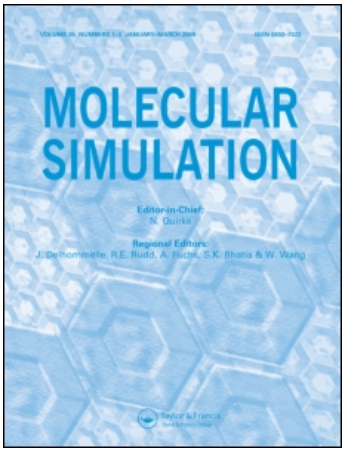

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Monte Carlo Simulation of $MCl^-(H_2O)_{<i>n</i>}$ (M = Li, Na) Clusters-Structures, Fluctuations and Possible Dissolving Mechanism

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MONTE CARLO SIMULATION OF $M^+Cl^-(H_2O)_n$ (M = Li, Na) CLUSTERS – STRUCTURES, FLUCTUATIONS AND POSSIBLE DISSOLVING MECHANISM

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Monte Carlo simulations of $M^+Cl^-(H_2O)_n$ (M = Li, Na) clusters at room temperature using new type of intermolecular potential function were performed to obtain the structural informations under the thermal equilibrium conditions, such as fluctuation of interionic-distance and orientation of water molecules around ion pairs. The lowest-energy geometries of these clusters were water-shared ion pairs, except $Li^+Cl^-(H_2O)$. From Monte Carlo results, we have found that shared water molecules may tend to place between a cation and an anion for their dipole-site stabilization interactions and play an important role for the dissolving process of ion pairs. A possible model for dissolving process of LiCl and NaCl salt into water was proposed.

KEY WORDS: Monte Carlo simulation, $M^+Cl^-(H_2O)_n$ cluster, optimized structure, dissolving process, fluctuation, averaged interionic distance.

1 INTRODUCTION

Ion pairs in crystals without solvent are strongly bound with each other by their electrostatic forces. However, most of them are easily dissolved in water. The informations about the three dimensional structure and the dissolving process of the ion pair in water is very important for the understandings of the chemical reactions in the solution and for the solvation effects. Therefore, the dissolving process of ion pairs in water has interested in both experimental and theoretical chemists for many years.

Although statistical behaviors such as radial distribution functions, angular distribution functions and coordination number of selected alkali halide solutions are widely investigated by X-ray diffraction [1, 2, 3] and by calculations using Monte Carlo (MC) and molecular-dynamics simulations [4–8], the role of solvent and three dimensional structure are not well explored [9].

In this paper, we have done Monte Carlo (MC) simulation of simple hydrated alkali halide clusters, $Li^+Cl^-(H_2O)_n$ and $Na^+Cl^-(H_2O)_n (n = 1 \sim 8)$ using new type of intermolecular potential function [10], and analyzed the role of solvent molecules for the dissolving process of ion pairs at room temperature. Hydrated ion clusters

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are suitable systems for this purpose, because the effects of microscopic interactions on the solvation can be clearly understood.

It has been already reported that there are two intermediate states for the dissolving process [11] in the solution. One is a contact ion pair and the other is a solvent separated ion pair [12]. These ion pairs are thought to be intermediate states of many chemical reactions.

The bond-bond type potential functions [13] with polarization terms [10] are used in this work. In this potential function, exchange type and charge transfer type interactions are expressed by the squares of overlap integrals between localized molecular orbitals for two interacting molecules. This type of potential function explicitly takes the lone pairs and LUMO's into consideration, which are important for charge transfer interactions between interacting molecules. Thus it is more realistic than the atom-atom potential functions such as Lennard-Jones [14] and Buckingham [15,16] potentials, in which all interactions are assumed to be isotropics. Bond-bond type potential functions without polarization terms have been successfully applied to MC simulations of hydrogen bonding systems, such as liquid water [17], liquid hydrogen fluoride [18] and liquid ammonia [19], and they revealed various new aspects of liquid structures. However, for a hydrated ion cluster, the effect of polarization due to the strong electric fields made by ions can not be disregarded.

2 COMPUTATIONAL METHODS

The interaction energies between molecules A and B in the cluster can be written as follows:

$$V_{AB} = \sum_{I}^{A}\sum_{J}^{B} C_{IJ} S_{IJ}^2 + \sum_{I}^{A}\sum_{K}^{B} C_{IK} S_{IK}^2 + \sum_{r}^{A}\sum_{s}^{B} \frac{Q_r Q_s}{R_{rs}} - \frac{1}{2}\sum_{i} \alpha_i E_i^2, \tag{1}$$

The details of this potential function are followed in the previous paper together with potential parameters [10,20]. Here our potential functions for the ion-water pair and for the water-water pair were simply scaled to reproduce the experimental binding energies. Optimized structures have been calculated using both our potential functions and *ab initio* Hartree-Fock level calculations using GAUSSIAN92 [21] program.

MC simulations were carried out using the Metropolis sampling algorithm [22] at 300°K. In each simulation, the system was equilibrated for the first 100k steps and statistical averages were taken over the next 200k steps. The periodic boundary conditions are not necessary for the MC simulations of the cluster systems and MC simulations have been done in a vacant box. For a large cluster or at high temperature, conformations in which a water molecule is far away from a given cluster appeared. Therefore, the cluster analysis method [23] was introduced to select the specific size of the cluster. The threshold energy used for the cluster analysis methods was -6.3 kJ/mol. Details of cluster analysis methods are also referred to the previous paper [20]. The fluctuation of interatomic-distance δ is the most useful

parmeter to see the melting transition of the small clusters. If N is the number of atoms in the system and r_{ij} is the interatomic-distance between i-th and j-th atoms, then δ is given by

$$\delta = \frac{2}{N(N-1)} \sum_{i>j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle} \tag{2}$$

We have sampled 100 configurations, each configuration is a geometry after generation of each 200 configurations, and analyzed the distribution of water molecules using geometrical parameter $r_{\mathrm{Li,O}}$, θ, and ϕ shown in Figure 1. When position vectors of Li^+, Cl^-, and an oxygen atom in water molecules are described by $\mathbf{R}_{\mathrm{Li}}$, $\mathbf{R}_{\mathrm{Cl}}$, and $\mathbf{R}_{\mathrm{O}}$, respectively, the distance between Li^+ ion and an oxygen atom in water molecules is $r_{\mathrm{Li,O}} = |\mathbf{r}_{\mathrm{Li,O}}| = |\mathbf{R}_{\mathrm{O}} - \mathbf{R}_{\mathrm{Li}}|$ and the distance between Li^+ ion and Cl^- ion is $r_{\mathrm{Li,Cl}} = |\mathbf{r}_{\mathrm{Li,Cl}}| = |\mathbf{R}_{\mathrm{Cl}} - \mathbf{R}_{\mathrm{Li}}|$. The angle θ and the angle ϕ in Figure 1 have the form:

$$\theta = \cos^{-1}\left(\frac{\mathbf{r}_{\mathrm{Li,Cl}} \cdot \mathbf{r}_{\mathrm{Li,O}}}{r_{\mathrm{Li,Cl}} r_{\mathrm{Li,O}}}\right), \tag{3}$$

and

$$\phi = \cos^{-1}\left(\frac{\mathbf{r}_{\mathrm{Li,O}} \cdot \mathbf{p}_{\mathrm{H_2O}}}{r_{\mathrm{Li,O}} |\mathbf{p}_{\mathrm{H_2O}}|}\right), \tag{4}$$

where $\mathbf{p}_{\mathrm{H_2O}}$ means the dipole moment direction of a water molecule.

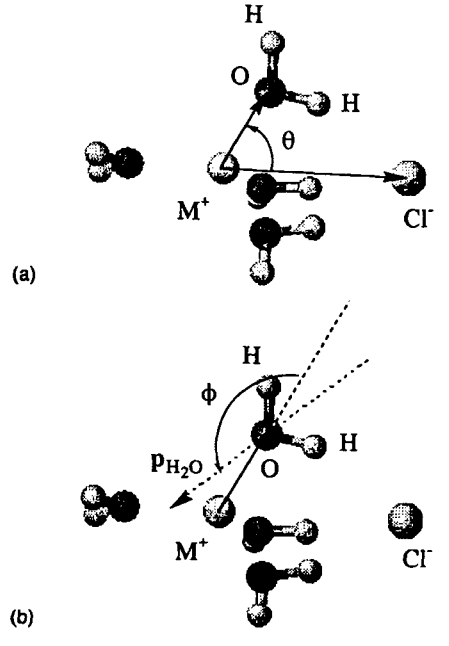

Figure 1 Structural parameters for $M^+Cl^-(H_2O)_n$ (M = Li, Na) clusters. $\mathbf{p}_{\mathrm{H_2O}}$ means the dipole moment vector of a water molecule.

3 RESULTS AND DISCUSSIONS

3.1 Optimized Structures

The optimized structures calculated by our potential functions have been compared with those obtained by *ab initio* calculations. The results are shown in Figures 2 &3 for the lowest energy geometries ($n = 1 \sim 4$) obtained from *ab initio* calculations. The interaction energies using non scaled potential functions are larger than *ab initio* results, whereas those using scaled potential funcitons are smaller. These disagreements may be due to non additivity effects on the interaction energies. However, many useful informations can be obtained from the following discussions. The geometrical features obtained by our potential functions are well agreement with *ab initio* results except for $Li^+Cl^-(H_2O)$ of scaled potential functions. Recently, Woon and Dunning [9] reported the *ab initio* cluster calculations for the diatomic

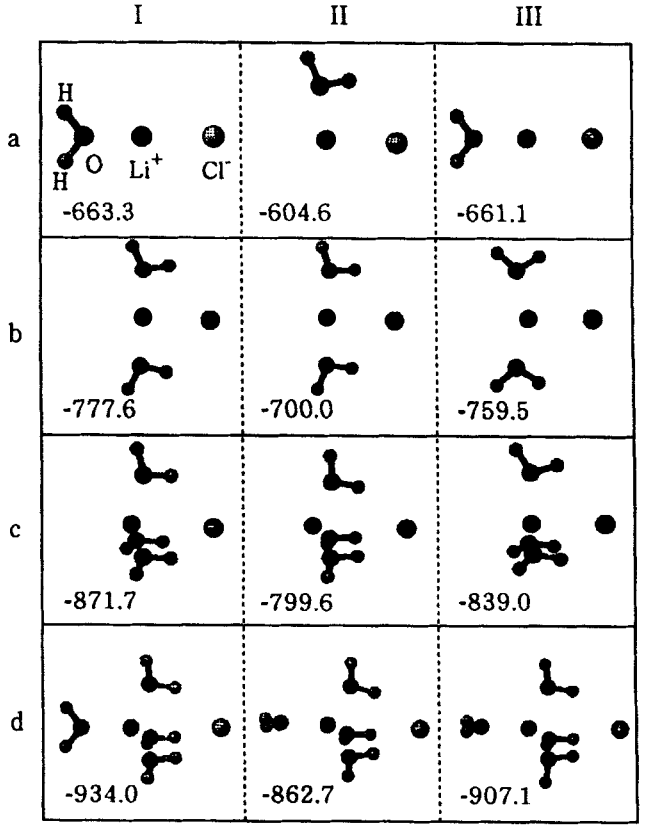

Figure 2 Comparison of the optimized structure for $Li^+Cl^-(H_2O)_n$ calculated using our potential functions and that obtained by *ab initio* calculations for the lowest energy geometry. From the left column non scaled potential (I) [20], scaled potential (II) [20] and *ab initio* results (III) (MINI-1 basis sets are used) are shown. The interaction energies are given in kJ/mol. (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, and (d) $n = 4$.

alkali halide with up to three water molecules. Our structures are quite similar with them. The structural feature is water shared ion pair [11] in the most stable structure for small $Li^+Cl^-(H_2O)_n (n = 2 \sim 4)$ and $Na^+Cl^-(H_2O)_n (n = 1 \sim 4)$ clusters. In $Li^+Cl^-(H_2O)$ the water molecule locates to be the linear arrangement and the cluster has C_{2v} symmetry, however all water molecules are shared by both Li^+ and Cl^- for $n = 2$ and 3. Additional water molecule locates on the opposite site of shared water molecules for $n = 4$. On the other hand, the first three water molecules are shared by Na^+ and Cl^- for $Na^+Cl^-(H_2O)_n (n = 1 \sim 3)$ clusters, then the fourth water molecule tends to coordinate to the cation on the opposite site of shared water molecules just like $Li^+Cl^-(H_2O)_4$ cluster.

3.2 *MC Results*

The fluctuations δ of the interionic-distances are shown in Figure 4. This figure shows a clear maximum at $n = 3$ and 4 for LiCl and NaCl pairs, respectively, where

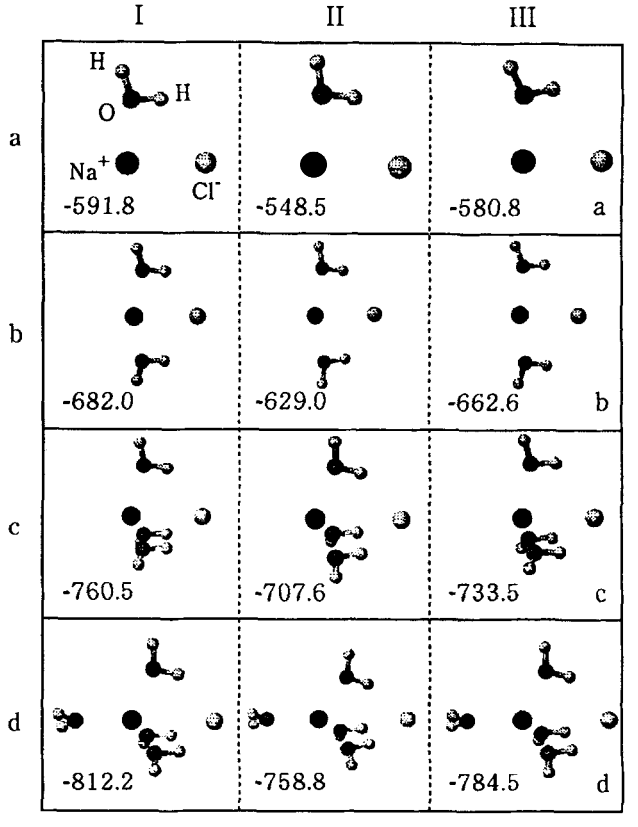

Figure 3 Comparison of the optimized structure for $Na^+Cl^-(H_2O)_n$ calculated using our potential functions and that obtained by *ab initio* calculations for the lowest energy geometry. From the left column non scaled potential (I) [20], scaled potential (II) [20] and *ab initio* results (III) (MINI-1 basis set are used) are shown. The interaction energies are given in kJ/mol. (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, and (d) $n = 4$.

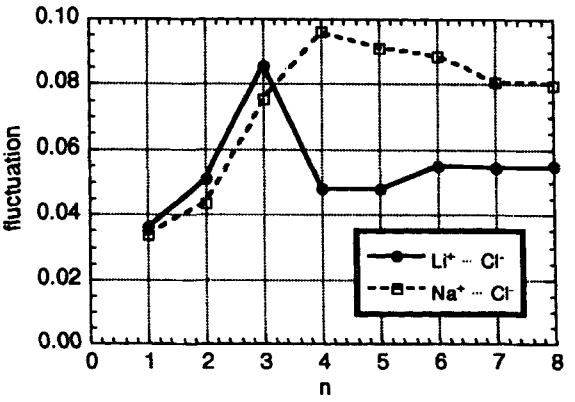

Figure 4 A plot of interionic distance fluctuation between $M^+ \cdots Cl^-$ for $M^+Cl^-(H_2O)_n$ cluster at T = 300 K obtained by MC simulation versus n. Solid line: M = Li, broken line: M = Na.

$Li^+Cl^-(H_2O)_3$ cluster has especially large fluctuation. The fluctuation δ is widely used to evaluate the melting point of the small cluster. Lindemann's criterion for melting said the melting transition occurs when this quantity passes through a value of 0.1 [24].

The positions of the oxygen atoms in water molecules have been collected over the 100 different configurations sampled over the whole simulation run. Their projections onto the $r\theta$-plane of this coordinate system are plotted in Figure 5 for the $Li^+Cl^-(H_2O)_n$ and $Na^+Cl^-(H_2O)_n$ $(3 < n < 5)$ clusters. The oxygen atoms in the first hydration shell of Li^+ and Na^+ ions are distributed at $r_{Li,O} \sim 1.9$ Å and $r_{Na,O} \sim 2.2$ Å, respectively. The other plots beyond this range correspond to the second hydration shell of the ion, which is appeared at $n = 5$ for $Li^+Cl^-(H_2O)_n$ and at $n = 4$ for $Na^+Cl^-(H_2O)_n$ clusters.

For $Li^+Cl^-(H_2O)_n$ clusters, as see at $n = 4$ in the first hydration shell of Li^+, water molecules can be found to be locally distributed in two distinct regions (Figure 2). The first group is in a region near the angle $\theta = 160°$ and the second is near $\theta = 60°$, which indicate that water molecules are nearly tetrahedraly located around a Li^+. We call the first group as in the 'A-region' and the second group as in the 'B-region', respectively. Thus shared water molecules are belonging to the B-region. These geometrical features can be easily understood looking at the energetically most stable structure of $Li^+Cl^-(H_2O)_4$ cluster shown in Figure 6. This result suggests that the small $Li^+Cl^-(H_2O)_n$ clusters are not an entropy favor but an enthalpy favor clusters. The present $r\theta$ plots from MC simulation have demonstrated size-dependent hydration structures of ions in small clusters. It has shown that the water molecules place mainly in B-region at $n = 3$, whereas additional water molecule places in A-region at $n = 4$. The angle θ for shared water molecules has become small with increasing the number of water molecules n.

For $Na^+Cl^-(H_2O)_n$ clusters, the MC results indicate the existence of a second hydration shell (which is the first hydration shell of Cl^-) around Na^+ ion at $n = 4$ (see Figure 5(e)), whereas in $Li^+Cl^-(H_2O)_4$ there is no such tendency (see Figure 5(b)). This fact suggests that the water molecules are rather loosely bounded by Na^+

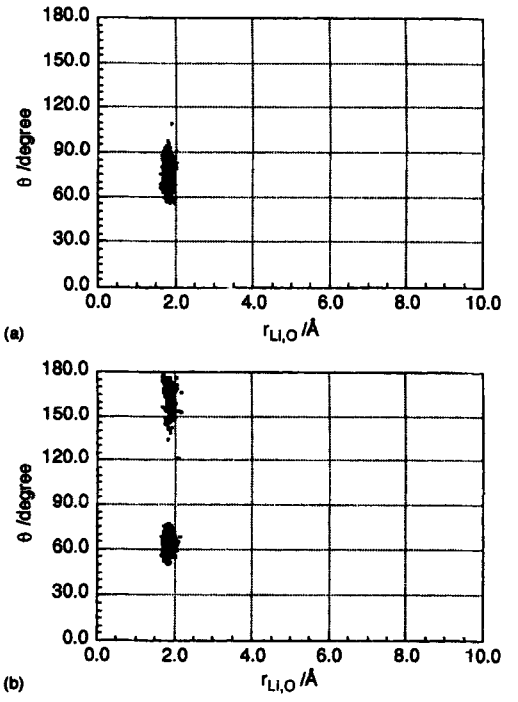

Figure 5 The projections onto the $r\theta$-plane of the positions of the oxygen atoms in water molecules. (a): $Li^+Cl^-(H_2O)_3$, (b): $Li^+Cl^-(H_2O)_4$, (c): $Li^+Cl^-(H_2O)_5$, (d): $Na^+Cl^-(H_2O)_3$, (e): $Na^+Cl^-(H_2O)_4$, (f): $Na^+Cl^-(H_2O)_5$.

than Li^+ and the entropy effects can not be ignored at room temperature. However, it has shown that the water molecules place mainly in B-region at $n = 3$ and additional water molecule mainly, places in A-region at $n = 4$. The angle θ for shared water molecules has also become small with increasing the number of water molecules n.

In Figure 7 the angle ϕ values at 300° K are plotted against the distance $r_{M.O}$. The ϕ values are large ($\phi = 150°$ for both Li^+ and Na^+) at the nearest distance which is corresponding to the first hydration shell of ion and decreases rather monotonically with increasing the distance for both kinds of clusters. These results are in reasonably agreement with those obtained from earlier study [6]. A distribution of $\cos\phi$ has already reported in the work for the electrolyte solution that it has a maximum at $\cos\phi = -1.0$ and its averaged value is -0.76 corresponding to $\phi = 139°$ for the first hydration shell of Li^+ and it is similar to the case of water molecules around Na^+ (average value of $\phi = 140°$) [6].

The pair energies for all molecular pairs of the most stable structures are given in Table 1 for $Na^+Cl^-(H_2O)_n (n = 2 \sim 4)$ clusters. There are 2, 3 and 3 rows for $n = 2, 3$ and 4 clusters, respectively, which are corresponding to the number of shared water molecules in B-region. These calculated results indicate that each water molecule in B-region is placed under almost the same conditions and takes a large portion of the overall stabilization energy. The interaction energies between the water molecules in A-region and Cl^- are repulsive at $n = 4$, whereas the interactions between shared

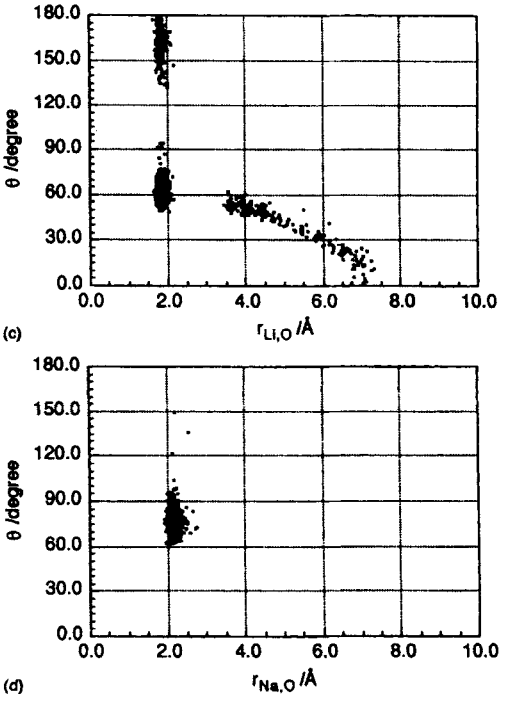

Figure 5 (c, d)

water molecules in B-region and Cl^- are attractive which is more stabilized as increasing the number of water molecules n. These facts suggest that the shared water molecules are bound more strongly by both Na^+ and Cl^- ions and it becomes more stable with increasing n. The water molecules in A-region are stabilized with Na^+ ion but it has repulsive interaction with Cl^- ion. Water molecules coordinating to the Na^+ are unfavorably orientated each other from an energetic standpoint of view. Since the angle θ becomes small and the shared water molecules become more stable with increasing n as mentioned above, we may expect that the water molecules in B-region tend to place between ion pairs.

When some water molecules place in B-region, stabilization energies due to $M^+...OH_2...Cl^-$ interaction may overcome unstabilization energies due to ion pair separation and water-water repulsive interactions. In this situation, a bit of energy may change the interionic-distance and the fluctuation δ between ion pair becomes larger.

We propose a new model for the dissolving process. Before discussing the dissolving process of a M^+Cl^- salt, let us examine the limit of the dissolved state, which is the saturated electrolyte solutions. From the solubility of a M^+Cl^- salt in water at 25°C [25], the average number of water molecules per a M^+Cl^- pair at the saturated electrolyte solution can be calculated. The results are listed in Table 2. From this table, we can see that the dissolved state of LiCl is very like as that of HCl in the aqueous solution. Thus Li^+ behaves as proton like. Actually, the optimized

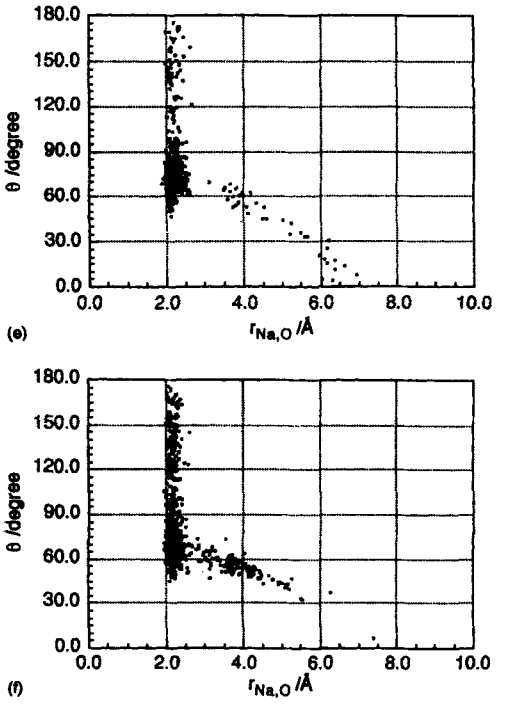

Figure 5 (e, f)

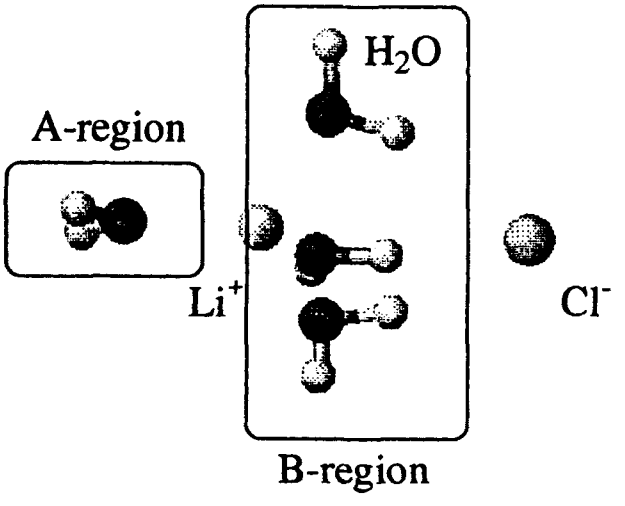

Figure 6 Illustrations of the A-region and the B-region for $Li^+Cl^-(H_2O)_4$ cluster.

structure of LiCl (H_2O) is very similar with that of $HCl \cdot H_2O$ shown in Figure 8. Referring the most stable structure for each $M^+Cl^-(H_2O)_n (n = 1 \sim 4)$ shown in Figures 2 and 3, we may expect the dissolving mechanism as follows;

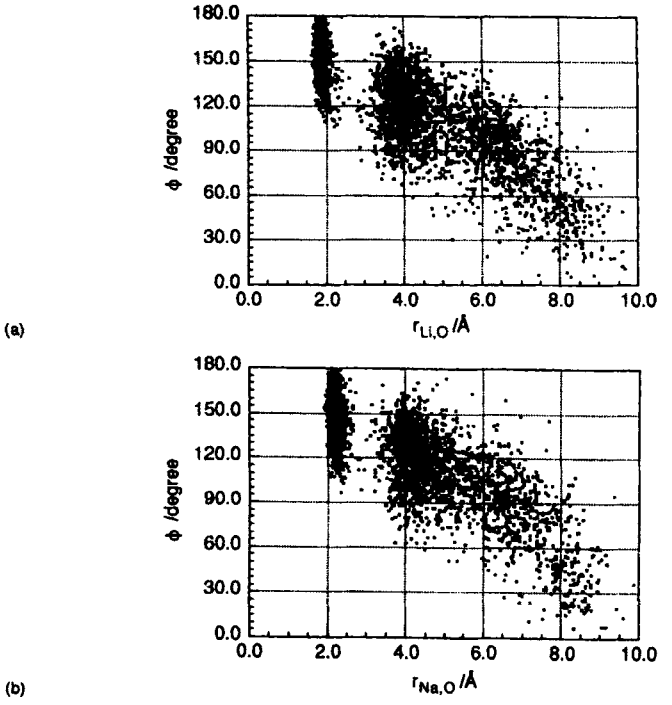

Figure 7 The projections onto the $r\phi$-plane of the positions of the oxygen atoms in water molecules. (a): $Li^+Cl^-(H_2O)_{15}$, (b): $Na^+Cl^-(H_2O)_{15}$.

Table 1 The pair interaction energy components between all molecular pairs for the most stable structure of $Na^+Cl^-(H_2O)_n$ ($2 \leqslant n \leqslant 4$).

hydration number n	*pair interaction energy / kJ mol^{-1} (see text)*						
	$Na^+\cdots Cl^-$	$Na^+\cdots A^a$	$Na^+\cdots B^a$	$Cl^-\cdots A^a$	$Cl^-\cdots B^a$	$A\cdots B^a$	$B\cdots B^a$
2	−459.6		−79.4		−15.6		3.4
			−79.4		−15.6		
3	−408.1		−84.3		−27.4		5.6
			−84.3		−27.4		5.6
			−84.3		−27.4		5.6
4	−350.5	−100.9	−89.9	19.7	−39.3	5.3	7.3
			−90.2		−39.0	5.3	7.3
			−90.2		−39.0	5.3	7.4

[a] "A" and "B" mean the water molecules in the A-region and in the B-region, respectively.

For LiCl salt, the first H_2O binds with Li^+ at A-region shown in Figure 6. Next, the second H_2O binds at B-region and then the first H_2O moves to the B-region, the third H_2O binds with LiCl at B-region. As reported in the previous paper [10], the interionic-distance $R(Li^+\cdots Cl^-)$ suddenly increase at $Li^+Cl^-(H_2O)_3$.

Table 2 Average number of water molecules per a M^+Cl^- (M = H, Li, Na, K) pair in the saturated electrolyte solution. Calculated from the data given in ref [25].

M^+	*Average number of water molecules per a* M^+Cl^-
H^+	3.0
Li^+	2.9
Na^+	9.1
K^+	11.6

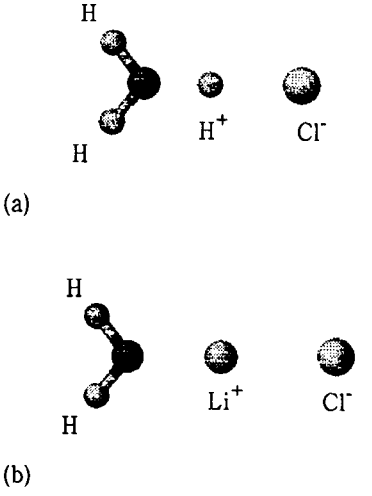

Figure 8 Optimized structures (RHF/MINI-1). (a): $HCl(H_2O)$, (b): $LiCl(H_2O)$.

We can say this is the dissolved state. Cl^- ion can be easily moved into water as shown in the previous paper [20].

On the other hand, for Na^+Cl^- salt, the first H_2O binds with Na^+Cl^- at B-region. The second, third and forth H_2O's also bind with Na^+Cl^- at B-region. And, the interionic-distance $R(Na^+...Cl^-)$ increases gradually with the increase of the number of H_2O molecule. $NaCl(H_2O)_4$ may be the dissolved state.

4 CONCLUSIONS

We have obtained the water shared ion pairs for small $Li^+Cl^-(H_2O)_n$ ($n = 2 \sim 4$) and $Na^+Cl^-(H_2O)_n$ ($n = 1 \sim 4$) clusters using our potential functions and *ab initio* calculations. We found that shared water molecules (in B-region) may tend to place between a cation and an anion for their dipole-site stabilization interactions. From the solubility of M^+Cl^- salt and optimized structure, we have found that Li^+ behaves as proton like in an aqueous solution. Thus, the dissolving process of ion pair is somewhat different between Li^+Cl^- and Na^+Cl^- pairs. It may be due to the

difference of the ionic radii. Finally, above mentioned calculations have reinforced our view that shared water molecuels play an important role for the dissolving process of ion pairs.

Acknowledgements

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