the concentration dependence of solute ion's behaviors in aqueous NaCl solution. In the dilute limit of solute, there must be no Na^+-Cl^- pair formation. However, it is very difficult to detect the existence of Na^+-Cl^- pairs experimentally. This prompts us to study the microscopical structure of aqueous NaCl by using MD simulation at three concentration conditions; 0.05 mol% (0.028M), 0.10 mol% (0.055M) and 0.50 mol% (0.276M).

In this work, we carried out two series of MD simulations. In the first series, Amber potential set [5] was adopted for NaCl-water and NaCl-NaCl interactions. This potential is constructed by a Lennard-Jones term and a Coulomb term. Parameters of this potential are taken from Amber force field [6,7]. These parameters were determined based on the energy of hydration of Na^+-water and Cl^--water. In the second series, Tosi-Fumi potential [8] was adopted as inter-ionic ones. This potential was made for solid alkali halide systems, such as crystalline NaCl and KCl. And, it is possible to reproduce their liquid structures, diffusion constants, electrical conductivities and viscosities very well [9]. Amber potential set was also employed for solution-water interactions in the second series.

MD simulation of low concentration condition requires a large scale system. We have developed a special-purpose computer, MDM (Molecular Dynamics Machine) [10–13], to carry out a large scale MD simulation. The MDM can perform very high-speed MD simulation of a Coulomb system using the Ewald method. The MDM consists of a MDGRAPE-2 part, a WINE-2 part and a host computer. The calculation speed of the MDM is 10-100 times faster than that of a general purpose computer. We used the MDM in the present work.

2. Methods

We carried out MD simulation of 64,000 water molecule and Na^+-Cl^- pairs. Three concentration conditions; 0.05 mol%, 0.10 mol% and 0.50 mol%, were employed in this simulation. The particle numbers are listed in Table 1. We used SPC/E model [14] for water molecule. The potential parameters of Na^+-water and Cl^--water were taken from Amber force field [6,7]. We adopted two types of potentials to calculate Na^+-Cl^- interaction.

Table 1: The number of particles

concentration	Water	Na	Cl	Total
0.05 mol%	63936	32	32	64000
0.10 mol%	63872	64	64	64000
0.50 mol%	63360	320	320	64000

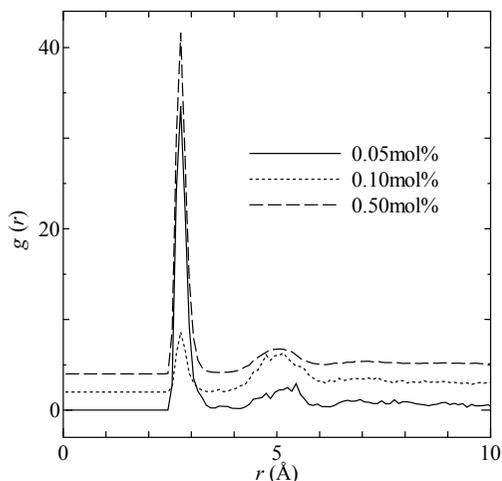Figure 1: The radial distribution functions of Na$^+$-Cl$^-$ with LJ+Coulomb potential.

Figure 2: The radial distribution functions of Na$^+$-Cl$^-$ with Tosi-Fumi potential.

One consists of LJ and Coulomb terms,

$$\phi_{ij}(r) = \frac{z_i z_j e^2}{r} + 4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r}\right)^{12} + \left(\frac{\sigma_{ij}}{r}\right)^6\right\} \quad (1)$$

The other was proposed by Tosi and Fumi [8],

$$\phi_{ij}(r) = \frac{z_i z_j e^2}{r} + A_{ij}\exp\left[B(\sigma_i + \sigma_j - r)\right] - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} \quad (2)$$

The potential parameters of eq. (1) was taken from Amber force field and that of eq. (2) was taken from literature [8]. These parameters are listed in Tables 2 and 3, respectively.

We calculated the interactions of all particle pairs without the cut-off of long-range interaction under the free boundary condition. The Ewald method was used to calculate Coulomb interaction under the periodic boundary condition. Time integration was performed with the leap-frog method, and one time step was set at 2.0×10^{-15}s. Total time step was 60,000 (300 ps). The first 50 ps was regarded as the equilibrium run. All results of this work were estimated from coordination data after 50 ps. The Nosé-Hoover [15] method is employed to control temperature in the *NVT* ensemble.

3. Results

We calculated the radial distribution functions to investigate the structure of Na$^+$-Cl$^-$. The radial
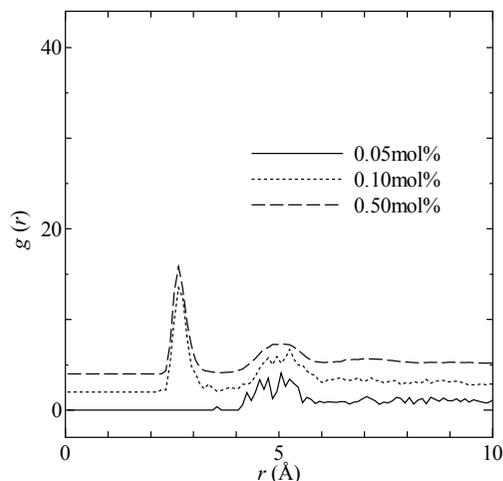
Table 2: Parameter of eq.(1)

	σ(Å)	ε(kcal/mol)	z_i
Na$^+$	3.33	0.0027	1.0
Cl$^-$	4.40	0.1	−1.0

Table 3: Parameters of eq.(2) (B=3.15 Å^{-1})

	A (10^{-19}J)	$\sigma_i+\sigma_j$ (Å)	C (10^{-79}Jm^6)	D (10^{-99}Jm^8)
++	0.4225	2.34	1.68	0.80
+−	0.3380	2.75	11.20	13.90
−−	0.2535	3.17	116.00	233.00

distribution functions by using LJ+Coulomb potential is shown in Fig. 1. These radial distribution functions have two clear peaks. The first peak is at $r \sim 2.7$ Å corresponding to the distance of contact ion pair (CIP), and the second peak is at $r \sim 5.1$ Å corresponding to solvent-separated ion pair (SSIP). These results agree with previous works [1,2,4]. The radial distribution functions in Tosi-Fumi potential system is shown in Fig. 2. These radial distribution functions also have two clear peaks and the peak positions are almost the same as those in LJ+Coulomb potential system (Fig. 1). The height of first peak of Fig. 1 is different from that of Fig. 2. The reason will be described in the next section.

The coordination number $n_{\text{Na+-Cl−}}$ was calculated by using the following equation.

Table 4: The coordination number of Na$^+$-Cl$^-$

mol %	Coordination number	
	LJ+Coulomb	Tosi-Fumi
0.05	0.0169	0.0000
0.10	0.0068	0.0156
0.50	0.1847	0.0746

Table 5: The life time of Na$^+$-Cl$^-$ pair

mol %	Life time	
	LJ+Coulomb	Tosi-Fumi
0.05	44.4	-
0.10	28.5	12.3
0.50	62.5	42.0

$$n_{\text{Na-Cl}} = \int_0^{r_0} 4\pi r^2 \rho g(r) dr, \quad (3)$$

where $r_0 (= 3.5$ Å) is the first minimum of radial distribution function and ρ is density of NaCl in the solution. The coordination numbers are listed in Table 4. These values correspond to the average number of Na$^+$-Cl$^-$ pairs.

The coordination number represents the static property of Na$^+$-Cl$^-$ pair. The time dependence of the total number of Na$^+$-Cl$^-$ pair and the life time were obtained to see the dynamic property of Na$^+$-Cl$^-$ pair. We regarded as a Na$^+$-Cl$^-$ pair as far as the distance between Na$^+$ and Cl$^-$ is smaller than 3.5 Å. The time dependence of the total number of Na$^+$-Cl$^-$ pair is shown in Fig. 3. Only the total number in 0.50 mol% system is drawn in this figure, because the values of 0.05 mol% and 0.10 mol% is very small (zero or one). The life times of Na$^+$-Cl$^-$ pair are listed in Table 5. We picked up Na$^+$-Cl$^-$ pairs every 0.5 ps after the equilibration run. Na+-Cl$_i$ pairs, which exist at the time after the equilibration run and the final step of simulation, were excluded from the calculation of the life time. The life time is estimated from Na$^+$-Cl$^-$ pairs which appear after the equilibration run and disappear before the final step of simulation.

The translational motion of water molecules and constituent ions are analyzed in terms of the diffusion constant D. It can be calculated from the mean square displacement by,

$$D = \lim_{t \to \infty} \frac{\left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle}{6t}. \quad (4)$$

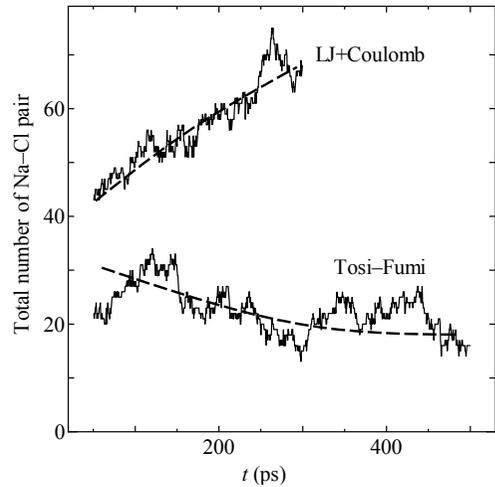The results of the diffusion constants are presented in Fig. 4 and Table 6.

Figure 3: The total number of Na$^+$-Cl$^-$ pari in 0.50mol% system. Dashed lines indicate tendency of results.

Table 6: The diffusion constants. The diffusion constants are expressed in unit of 10^{-5}cm^2/s

mol%	LJ+Coulomb			Tosi-Fumi		
	Na$^+$	Cl$^-$	Water	Na$^+$	Cl$^-$	Water
0.05	1.30	1.75	2.73	1.53	1.75	2.74
0.10	1.50	1.80	2.72	1.32	1.73	2.73
0.50	1.38	1.62	2.65	1.39	1.67	2.64

4. Discussion

The height of the first peak of radial distribution function in LJ+Coulomb potential system is higher than that in Tosi-Fumi potential system. And the coordination number of LJ+Coulomb potential is larger than that of Tosi-Fumi potential. These results indicate that the number of Na$^+$-Cl$^-$ pair in LJ+Coulomb potential system is larger than that in Tosi-Fumi potential system. Actually, this phenomenon is confirmed from the time dependence of the number and the life time of Na$^+$-Cl$^-$ pair. Furthermore, it is recognized that the number of Na$^+$-Cl$^-$ pair in LJ+Coulomb potential system increases with time and there is no convergence. This behavior indicates that the strength of Na$^+$-Cl$^-$ interaction of LJ+Coulomb is too strong. On the other hand, the number of Na$^+$-Cl$^-$ pair almost keeps a constant value in Tosi-Fumi potential system. These facts suggest that a small but stable formation of Na$^+$-Cl$^-$ pair is produced by Tosi-Fumi potential rather than LJ+Coulomb one.
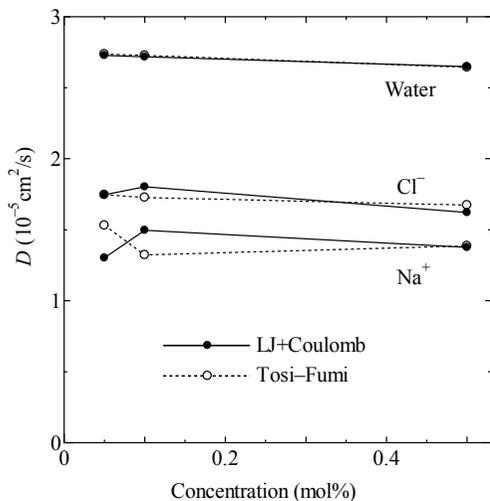
Figure 4: The diffusion constants

The diffusion constants of the constituents decrease with increasing the concentration. These results agree with previous works [1,4]. The diffusion constant of water in LJ+Coulomb potential system agree with that in Tosi-Fumi potential system. The fluctuation of the diffusion constants of Na^+ and Cl^- is large at the low concentration systems, because the particle numbers of Na^+ and Na^+-Cl^- are much smaller than that of water. Noteworthy is that the diffusion constants in LJ+Coulomb and Tosi-Fumi potential system are almost identical. The life time in LJ+Coulomb potential system is longer than that in Tosi-Fumi potential system, but the diffusion constants are almost the same in both systems. It indicate that the strength of Na^+-Cl^- bond does not affect directly the translational motion of Na^+ and Cl^-. It is known that Na^+-Cl^- pair has a cooperative motion in aqueous solution.

From the present results, it is difficult to decide the dilute limit of concentration forming the Na^+-Cl^- pairs. We found, however, the concentration in which there is no Na^+-Cl^- pair from the result of radial distribution function (Fig. 2) in Tosi-Fumi potential system. Therefore, it seems that the concentration of dilute limit is around 0.05 mol% or less.

References and Notes

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