## Hydration and Association of Alkaline Earth Metal Chloride Aqueous Solution under Supercritical Condition

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**Molecular dynamics method is used to simulate alkaline earth metal (magnesium, calcium, strontium and barium) chloride aqueous solution under ambient and supercritical condition. The Aqvist's potential is taken due to its complete coverage and good results. SPC/E model is used to describe the interaction of water molecules. Ion association under supercritical condition is studied in view of the microstructure of solution. The results of simulation indicate that the solvent-separated ion pair is the main association pattern in dilute magnesium chloride solution and the microstructure of alkaline earth metal aqueous solution is a synergistic action of hydration and association.**

*Keywords*: Hydration; Association; Microstructure; Alkaline earth metal; Supercritical

## INTRODUCTION

Interest in ion behaviors in water stems from the importance of water as a solvent that is wildly used in laboratory and industry. Theoretical and experimental studies of ions in water are well reviewed in many monographs [1–3]. In the past two decades, with the rapid development of computer technology, computer simulation has become a powerful tool for understanding and predicting the physicochemical properties of those solutions at the microcosmic level [4].

Most of the published simulations focus on the alkaline metal solution, especially on sodium chloride [5–16]. On the contrary, the researches about the alkaline earth metal aqueous solution are relatively few in spite of its wide use in chemical engineering and environmental industry. Compared with alkaline metal ion, alkaline earth metal ion has more charges;

but its conductivity does not behave as its charge increases, which is considered for the formation of ion pair. However, due to the multiplicity of components, the molecular simulation of concentrated electrolyte solution is very costly. What's more, it needs a long time for simulation (ordinarily greater than 100 ps) to observe the interaction between the hydrated ion and water molecules around it. All of the above leads most published simulations to deal with single ion or ion pair in aqueous solution [5–18], although there are still some papers involved in the concentrated solution [16]. In this paper, dilute solution was adopted in simulation. In order to investigate the interaction between cation and anion, the solution consists of one cation and one anion with solvent water.

In this simulation work, the solution at supercritical condition is also studied. The hydration and association of alkaline earth metal ions are observed. To our knowledge, the published computer simulations about alkaline earth metal aqueous solution [19–30] did not refer the supercritical condition. This paper will firstly give the systematical microcosmic information of alkaline earth metal aqueous solution, especially the ion pair behavior, by molecular dynamics simulation.

## DETAILS OF SIMULATION

The ion–ion, ion–site, site–site potential function used in this work has a unique form as:

$$u_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon_0}\sum_{j\neq i}\frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] \quad (1)$$

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TABLE I    Potential parameters

| Site | $q$(e) | $\sigma$ (Å) | $\varepsilon$ (kcal.mol$^{-1}$) |
|------|--------|--------------|--------------------------------|
| Mg$^{2+}$ | 2 | 1.3979 | 0.8750 |
| Ca$^{2+}$ | 2 | 2.3609 | 0.4497 |
| Sr$^{2+}$ | 2 | 3.1024 | 0.1182 |
| Ba$^{2+}$ | 2 | 3.7862 | 0.0471 |
| Cl$^-$ | $-1$ | 4.401 | 0.1000 |
| O$_W$ | $-0.8476$ | 3.1655 | 0.1554 |
| H$_W$ | 0.4238 | 0 | 0 |

where the $i$, $j$ represent different ion or site. $\varepsilon_{ij}$ and $\sigma_{ij}$ are the Lennard–Jones parameters for the interaction between the $i$ and $j$, while the Coulomb term incorporates the electrostatic interactions between $i$ and $j$.

The parameters of potential function are listed in Table I. The parameters of SPC/E water are from Brenderson [28], the cation-water parameters are from Aqvist *et al.* [22] and the chloride-water parameters are from Rasaiah *et al.* [9,10]. The Lorenze–Berthelot combining rules are used to define the cross parameters:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \qquad (2)$$

The simulation is run by the general purposed MD code: MOLDY [31]. The simulation system consists of 510 water molecules, one alkaline earth metal ion and one chloride ion. The initial configuration is generated by "skew start" method [31]. In the ambient condition, this solution is "dilute" enough, i.e. its behavior like the system with one ion only, so called infinite dilute solution in many previous published simulation works. The simulation ensemble is NVT, where temperature is controlled by Nose–Hoover method and long range Coulomb force is handled by the Ewald sum. One million steps preceded with

the time step 0.5 fs. The last 0.5 million steps are dumped every 10 steps and used to get results. Two state points, one at ambient temperature (298.15 K, 0.997 g/cm$^3$) and the other at supercritical condition (683.15 K, 0.35 g/cm$^3$), are studied in this paper.

## RESULTS AND DISCUSSION

### Radial Distribution Functions (RDF) and Coordinate Number

In this paper, the Radial Distribution Functions (RDF) between alkaline earth metal ions and water are computed from the last 250 ps.

All the RDFs of cation-oxygen have two obvious peaks. The first is sharp and high and the second is low and wide relatively. The distances between oxygen and cation where the peak occurs are in the order Mg$^{2+}$ < Ca$^{2+}$ < Sr$^{2+}$ < Ba$^{2+}$, and the height of peaks are in the sequence Mg$^{2+}$ > Ca$^{2+}$ > Sr$^{2+}$ > Ba$^{2+}$. (Fig. 1)

Comparing the RDF in ambient and supercritical condition, the positions of the first peak remain nearly the same, but the peak heights increase with the decrease in density. For the second peak, the position of peak moves to distant location in supercritical condition. Thus, the interaction between the ion and water molecules in the second hydration shell becomes weaker when the temperature increased beyond supercritical temperature. Not like the alkaline metal ions, the alkaline earth ion's first hydration shells are clearly separated from the second hydration shell at ambient temperature. However, as to the supercritical condition studied in this work, the first hydration shells and the second hydration shells of alkaline earth metal ions interlace each other except magnesium chloride solution.
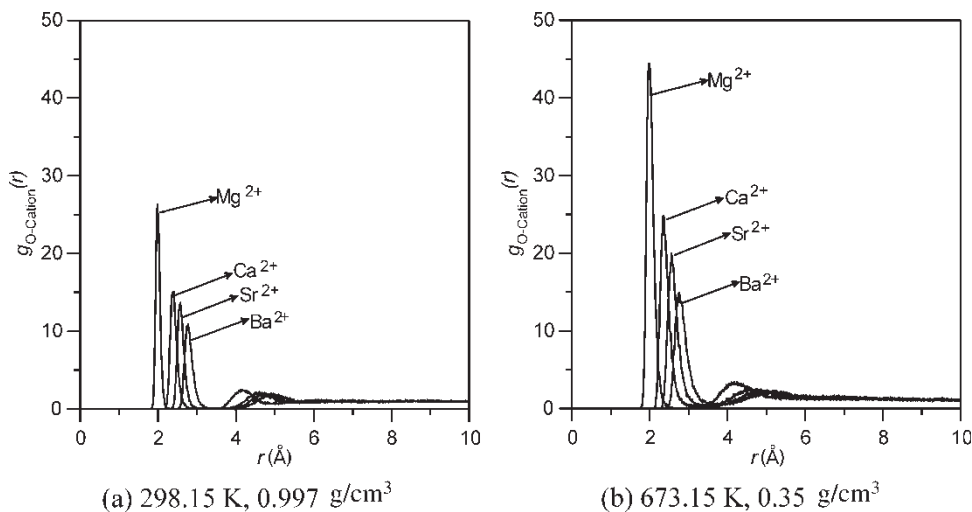


(a) 298.15 K, 0.997 g/cm$^3$          (b) 673.15 K, 0.35 g/cm$^3$

FIGURE 1    Radial distribution function of cation-oxygen.

TABLE II   RDF peaks and coordinate numbers of various ions

| | State | rmax | Rmin | rmax | Rmin | Num1 | Num2 |
|---|---|---|---|---|---|---|---|
| Mg$^{2+}$ | Ambient | 1.98 | 2.90 | 4.15 | 4.90 | 6.0 | 13.3 |
| | | 2.12[21] | 3.1[23] | 4.40[21] | | 6.0[21] | 12[21] |
| | | 2.12[32] | | 4.1[32] | | 6[32] | 12[32] |
| | | 2.00[22] | | | | 6.2[23] | |
| | | 2.2[23] | | | | 6[37] | |
| | | 2.1[37] | | | | 6−8[37,38] | |
| | | 2.1[39] | | | | 6[39] | |
| | | 2.05[19] | | | | 6[19] | |
| | SC | 1.98 | 2.95 | 4.20 | 5.30 | 6.0 | 11.0 |
| Ca$^{2+}$ | Ambient | 2.39 | 3.30 | 4.60 | 5.40 | 7.6 | 17.4 |
| | | 2.40[21] | 3.31[29] | 4.66[21] | | 7.01[21] | 20[21] |
| | | 2.39[33] | 3.5[23] | | | 6.98[33] | |
| | | 2.46[29] | 3.2−3.7[25] | | | 8.0[29] | |
| | | 2.40[22] | | | | 8.0[23] | |
| | | 2.5[23] | | | | 9[26] | |
| | | 2.4[37] | | | | 6−8[37,38] | |
| | | 2.4[25] | | | | 6−10[40] | |
| | | 2.45[19] | | | | 8[19] | |
| | SC | 2.35 | 3.30 | 4.65 | 6.10 | 5.9 | 14.8 |
| Sr$^{2+}$ | Ambient | 2.67 | 3.40 | 4.80 | 5.80 | 8.1 | 20.9 |
| | | 2.58[22] | 3.7[23] | | | 9.0[30] | |
| | | 2.60[30] | | | | 8.5[35] | |
| | | 2.61[34] | | | | 9.8[26] | |
| | | 2.57[35] | | | | 8−10[1] | |
| | | 2.70[36] | | | | 9.1[23] | |
| | | 2.63[26] | | | | 6−8[37,38] | |
| | | 2.53[1] | | | | 10[41] | |
| | | 2.9[23] | | | | | |
| | | 2.6[37] | | | | | |
| | | 2.6[38] | | | | | |
| | SC | 2.55 | 3.55 | 4.85 | 6.40 | 6.4 | 16.2 |
| Ba$^{2+}$ | Ambient | 2.78 | 3.70 | 4.95 | 6.00 | 8.9 | 22.8 |
| | | 2.77[22] | | | | 9.4[30] | |
| | | 2.80[30] | | | | 6[30] | |
| | | 2.89[34] | | | | 8.5[35] | |
| | | 2.73[35] | | | | 6−8[1] | |
| | | 2.92[36] | | | | | |
| | | 2.75,2.90[1] | | | | | |
| | SC | 2.75 | 3.80 | 5.20 | 6.80 | 7.0 | 18.8 |
| Cl$^−$ | Ambient | 3.21 | 3.90 | 4.95 | 6.20 | 7.2 | 24.5 |
| | SC | 3.20 | 4.40 | 5.70 | 6.90 | 7.8 | 19.3 |

In Table II, $g_{io}$, the RDF of ion and oxygen and the coordinate number are listed. The results are compared with the simulation performed in published papers. In ambient temperature, the first peak position and coordinate number agree well with most of the previous work, which means that the simulated system is large enough to work out the properties of the "single ion" system (so called infinite dilute).

## Residence Time

The residence time describes stability of the water molecule around the ion. The length of residence time intimates with strength of hydration. Many previous results on alkaline metal solution support the fact that the hydration decreases dramatically at supercritical condition. In this paper, the hydration of alkaline earth metal ion at supercritical condition was systematically analyzed.

The residence time is calculated from the time correlation function defined by

$$R(t) = \frac{1}{N_h} \sum_{i=1}^{N_h} \langle \theta_i(t)\theta_i(0) \rangle \tag{3}$$

Here $\theta_i(t)$ is the Heaviside unit step function, which is one if a water molecule is in the coordination shell of the ion at $t$ and zero otherwise, and $N_h$ is the hydration number of this shell.

The residence time correlation functions of alkaline earth ions at different conditions are drawn in Fig. 2.

The residence time of water in the hydration shell can be calculated by integrating the residence time correlation function

$$\tau = \int_0^\infty R(t)\, dt \tag{4}$$

However, the simulation time in a feasible MD simulation is finite, and it is more convenient to

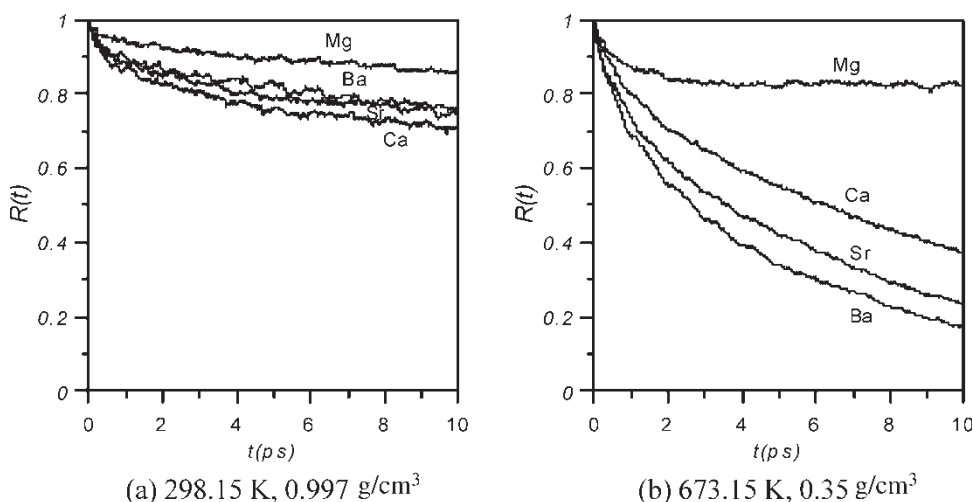(a) 298.15 K, 0.997 g/cm³       (b) 673.15 K, 0.35 g/cm³

FIGURE 2   The residence time correlation function.

obtain the residence time by fitting the residence time correlation function with the function below:

$$R(t) \approx \exp\left(\frac{-t}{\tau}\right) \quad (5)$$

This equation is especially useful when $\tau$ is large. In this paper, the residence time is obtained by numerical integration of the time correlation function from 0 to 10 ps, with the remainder calculated by fitting time correlation function at large times to an exponential decay. The results are shown in Table III. The results of alkaline metal ions published by other researcher are also listed for comparison.

From Table III, the residence time follows the order $Mg^{2+} \approx Li^+ > Sr^{2+} \approx Ba^{2+} > Ca^{2+} > Na^+ > Rb^+ \approx Cs^+ > K^+$ at ambient condition, while at supercritical condition (683.15 K, 0.35 g/cm³) it becomes $Mg^{2+} \gg Ca^{2+} > Sr^{2+} > Li^+ > Ba^{2+} > Na^+ > Rb^+ \approx Cs^+$.

It is very interesting that the hydration ability of K ion is weakest in alkaline metal ion at ambient temperature, and for alkaline earth metal ion, it is Ca ion. This phenomenon is caused by two reasons: on the one hand, the hydration ability rises when the radius of ion decreases; on the other hand, the hydration ability rises while the electrostatic interaction of the ion and water molecule becomes stronger (This is also proved in our previous paper [18], where the ion charge is changed to compare their hydration abilities, and was proved by other researchers' work [44]). These two properties vary inversely in one column of the element periodical table, which generates a minimum. At supercritical condition, the hydration abilities of most ions decrease due to the formation of the ion pair: the residence time values of different ions at that condition are very close comparing with those at ambient condition, except magnesium ion. This is because the association type of magnesium ion and chloride ion is different from others.

### Ion Association

Although the alkaline earth metal ions are more likely to form the ion pair than alkaline metal ions, it is found in this simulation work that there is almost

TABLE III   Residence time of different ions

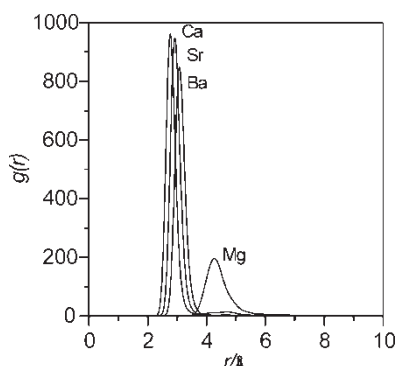| | $\tau_{cation}$ (ps) | | | | | $\tau_{Anion}$ (ps) | |
|---|---|---|---|---|---|---|---|
| | Ambient | | SC | | | Ambient | SC |
| | 1st shell | 2nd shell | 1st shell | 2nd shell | | | |
| LiCl | 55[10] | | 6.1[10] | | | | |
| | 51[42] | | | | | | |
| NaCl | 20[10,42] | | 2.7[10] | | | | |
| KCl | 9[42] | | | | | | |
| | 9.4[43] | | | | | | |
| RbCl | 10[10,42] | | 2.0[10] | | | | |
| CsCl | 10[10,42] | | 1.9[10] | | | | |
| MgCl₂ | 60.7 | 10.6 | 45.2 | 2.5 | | 11.9 | 3.9 |
| CaCl₂ | 25.9 | 7.2 | 9.8 | 3.1 | | 10.9 | 4.4 |
| SrCl₂ | 33.0 | 8.2 | 6.7 | 3.0 | | 9.8 | 4.6 |
| BaCl₂ | 31.8 | 8.4 | 5.5 | 3.3 | | 7.1 | 3.6 |

FIGURE 3    The RDF of ion pair.

no ion pair at ambient condition. At supercritical condition (683.15 K, 0.35 g/cm$^3$), the ion pair appears in all the solutions studied in this paper; however, the association types of ion pairs are different. The RDF of cation and anion can be used to depict the different association type. These are shown in Fig. 3.

From Fig. 3, it is clear that the peak of Ca–Cl, Sr–Cl, Ba–Cl appear at about 3 Å, while the magnesium chloride RDF has a peak value at 4.6 Å (The same simulation was run ten times at ten computers with different initial configuration; all the results show that Mg–Cl radial distribution function has a peak at this range), which is larger than the sum of crystal radii for $Mg^{2+}$ ion and $Cl^-$ ion 2.45 Å [3]. This indicates that the solvent-separated ion pair is the main association pattern in infinite dilute magnesium chloride solution and the microstructure of alkaline earth metal aqueous solution is a synergistic action of hydration and association.

## CONCLUSION

In this paper, systematical MD simulation was proceeded to investigate the alkaline earth solution at ambient condition and supercritical condition. With the data in published papers, the strength of hydration for different alkaline and alkaline earth ions was obtained quantitatively. Comparing the residence time of water molecules inside the first hydration shell of metal ions, the strength of hydration between alkaline and alkaline earth ions was obtained. The sequence at ambient temperature is $Mg^{2+} \approx Li^+ > Sr^{2+} \approx Ba^{2+} > Ca^{2+} > Na^+ > Rb^+ \approx Cs^+ > K^+$, and the reason of the appearance of the minimum for same main group ions is that both the smaller diameters of ions and the stronger electrostatic interaction between ion and water molecules tend to enhance the hydration ability. The sequence at supercritical condition (683.15 K, 0.35 g/cm$^3$) becomes $Mg^{2+} \gg Ca^{2+} > Sr^{2+} > Li^+ > Ba^{2+} > Na^+ > Rb^+ \approx Cs^+$.

The ion association is also studied. At ambient temperature, there is no association between all kinds of positive and negative ions; while under supercritical condition studied in this paper, the association type of $Mg^{2+}$ ion and $Cl^-$ ion is different from those of other alkaline earth metal ions. The solvent-separated ion pair is the main association pattern in magnesium chloride solution while for other ion pairs, direct association.

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