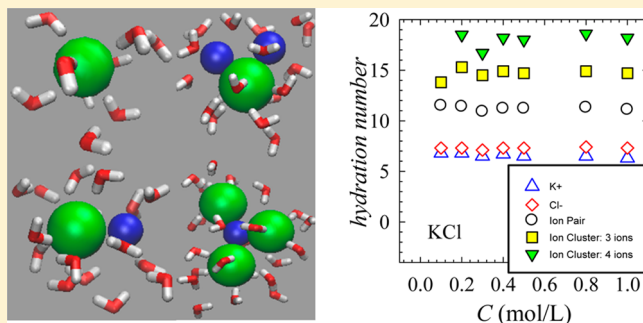


# Hydrated Ions: From Individual Ions to Ion Pairs to Ion Clusters

Houyang Chen\* and Eli Ruckenstein\*

Department of Chemical and Biological Engineering, State University of New York at Buffalo, Buffalo, New York 14260-4200, United States

**ABSTRACT:** The structure of hydrated ions plays a central role in chemical and biological sciences. In the present paper, five ions, namely,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , are examined using molecular dynamics simulations. In addition to hydrated individual ions and ion pairs identified previously, hydrated ion clusters containing 3, 4, 5, or more ions are identified in the present paper. The dependence of hydration numbers and mole fractions of individual ions, ion pairs, and larger ion clusters on the electrolyte concentration is determined. As the electrolyte concentration increases, the mole fraction of hydrated individual ions decreases, and the mole fraction of hydrated larger ion clusters increases. The results also reveal that the hydrogen bonding numbers of the  $\text{H}_2\text{O}$  molecules of the first hydration shells of individual ions, ion pairs, and larger ion clusters are insensitive to the electrolyte concentration, but sensitive to the nature and conformation of ions.



## INTRODUCTION

Hydration of ions plays a significant role in the chemical<sup>1</sup> and biological sciences,<sup>2</sup> etc. In most of the previous studies, only hydrated individual ions were identified. The hydration number of ions and the free energy of ion hydration were determined experimentally by proton nuclear magnetic resonance (proton NMR),<sup>3</sup> X-ray Compton scattering,<sup>4</sup> neutron scattering,<sup>5</sup> and theoretically by density functional theory,<sup>6,7</sup> perturbation theory,<sup>8</sup> as well as molecular simulations.<sup>9–11</sup> For additional information, one can see refs 12–14 and the references therein. In addition to hydrated individual ions, the presence of hydrated ion pairs were also noted. Most studies on hydrated ion pairs involve their free energies of hydration<sup>15–17</sup> and their structure.<sup>18,19</sup> For more information regarding ion pairing, one can see refs 20 and 21 and the references therein.

In previous papers,<sup>3–10,12–21</sup> the focus was on hydrated individual ions and hydrated ion pairs. However, how many hydrated individual ions and ion pairs are present in solutions was not determined. Furthermore, ion clusters and how many there are have not been identified and calculated. In our previous paper, ion clusters were identified for a nanomembrane in an electrolyte solution.<sup>11</sup> Two issues are considered in this paper. The first one is concerned with the dependence of the mole fractions and the hydration numbers of hydrated individual ions, ion pairs, and larger ion clusters on electrolyte concentration. The second one is the dependence of the hydrogen bonding number of all  $\text{H}_2\text{O}$  molecules of the first hydration layer on the electrolyte concentration and nature of ions. In addition, we emphasize that in the current paper, we use the TIP3P model<sup>22,23</sup> for the water molecules. However, different force fields may provide different results. In our ongoing work, we calculate the hydration number of ions, ion pairs, and ion clusters using molecular simulation with different

force fields, including the AMOEBA force field,<sup>24–26</sup> and quantum density functional theory.

## SIMULATION DETAILS

Molecular dynamics simulations were carried out using the nanoscale molecular dynamics (NAMD) program (version 2.9).<sup>27</sup> Snapshots were obtained using the Visual Molecular Dynamics (VMD) program.<sup>28</sup> The CHARMM 27 force field<sup>29,30</sup> and the TIP3P model<sup>22,23</sup> were employed for ions and water, respectively. The long-range Coulomb interactions were calculated using the particle-mesh Ewald (PME) method.<sup>31</sup> After minimization at 0 K, the temperature was raised to 300 K, and 4 ns isothermal–isobaric ensemble (NPT ensemble) simulations were carried out. Finally, 120 ns canonical ensemble (NVT ensemble) simulations were performed with a time step of 2.0 fs. In this paper, the electrolyte concentration in aqueous solutions was varied from 0.1 to 1.0 M. Each system possessed more than 30 000 atoms.

## RESULTS AND DISCUSSION

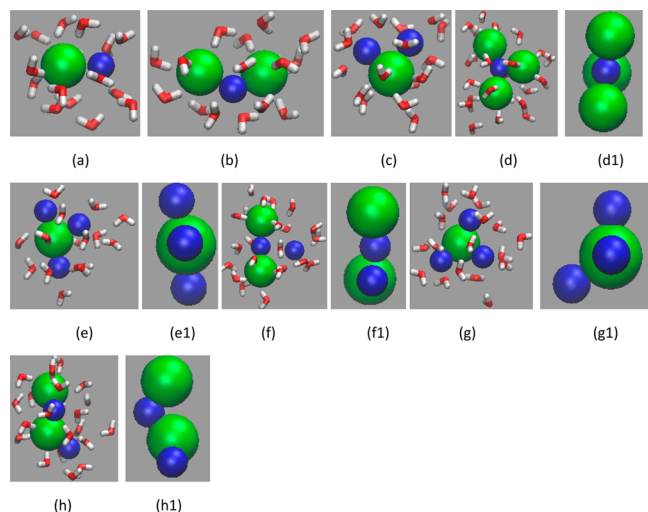
As examples, four electrolyte solutions,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ , were examined. An ion pair or ion cluster was formed when an ion(s) was(were) trapped in the first hydration shell of another ion. A water molecule belongs to the hydration shell of an individual ion or an ion pair or a larger ion cluster when the distance between its oxygen atom and the nearest ion is smaller than the distance of the first hydration shell of the corresponding individual ion. We calculated the hydration numbers of individual ion both by the above procedure and the

Received: July 15, 2015

Revised: September 2, 2015

radial distribution function, and found that they provide the same results. For example, the hydration number of  $\text{Na}^+$  under 0.1 mol/L is  $5.4 \pm 0.1$  for both the present procedure and the radial distribution function. For the hydration numbers of ion pairs and ion clusters, we use only the present procedure because the radial distribution functions cannot provide the hydration numbers for ion pairs and ion clusters.

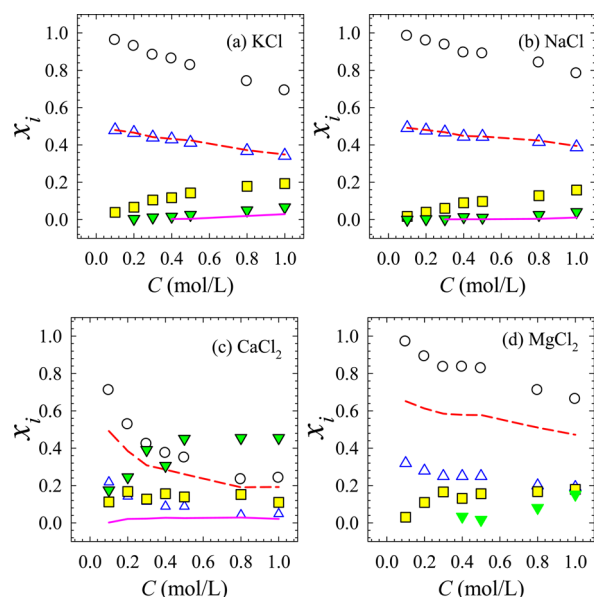
The conformations of hydrated ion pairs and larger ion clusters are presented in Figure 1. An ion pair has a linear



**Figure 1.** Snapshots of hydrated ion pairs and ion clusters: (a) hydrated cation-anion pair; (b) hydrated anion-cation-anion cluster; (c) hydrated cation-anion-cation cluster; (d and d1) hydrated anion-anion-cation-anion cluster; (e, e1, g, and g1) hydrated cation-cation-anion-cation cluster; (f, f1, h and h1) cation-anion-cation-anion cluster. Red: oxygen atoms of water; white: hydrogen atoms of water; green: chlorine ions; blue: cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ).

structure (Figure 1a). In our simulations, contact ion-pairs were identified, and no solvent separating ion-pairs was found; only cation-anion pairs were present. A hydrated cluster with three ions (one cation and two anions, or two cations and one anion) possesses a “V”-shape structure (Figure 1b,c). A hydrated cluster with four ions can have the structure of a planar triangle (Figure 1d–f), of a triangular pyramid (Figure 1g), and of an alternative cation-anion arrangement (Figure 1h). The structure of alternative cation-anion structure can have several conformations, among which one is linear (i.e., four ions in line) and another has a planar “N”-shape of cation-anion. Both the ion pairs and the ion clusters are composed of cation(s) and anion(s). We did not find that ion pairs or larger ion clusters are composed of only cations or anions. When an individual ion is introduced into the bulk water, some hydrogen bonds (H-bonds) between the water molecules are broken, resulting in the reorientation of water molecules around the ions. When hydrated ion pairs or larger ion clusters are formed, they will further break H-bonds. The water molecules around the ion pairs and particularly ion clusters are disordered. It should be mentioned that the ion pairs and larger ion clusters can be negatively charged, positively charged, or neutral.

Figure 2 plots the mole fractions ( $x_i$ ) of hydrated individual ions, of ions involved in hydrated ion pairs and in hydrated ion clusters as functions of electrolyte concentration  $C$ . For KCl or NaCl solutions, as the electrolyte concentration increases, the



**Figure 2.** Mole fraction ( $x_i$ ) of hydrated individual cation (triangle up), hydrated individual anion (dashed line), hydrated individual ions (both cation and anion, circle), hydrated ion pairs (square), and hydrated ion clusters with three ions (triangle down) and four ions (solid line) as functions of electrolyte concentration  $C$ .

mole fractions of hydrated individual cations and hydrated individual anions decrease, but the mole fractions of hydrated ion clusters with three ions and four ions increase. This occurs because, as the electrolyte concentration increases, the probability of individual ions to form ion pairs or larger ion clusters increases. For  $C = 0.1$  mol/L, most ions are present in water as individual ions (with mole fractions larger than 0.95). However, for  $C = 1.0$  mol/L, the mole fractions of individual ions decrease to 0.84 and 0.70 for NaCl and KCl, respectively.

For  $\text{CaCl}_2$  solutions, as the electrolyte concentration increases, the mole fractions of hydrated individual ions decrease, and the mole fraction of hydrated clusters with three ions increases. The mole fraction of individual ions is approximately 0.71 at  $C = 0.1$  mol/L, much smaller than the mole fractions of hydrated individual ions in aqueous KCl and NaCl solutions at the same concentration. The mole fraction of hydrated individual ions decreases to 0.24 for an electrolyte concentration of 1.0 mol/L.

For a  $\text{MgCl}_2$  solution, as the electrolyte concentration increases, the mole fractions of hydrated individual Mg and Cl ions decrease, and the mole fractions of hydrated ion pairs and larger ion clusters with three ions increase. It should be mentioned that in  $\text{MgCl}_2$  solutions, one can ignore the ion clusters with four or more ions because their mole fractions are extremely low.

Figure 2 shows that, for a selected electrolyte concentration, the mole fractions of hydrated individual cation ions follows the order  $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ .

The hydration numbers (considered as the number of water molecules in the first hydration shell) of individual ions, ion pairs, and larger ion clusters were calculated and listed in Table 1. In a KCl solution, as the electrolyte concentration  $C$  increases, the hydration number of  $\text{K}^+$  decreases from 6.8 (at  $C = 0.1$  mol/L) to 6.3 (at  $C = 1.0$  mol/L). A similar behavior of the hydration numbers of individual ions was found experimentally by Mancinelli et al.<sup>32</sup> As the electrolyte

**Table 1. Average Hydration Number of Individual Ions, Ion Pairs, and Larger Ion Clusters for KCl, NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> Solutions with Various Concentration C**

| $C_{\text{KCl}}$    | K (free ion)  | Cl (free ion) | ion pair   | clusters with 3 ions | cluster with 4 ions  |
|---------------------|---------------|---------------|------------|----------------------|----------------------|
| 0.1                 | 6.8 ± 0.3     | 7.3 ± 0.3     | 11.5 ± 1.5 | -----                | -----                |
| 0.2                 | 6.8 ± 0.2     | 7.3 ± 0.2     | 11.4 ± 1.0 | 15.3 ± 1.8           | -----                |
| 0.3                 | 6.5 ± 0.2     | 7.1 ± 0.2     | 10.9 ± 0.7 | 14.5 ± 1.9           | -----                |
| 0.4                 | 6.7 ± 0.2     | 7.3 ± 0.2     | 11.2 ± 0.6 | 14.9 ± 1.8           | 18.2 ± 2.8           |
| 0.5                 | 6.5 ± 0.1     | 7.3 ± 0.2     | 11.2 ± 0.5 | 14.7 ± 1.5           | 18.0 ± 2.8           |
| 0.8                 | 6.5 ± 0.1     | 7.4 ± 0.1     | 11.3 ± 0.3 | 14.9 ± 0.9           | 18.6 ± 1.6           |
| 1.0                 | 6.3 ± 0.1     | 7.3 ± 0.1     | 11.1 ± 0.3 | 14.7 ± 0.8           | 18.2 ± 1.4           |
| $C_{\text{NaCl}}$   | Na (free ion) | Cl (free ion) | ion pair   | clusters with 3 ions | cluster with 4 ions  |
| 0.1                 | 5.4 ± 0.1     | 7.4 ± 0.3     | 10.7 ± 1.0 | -----                | -----                |
| 0.2                 | 5.5 ± 0.1     | 7.3 ± 0.2     | 10.3 ± 1.2 | 13.2 ± 1.1           | -----                |
| 0.3                 | 5.4 ± 0.1     | 7.3 ± 0.2     | 10.2 ± 0.9 | 13.4 ± 2.0           | 15.4 ± 2.4           |
| 0.4                 | 5.4 ± 0.1     | 7.1 ± 0.2     | 9.9 ± 0.6  | 12.8 ± 1.5           | 15.7 ± 1.8           |
| 0.5                 | 5.5 ± 0.1     | 7.1 ± 0.1     | 9.9 ± 0.5  | 13.1 ± 1.4           | 15.7 ± 2.3           |
| 0.8                 | 5.4 ± 0.1     | 7.3 ± 0.1     | 10.3 ± 0.4 | 13.3 ± 1.2           | 16.0 ± 2.3           |
| 1.0                 | 5.5 ± 0.1     | 7.3 ± 0.1     | 10.3 ± 0.3 | 13.5 ± 0.9           | 16.7 ± 1.7           |
| $C_{\text{CaCl}_2}$ | Ca (free ion) | Cl (free ion) | ion pair   | clusters with 3 ions | clusters with 4 ions |
| 0.1                 | 6.7 ± 0.3     | 7.3 ± 0.3     | 9.5 ± 1.0  | 12.5 ± 1.0           | 15.8 ± 1.8           |
| 0.2                 | 6.7 ± 0.3     | 7.3 ± 0.2     | 9.2 ± 0.6  | 12.7 ± 0.6           | 15.0 ± 1.9           |
| 0.3                 | 6.6 ± 0.2     | 7.0 ± 0.2     | 8.9 ± 0.5  | 12.3 ± 0.3           | 14.4 ± 1.8           |
| 0.4                 | 6.6 ± 0.3     | 7.2 ± 0.2     | 9.4 ± 0.4  | 12.6 ± 0.4           | 15.2 ± 1.7           |
| 0.5                 | 6.6 ± 0.2     | 6.8 ± 0.2     | 8.8 ± 0.4  | 12.1 ± 0.2           | 13.9 ± 1.8           |
| 0.8                 | 6.4 ± 0.3     | 7.4 ± 0.2     | 9.5 ± 0.3  | 13.4 ± 0.2           | 15.4 ± 1.5           |
| 1.0                 | 6.4 ± 0.3     | 7.0 ± 0.1     | 8.8 ± 0.3  | 12.7 ± 0.2           | 13.1 ± 1.4           |
| $C_{\text{MgCl}_2}$ | Mg (free ion) | Cl (free ion) | Ion Pair   | Clusters with 3 ions |                      |
| 0.1                 | 5.6 ± 0.2     | 7.0 ± 0.2     | 8.5 ± 1.6  | -----                |                      |
| 0.2                 | 5.7 ± 0.1     | 7.0 ± 0.2     | 9.0 ± 0.5  | -----                |                      |
| 0.3                 | 5.6 ± 0.1     | 7.0 ± 0.1     | 8.9 ± 0.4  | -----                |                      |
| 0.4                 | 5.7 ± 0.1     | 7.1 ± 0.1     | 8.8 ± 0.4  | 12.0 ± 1.0           |                      |
| 0.5                 | 5.7 ± 0.1     | 7.3 ± 0.1     | 9.3 ± 0.3  | 11.9 ± 1.6           |                      |
| 0.8                 | 5.6 ± 0.1     | 7.0 ± 0.1     | 9.0 ± 0.2  | 11.8 ± 0.5           |                      |
| 1.0                 | 5.6 ± 0.1     | 7.0 ± 0.1     | 8.9 ± 0.2  | 12.0 ± 0.3           |                      |

concentration  $C$  increases, the hydration number of  $\text{Cl}^-$  remains constant and approximately 7.3. The hydration numbers of ion pairs, ion clusters with three ions, and ion clusters with four ions are 10.9–11.5, 14.5–15.3, and 18.0–18.6, respectively. (The range of values is a result of the dependence of the hydration number on electrolyte concentration.)

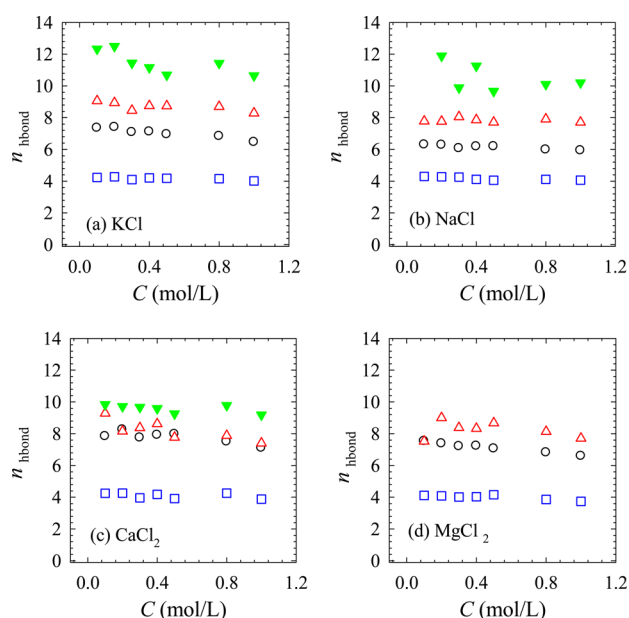
For a NaCl solution, as the electrolyte concentration increases, the hydration numbers are 5.4–5.5, 7.1–7.3, 9.9–10.3, 12.8–13.2, and 15.4–16.0 for individual  $\text{Na}^+$ , individual  $\text{Cl}^-$ , ion pairs, ion clusters with three ions, and ion cluster with four ions, respectively. The hydration number of individual  $\text{Na}^+$  agrees with the result (5.3) experimentally provided by Mancinelli et al.<sup>32</sup> and the result (5.5) theoretically provided by Straatsma and Berendsen.<sup>9</sup> Our results show that the hydration numbers of individual  $\text{Na}^+$  is almost insensitive to electrolyte concentration.

For  $\text{CaCl}_2$  solutions, as the electrolyte concentration increases, the hydration numbers of individual  $\text{Ca}^{2+}$ , individual  $\text{Cl}^-$ , ion pair, cluster with three ions, and cluster with four ions, are in the ranges 6.4–6.7, 6.8–7.4, 8.8–9.5, 12.1–13.4, and 13.1–15.8, respectively.

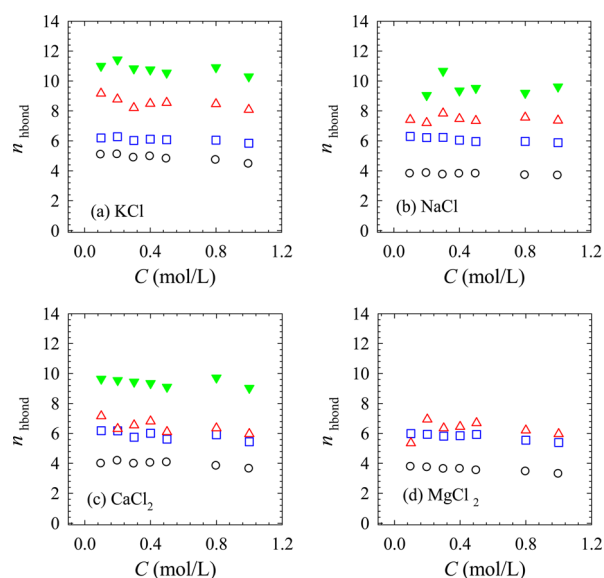
For  $\text{MgCl}_2$  solutions, when the electrolyte concentration varies from 0.1 to 1.0 mol/L, the hydration numbers of  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , ion pair, and clusters with three ions, are in the ranges 5.6–5.7, 7.0–7.3, 8.5–9.0, and 11.8–12.0, respectively. The hydration number of individual  $\text{Mg}^{2+}$  ion is in agreement with

the first-principles molecular dynamics result (5.8) provided by Tommaso and de Leeuw.<sup>33</sup> However, in Tommaso and de Leeuw's work, no ion pairs or larger ion clusters were investigated.

To provide information regarding the structure of water beyond the first hydration shell of any individual ion, ion pair, or larger ion cluster, the hydrogen bonding numbers were calculated. A hydrogen bond is generated when the distance between the donor O atom in one water molecule and acceptor O atom in the other water molecule is less than 3.5 Å and the angle  $\text{O}-\text{H}\cdots\text{O}$  is less than 30°. <sup>28</sup> When the  $\text{H}_2\text{O}$  molecules of the first hydration shell of any individual ion, ion pair, or larger ion cluster are present as donors, for any KCl solution, the hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shell of individual  $\text{K}^+$ , individual  $\text{Cl}^-$ , ion pairs, and ion clusters with three ions are in the ranges 6.46–7.35, 4.02–4.28, 8.29–9.06, and 10.65–12.50, respectively (Figure 3a). From Table 1, one can see that the hydration numbers of  $\text{K}^+$  and  $\text{Cl}^-$  are around 7. However, the hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shell of individual  $\text{K}^+$  is much larger than those from  $\text{Cl}^-$ . This is caused by the orientation of water molecules around the ions. The O atoms in  $\text{H}_2\text{O}$  prefer  $\text{K}^+$  and the H atoms prefer  $\text{Cl}^-$ . Hence, the  $\text{H}_2\text{O}$  molecules around  $\text{K}^+$  prefer to be donors, while the  $\text{H}_2\text{O}$  molecules around  $\text{Cl}^-$  prefer to be acceptors (this conclusion is confirmed by both Figures 3 and 4). The hydrogen bonding number for all  $\text{H}_2\text{O}$  molecules in the first shell of ion clusters with three ions possess larger



**Figure 3.** Hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shell of individual  $Q$  ( $Q = \text{K}^+, \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$ , circle), individual  $\text{Cl}^-$  (square), ion pair (triangle up), and ion cluster with three ions (triangle down) as functions of electrolyte concentration when the  $\text{H}_2\text{O}$  of the first hydration shell of individual ion, ion pair, or ion cluster present as donors.



**Figure 4.** Hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shell of individual  $Q$  ( $Q = \text{K}^+, \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$ , circle), individual  $\text{Cl}^-$  (square), ion pair (triangle up), and ion cluster with three ions (triangle down) as functions of electrolyte concentration when the  $\text{H}_2\text{O}$  of the first hydration shell of individual ion, ion pair or larger ion cluster are present as acceptors.

fluctuations than those from individual ions and ion pairs. This occurs because the ion clusters with three ions can acquire various conformations, which provide different hydrogen bonding networks. The hydrogen bonding numbers in NaCl solutions have a similar behavior (Figure 3b).

For  $\text{CaCl}_2$  solutions at a selected concentration, the hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first shell of  $\text{Ca}^{2+}$  is close to those of ion pairs (Figure 3c). The hydrogen

bonding number of all  $\text{H}_2\text{O}$  molecules of the first shell of  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , ion pairs, and ion clusters with three ions follows the order  $\text{Cl}^- < \text{Ca}^{2+} \sim$  ion pairs < ion clusters. For  $\text{MgCl}_2$  solutions, the hydrogen bonding number of  $\text{H}_2\text{O}$  of the first shell of  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and ion pairs follows  $\text{Cl}^- < \text{Mg}^{2+} <$  ion pair (Figure 3d).

Based on Table 1 and Figure 3, the hydrogen bonding number per  $\text{H}_2\text{O}$  molecule of the first hydration shell was obtained when all  $\text{H}_2\text{O}$  molecules of the first hydration shell of ions, ion pairs, and larger ion clusters are present as donors. In KCl solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule were 1.02–1.09, 0.55–0.59, 0.74–0.79, and 0.72–0.82 for  $\text{H}_2\text{O}$  molecules of the first hydration shell of individual  $\text{K}^+$ , individual  $\text{Cl}^-$ , ion pairs, and ion clusters with three ions, respectively. In NaCl solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule were 1.10–1.15, 0.56–0.59, 0.75–0.80, and 0.73–0.92 for the  $\text{H}_2\text{O}$  molecules of the first hydration shell of individual  $\text{Na}^+$ , individual  $\text{Cl}^-$ , ion pair and ion clusters with three ions, respectively. In  $\text{CaCl}_2$  solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule are 1.17–1.24, 0.56–0.59, 0.82–0.98, and 0.73–0.79 for  $\text{H}_2\text{O}$  of the first hydration shell of individual  $\text{Ca}^{2+}$ , individual  $\text{Cl}^-$ , ion pair and ion clusters with three ions, respectively. In  $\text{MgCl}_2$  solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule are 1.21–1.30, 0.55–0.59, and 0.88–1.00 for  $\text{H}_2\text{O}$  of the first hydration shell of individual  $\text{Ca}^{2+}$ , individual  $\text{Cl}^-$ , and ion pair, respectively.

We also provide hydrogen bonding information when the  $\text{H}_2\text{O}$  of the first hydration shell of individual ions, ion pairs, or larger ion clusters are present as acceptors. Generally, for a selected electrolyte concentration, the hydrogen bonding number of a  $\text{H}_2\text{O}$  molecule of the first hydration shell of ion, ion pairs, and larger ion clusters with three ions follows the order: ion clusters with three ions > ion pairs >  $\text{Cl}^- > Q$ , where  $Q = \text{K}^+, \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$  (Figure 4). In KCl solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule of the first shell are in the ranges 0.70–0.75, 0.80–0.87, 0.73–0.80, and 0.70–0.80 for individual  $\text{K}^+$ , individual  $\text{Cl}^-$ , ion pair, and ion clusters with three ions, respectively. Based on Table 1 and Figure 4, one can also obtain the hydrogen bonding number per  $\text{H}_2\text{O}$  molecule of the first hydration shell whose water molecules act as acceptors. For NaCl solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule are in the ranges 0.68–0.71, 0.81–0.86, 0.70–0.77, and 0.69–0.74 for individual  $\text{Na}^+$ , individual  $\text{Cl}^-$ , ion pair and ion clusters with three ions, respectively. For  $\text{CaCl}_2$  solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule are 0.59–0.63, 0.70–0.85, 0.66–0.76, and 0.73–0.78 for individual  $\text{Ca}^{2+}$ , individual  $\text{Cl}^-$ , ion pairs, and ion clusters with three ions, respectively. For  $\text{MgCl}_2$  solutions, the hydrogen bonding numbers per  $\text{H}_2\text{O}$  molecule are 0.61–0.68, 0.79–0.86, and 0.63–0.78 for individual  $\text{Ca}^{2+}$ , individual  $\text{Cl}^-$ , and ion pairs, respectively.

The hydrogen bonding between the water molecules of the first hydration shell of individual ions, ion pairs, or larger ion clusters are small. For all the water molecules of the first hydration shell of individual ions, the values are smaller than 0.4. The values of hydrogen bonds are smaller than 1.5 and 2 for all water molecules of the first hydration shells of ion pairs and larger ion clusters with three ions, respectively. From Figures 3 and 4, one can conclude that the hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shells of individual ions, ion pairs, and larger ion clusters are almost insensitive to the electrolyte concentration; they are sensitive to the nature of ions, ion pairs, and ion clusters.



## CONCLUSION

In conclusion, by employing molecular dynamics simulations, the ion structures and their hydration numbers in aqueous solution were determined for individual ions, ion pairs, and larger ion clusters. The hydration numbers of hydrated individual  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions are insensitive to the electrolyte concentration, whereas those of hydrated individual  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions are weakly sensitive. As the electrolyte concentration increases, the hydration numbers of ion pairs and larger ion clusters change little. However, the ion structures and their mole fractions are electrolyte concentration-dependent. For ion clusters of  $\text{MgCl}_2$ , only those with three ions could be identified. For  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$  solutions, ion clusters with three, four, five or even more ions, were found, but for clusters with more than four ions, the mole fractions were extremely low. Our results show that the nature and conformation of ions play a significant role in the hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shells of individual ions, ion pairs, and larger ion clusters. The hydrogen bonding numbers of  $\text{H}_2\text{O}$  of the first hydration shells are insensitive to the electrolyte concentration. When  $\text{H}_2\text{O}$  of the first hydration shell are donors, the hydrogen bonding number per  $\text{H}_2\text{O}$  molecule follows the order  $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$  for individual cations, the order  $\text{K}^+ \sim \text{Na}^+ < \text{Ca}^{2+} \sim \text{Mg}^{2+}$  for ion pairs, and the order  $\text{K}^+ \sim \text{Na}^+ \sim \text{Ca}^{2+}$  for ion clusters with three ions. When the  $\text{H}_2\text{O}$ s of the first hydration shell are acceptors, the hydrogen bonding number per  $\text{H}_2\text{O}$  molecule follows the order  $\text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$  for individual cations, the order  $\text{K}^+ \sim \text{Na}^+ \sim \text{Ca}^{2+} \sim \text{Mg}^{2+}$  for ion pairs, and the order  $\text{K}^+ \sim \text{Na}^+ \sim \text{Ca}^{2+}$  for ion clusters with three ions.

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [hchen23@buffalo.edu](mailto:hchen23@buffalo.edu) (H. C.).

\*E-mail: [feaeliru@buffalo.edu](mailto:feaeliru@buffalo.edu) (E.R.).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We wish to thank the Center for Computational Research in State University of New York at Buffalo for the computer time provided. H.C. is also grateful for the financial support from the National Natural Science Foundation of China (No. 21206049).

## REFERENCES

- (1) Shikano, K.; Kudo, K.; Kobayashi, K. Radiochemical separation of fluorine using hydrated tin dioxide as an inorganic ion exchanger. *J. Radioanal. Chem.* **1982**, *74*, 73–84.
- (2) Mason, P. E.; Neilson, G. W.; Dempsey, C. E.; Barnes, A. C.; Cruickshank, J. M. The hydration structure of guanidinium and thiocyanate ions: implications for protein stability in aqueous solution. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 4557–4561.
- (3) Swift, T. J.; Sayre, W. G. Determination of hydration numbers of cations in aqueous solution by means of proton NMR. *J. Chem. Phys.* **1966**, *44*, 3567–3574.
- (4) Nygård, K.; Hakala, M.; Manninen, S.; Hämäläinen, K.; Itou, M.; Andrejczuk, A.; Sakurai, Y. Ion hydration studied by x-ray compton scattering. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 024208.
- (5) Mason, P. E.; Wernersson, E.; Jungwirth, P. Accurate description of aqueous carbonate ions: an effective polarization model verified by neutron scattering. *J. Phys. Chem. B* **2012**, *116*, 8145–8153.
- (6) Barnett, R. N.; Landman, U. Hydration of sodium in water clusters. *Phys. Rev. Lett.* **1993**, *70*, 1775–1778.

- (7) Iyengar, S. S.; Petersen, M. K.; Day, T. J. F.; Burnham, C. J.; Teige, V. E.; Voth, G. A. The properties of ion-water clusters. I. the protonated 21-water cluster. *J. Chem. Phys.* **2005**, *123*, 084309.
- (8) Hummer, G.; Pratt, L. R.; García, A. E. Free energy of ionic hydration. *J. Phys. Chem.* **1996**, *100*, 1206–1215.
- (9) Straatsma, T. P.; Berendsen, H. J. C. Free energy of ionic hydration: analysis of a thermodynamic integration technique to evaluate free energy differences by molecular dynamics simulations. *J. Chem. Phys.* **1988**, *89*, 5876–5886.
- (10) Koneshan, S.; Rasaiah, J. C. Computer simulation studies of aqueous sodium chloride solutions at 298 and 683 K. *J. Chem. Phys.* **2000**, *113*, 8125–8137.
- (11) Chen, H.; Ruckenstein, E. Nanomembrane containing a nanopore in an electrolyte solution: a molecular dynamics approach. *J. Phys. Chem. Lett.* **2014**, *5*, 2979–2982.
- (12) Ohtaki, H.; Radnai, T. Structure and dynamics of hydrated ions. *Chem. Rev.* **1993**, *93*, 1157–1204.
- (13) Robertson, W. H.; Johnson, M. A. Molecular aspects of halide ion hydration: the cluster approach. *Annu. Rev. Phys. Chem.* **2003**, *54*, 173–213.
- (14) Abel, B. Hydrated interfacial ions and electrons. *Annu. Rev. Phys. Chem.* **2013**, *64*, 533–552.
- (15) Dang, L. X.; Pettitt, B. M. A theoretical study of like ion pairs in solution. *J. Phys. Chem.* **1990**, *94*, 4303–4308.
- (16) Luo, Y.; Jiang, W.; Yu, H.; MacKerell, A. D.; Roux, B. Simulation study of ion pairing in concentrated aqueous salt solutions with a polarizable force field. *Faraday Discuss.* **2013**, *160*, 135–149.
- (17) Pluhařová, E.; Marsalek, O.; Schmidt, B.; Jungwirth, P. Ab initio molecular dynamics approach to a quantitative description of ion pairing in water. *J. Phys. Chem. Lett.* **2013**, *4*, 4177–4181.
- (18) Belch, A. C.; Berkowitz, M.; McCammon, J. A. Solvation structure of a sodium chloride ion pair in water. *J. Am. Chem. Soc.* **1986**, *108*, 1755–1761.
- (19) Peslherbe, G. H.; Ladanyi, B. M.; Hynes, J. T. Structure of NaI ion pairs in water clusters. *Chem. Phys.* **2000**, *258*, 201–224.
- (20) Marcus, Y.; Hefter, G. Ion pairing. *Chem. Rev.* **2006**, *106*, 4585–4621.
- (21) Suits, A. G.; Hepburn, J. W. Ion pair dissociation: spectroscopy and dynamics. *Annu. Rev. Phys. Chem.* **2006**, *57*, 431–465.
- (22) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.* **1983**, *79*, 926–935.
- (23) Zhu, F. Q.; Schulten, K. Water and proton conduction through carbon nanotubes as models for biological channels. *Biophys. J.* **2003**, *85*, 236–244.
- (24) Grossfield, A.; Ren, P.; Ponder, J. W. Ion solvation thermodynamics from simulation with a polarizable force field. *J. Am. Chem. Soc.* **2003**, *125*, 15671–15682.
- (25) Ren, P.; Ponder, J. W. Temperature and pressure dependence of the AMOEBA water model. *J. Phys. Chem. B* **2004**, *108*, 13427–13437.
- (26) Ponder, J. W.; Wu, C.; Ren, P.; Pande, V. S.; Chodera, J. D.; Schnieders, M. J.; Haque, I.; Mobley, D. L.; Lambrecht, D. S.; DiStasio, R. A.; Head-Gordon, M.; Clark, G. N. I.; Johnson, M. E.; Head-Gordon, T. Current status of the AMOEBA polarizable force field. *J. Phys. Chem. B* **2010**, *114*, 2549–2564.
- (27) Phillips, J. C.; Braun, R.; Wang, W.; Gumbart, J.; Tajkhorshid, E.; Villa, E.; Chipot, C.; Skeel, R. D.; Kalé, L.; Schulten, K. Scalable molecular dynamics with NAMD. *J. Comput. Chem.* **2005**, *26*, 1781–1802.
- (28) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38.
- (29) Foloppe, N.; MacKerell, A. D., Jr. All-atom empirical force field for nucleic acids: I. Parameter optimization based on small molecule and condensed phase macromolecular target data. *J. Comput. Chem.* **2000**, *21*, 86–104.
- (30) MacKerell, A. D.; Banavali, N. K. All-atom empirical force field for nucleic acids: II. application to molecular dynamics simulations of DNA and RNA in solution. *J. Comput. Chem.* **2000**, *21*, 105–120.

- (31) Darden, T.; York, D.; Pedersen, L. Particle mesh Ewald: an  $N \cdot \log(N)$  method for Ewald sums in large systems. *J. Chem. Phys.* **1993**, *98*, 10089–10092.
- (32) Mancinelli, R.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. Hydration of sodium, potassium, and chloride ions in solution and the concept of structure maker/breaker. *J. Phys. Chem. B* **2007**, *111*, 13570–13577.
- (33) Tommaso, D. D.; de Leeuw, N. H. Structure and dynamics of the hydrated magnesium ion and of the solvated magnesium carbonates: insights from first principles simulations. *Phys. Chem. Chem. Phys.* **2010**, *12*, 894–901.