Dynamic and Static Properties of Aqueous NaCl Solutions at 25°C as a Function of NaCl Concentration: A Molecular Dynamics Simulation Study

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Received 20 October 2020; Revised 11 November 2020; Accepted 23 November 2020; Published 9 December 2020

Academic Editor: Bryan M. Wong

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We present the result of molecular dynamics (MD) simulations to calculate the molar conductivity \( \Lambda_m \) of NaCl in SPC/E water at 25°C as a function of NaCl concentration \( c \) using Ewald sums employing a velocity Verlet algorithm. It is found that the MD result for \( \Lambda_m \) with Ewald parameter \( \kappa = 0.10 \text{ Å}^{-1} \) gives the closest one to the experimental data and that the obtained radial distribution functions \( g_{ii}(r) \) with \( \kappa = 0.10 \text{ Å}^{-1} \) show a dramatic change with a very deep minimum of \( g_{NaCl}(r) \) and, as a result, sharp maxima of \( g_{NaNa}(r) \) and \( g_{ClCl}(r) \) at the distance 9.95 Å, which indicates a characteristic of ionic atmosphere, the basis of the Debye–Hückel theory of ionic solutions. The static and dynamic properties of NaCl (aq) solutions are analyzed in terms of radial distribution functions, hydration numbers, coordination numbers around \( Na^+ \) and \( Cl^- \), residence times of water around \( Na^+ \) and \( Cl^- \), water diffusion, and ion-ion electrostatic energies to explain the behavior of the molar conductivity \( \Lambda_m \) of NaCl obtained from our MD simulations.

1. Introduction

The theory that an electrolyte is dissolved in water and dissociated into ions was proposed by Arrhenius (Arrhenius’s theory of electrolytic dissociation), who won the Nobel Prize in Chemistry in 1903, in his doctoral degree in 1884. Before this theory was raised, it was well known that a solution dissolved in an electrolyte passes electricity, and Faraday explained that the electrolyte dissolved in water is decomposed into charged ions by the action of this electricity. By measuring the molar electrical conductivity according to the concentration of various salt solutions, Kohlrausch obtained the relation (equation (1)) between the molar conductivity \( \Lambda_m \) and the molar concentration \( c \) of a strong electrolyte (Kohlrausch’s law), and he found that each ion moved independently in an electric field. In the case of an electrolyte dissolved in a solvent and dissociated into \( v_+ \) cations and \( v_- \) anions, the limiting molar conductivity \( \Lambda_m^\circ \) in an infinitely dilute solution is related to the limiting molar conductivities \( \lambda_+^\circ \) and \( \lambda_-^\circ \) of each ion, as shown in equation (2) (Kohlrausch’s law of the independent migration of ions).

\[
\Lambda_m = \Lambda_m^\circ - Ke^{1/2},
\]

(1)

where \( K \) is a constant.

\[
\Lambda_m^\circ = v_+\lambda_+^\circ + v_-\lambda_-^\circ,
\]

(2)

where the limiting molar conductivities of \( Na^+ \) and \( Cl^- \) at 25°C are measured as 5.01 and 7.63 mS m\(^{-2}\) mol\(^{-1}\) experimentally [1].

In 1925, Onsager extended the Debye–Hückel theory of electrolyte solutions, published two years ago, to come up with the Debye–Hückel–Onsager theory, which became an integral part of his Nobel Prize winning achievements. Around some ions, ions with opposite charges are surrounded by electrostatic forces. In the absence of an external electric field, the distribution of counter ions around the central ion is symmetric. However, when the electric field...
acts, the ions at the center and the ions around them receive forces in opposite directions to create an asymmetric ionic atmosphere, and thereby, an electrostatic force acts in the direction opposite to the direction in which the ions move. The higher the concentration of the electrolyte, the greater this effect becomes, and thus, the molar conductivity becomes less than in a dilute solution. This reduction of the ions’ molar conductivity is called the relaxation effect.

Another effect of the ionic atmosphere is the electrophoretic effect. Ions are hydrated with solvent molecules, and these solvent molecules move with the ions. Since the central ions and the surrounding ions move in opposite directions, the central ions move against the flow of the solvent moving together with the surrounding ions. Onsager took these two points into consideration and treated the ion motion as a zigzag Brownian motion rather than a straight line in the electric field and derived the following molar conductivity equation. The Debye–Hückel–Onsager theory is an attempt to obtain quantitative expressions which leads to a Kohrausch-like expression:

\[ \Lambda_m = \Lambda_m^0 - (A + B \Lambda_m^0) c^{1/2}, \]  

(3)

where \( A \) and \( B \) are coefficients determined by temperature and the dielectric constant and viscosity of the solvent. The numerical values of \( A \) and \( B \) in water are 6.02 mS m\(^{-2}\) mol\(^{-1}\) (mol L\(^{-1}\))\(^{1/2}\) and 0.229 (mol L\(^{-1}\))\(^{1/2}\) [1]

A systematic conductivity study of sodium chloride-water + 1, 4-dioxane in dilute solutions (\( c < 0.01 \) mol dm\(^{-3}\)) [2] has been conducted covering a broad solvent composition range at temperatures from 5 to 35°C. Accurate viscosity and permittivity data were determined for the organic solvent system. Evaluation of the limiting molar conductivities \( \Lambda_m^0 \), ionic conductivities \( \Lambda_i^0 \) and \( \Lambda_o^0 \), and the association constant \( K_A \) is based on the chemical model [3] of electrolyte solutions, including short-range forces. In the next paper [4], they reported on an extension of this study to concentrated solutions, covering the temperature range from 5 to 35°C at a solvent mole fraction of dioxane from \( x_D = 0.20 \) to 0.65 and electrolyte concentration up to the limit of salt solubility in the respective mixtures and up to 5 mol dm\(^{-3}\) in water. Data analysis is based on the mean spherical approximation (MSA) [5]. Comparison is made with the data representation by the empirical Casteel–Amis equation [6]. The association constants of the MSA are compared with those from chemical model calculations at low concentrations (ICCM). Later on, an investigation of ion-pairing of alkali metal halides in aqueous solutions using the electrical conductivity and the Monte Carlo computer simulation methods was reported. [7]

In our previous paper [8], we reported molecular dynamics (MD) simulations for the ionic mobilities \( \mu \) of Na\(^+\) and Cl\(^-\) ions, in the system of Na\(^+\) (or Cl\(^-\)) ion + 1023 water molecules, at 25°C using reaction field correction (RFC), simple truncation (ST), and Ewald sums employing Gear’s fifth order predictor-corrector and velocity Verlet algorithms. We found that MD simulations using Ewald sum with \( \kappa = 0.20-0.30 \) Å\(^{-1}\) employing a velocity Verlet algorithm gives the best result for \( \mu_{Na^+} \) and \( \mu_{Cl^-} \) at 25°C, even though the calculated \( \mu_{Na^+} \) overestimates the experimental data and the \( \mu_{Cl^-} \) underestimates them. This behavior of \( \mu_{Na^+} \) is opposite to that reported in our other MD simulations [9].

In this study, we have carried out MD simulations to calculate the molar conductivity \( \Lambda_m \) of NaCl in SPC/E water at 25°C as a function of NaCl concentration (\( c \)) using Ewald sums employing a velocity Verlet algorithm. The primary goal of this study is to analyze radial distribution functions, hydration numbers, coordination numbers, residence times, and ion-ion electrostatic energies water diffusion to understand the behavior of the ionic atmosphere around Na\(^+\) and Cl\(^-\) ions through our MD simulations. This paper is organized as follows: Section 2 contains a brief description of molecular models and MD simulation methods followed by Section 3, which presents the results of our simulations. Our conclusion is summarized in Section 4.

2. Molecular Models and Molecular Dynamics Simulation Details

In order to establish systems of electrolyte solution of NaCl for MD simulation, we consider a system of \( c = 1 \) mol concentration (mol/L) of NaCl solution with 36 of Na\(^+\) and Cl\(^-\) ions at 25°C. Then, the volume of this solution is simply equal to \( V = V_{soln} = 36000 \) cm\(^3\)/\( N_A \) with \( N_A \), Avogadro’s number, which is the fixed volume for all the current MD simulations of NaCl in electrolyte systems, which gives the length of simulation box \( L = 39.1009 \) Å. It is very hard to find the relation between the molar concentration \( c \) and the density of the solution \( (\rho, g/cm^3) \) of NaCl solution in the literature. Instead, we use the experimental data of the weight percent \( (\% W_{NaCl}) \) and the density \( (\rho, g/cm^3) \) of NaCl solutions (Table 1) to find the numbers of ions \( (N_{NaCl}) \) and water \( (N_w) \). First, the relationship between \( \rho_i \) and \( \% W_{NaCl} \) is obtained by using the least squares method from Table 1.

\[ \rho_i = 0.007583338535 W_{NaCl} + 0.9942949 (g/cm^3). \]  

(4)

For \( c = 1 \) mol/L of \( N_{NaCl} = 36 \) with \( V = 36000 \) cm\(^3\)/\( N_A \),

\[ \rho_i = (18.0152N_w + 36 \times 58.4433)/36000 (g/cm^3). \]  

(5)

Also,

\[ \% W_{NaCl} = (36 \times 58.4433)/(18.0152N_w + (36 \times 58.4433)) \times 100. \]  

(6)

Substituting equations (5) and (6) into equation (4), we obtain \( N_w = 1956 \). Numbers of water molecules for given \( c \) are obtained using the same process and listed in Table 2.

The SPC/E model [10] was adopted for water-water and ion-water. The pair potential between water and ion has the TIPS form [11]:

\[ v_{iw} = 4 \epsilon_{io} \left[ \left( \frac{\sigma_{io}}{r_{io}} \right)^{12} - \left( \frac{\sigma_{io}}{r_{io}} \right)^{6} \right] + \sum_{j \neq i} \frac{q_i q_j}{r_{ij}}, \]  

(7)

where \( \sigma_{io} \) and \( \epsilon_{io} \) are Lennard–Jones (LJ) parameters between oxygen on a water molecule and an ion \( i \), \( q_i \) is the charge at site \( j \) in water, and \( q_i \) is the charge on ion \( i \).
Table 1: Experimental data between %W_{NaCl} and \( \rho_t \) at 25°C. The relationship (\( \rho_t = 0.00758333853 \% W_{NaCl} + 0.9942949 \)) is obtained by using the least squares method.

<table>
<thead>
<tr>
<th>%W_{NaCl}</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_t ) (g/cm(^3))</td>
<td>1.00409</td>
<td>1.01112</td>
<td>1.02530</td>
<td>1.03963</td>
<td>1.05412</td>
<td>1.06879</td>
<td>1.08356</td>
</tr>
<tr>
<td>%W_{NaCl}</td>
<td>14</td>
<td>16</td>
<td>18</td>
<td>20</td>
<td>22</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td>( \rho_t ) (g/cm(^3))</td>
<td>1.09872</td>
<td>1.11401</td>
<td>1.12954</td>
<td>1.14533</td>
<td>1.16140</td>
<td>1.17760</td>
<td>1.19443</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Diffusion Coefficient. \( D_{Na^+} \) and \( D_{Cl^-} \) at 25°C in SPC/E water were obtained from mean square displacements (MSDs), equation (9), of Na\(^+\) and Cl\(^-\) from our MD simulations using Ewald sum with \( \kappa = 0.05-0.25 \text{Å}^{-1} \) employing a velocity Verlet algorithm. We have listed sum of Na\(^+\) and Cl\(^-\) diffusion coefficients \( D = D_{Na^+} + D_{Cl^-} \) in Table 3 and compared \( D \) as a function of molar concentration (\( c \)) of NaCl with the experimental data [23] in Figure 1. Figure 1 shows
Table 3: Diffusion coefficients \((D, 10^{-9} \text{ m}^2\text{ sec}^{-1})\) of NaCl in SPC/E water at 25°C employing a velocity Verlet algorithm, where \(n\) is the number of (Na\(^+\) or Cl\(^-\)) ion(s).

<table>
<thead>
<tr>
<th>System (n)</th>
<th>(\kappa = 0.05)</th>
<th>(\kappa = 0.10)</th>
<th>(\kappa = 0.15)</th>
<th>(\kappa = 0.20)</th>
<th>(\kappa = 0.25)</th>
<th>Best to exp.</th>
<th>((\kappa, \text{ Å}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (1)</td>
<td>5.73</td>
<td>5.06</td>
<td>5.08</td>
<td>4.56</td>
<td>4.61</td>
<td>A1 (0.25)</td>
<td>4.61</td>
</tr>
<tr>
<td>A2 (2)</td>
<td>4.65</td>
<td>3.85</td>
<td>3.82</td>
<td>3.94</td>
<td>3.73</td>
<td>A2 (0.25)</td>
<td>3.73</td>
</tr>
<tr>
<td>A3 (4)</td>
<td>3.91</td>
<td>3.46</td>
<td>3.64</td>
<td>3.47</td>
<td>3.15</td>
<td>A3 (0.25)</td>
<td>3.15</td>
</tr>
<tr>
<td>A4 (8)</td>
<td>3.50</td>
<td>3.20</td>
<td>3.28</td>
<td>3.22</td>
<td>2.98</td>
<td>A4 (0.25)</td>
<td>2.98</td>
</tr>
<tr>
<td>A5 (18)</td>
<td>3.05</td>
<td>2.82</td>
<td>3.17</td>
<td>3.00</td>
<td>2.69</td>
<td>A5 (0.25)</td>
<td>2.69</td>
</tr>
<tr>
<td>A6 (36)</td>
<td>2.43</td>
<td>2.48</td>
<td>2.86</td>
<td>2.86</td>
<td>2.65</td>
<td>A6 (0.05)</td>
<td>2.43</td>
</tr>
<tr>
<td>A7 (72)</td>
<td>1.81</td>
<td>2.05</td>
<td>2.46</td>
<td>2.48</td>
<td>2.36</td>
<td>A7 (0.10)</td>
<td>2.05</td>
</tr>
<tr>
<td>A8 (108)</td>
<td>1.41</td>
<td>1.64</td>
<td>2.07</td>
<td>2.10</td>
<td>2.02</td>
<td>A8 (0.10)</td>
<td>1.64</td>
</tr>
<tr>
<td>A9 (144)</td>
<td>1.14</td>
<td>1.34</td>
<td>1.69</td>
<td>1.78</td>
<td>1.73</td>
<td>A9 (0.10)</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Figure 1: Comparison of the diffusion coefficients \((D = D_{Na^+} + D_{Cl^-})\) of NaCl at 25°C as a function of the molar concentration \((c)\) of NaCl for given Ewald sum parameters \((\kappa)\) employing a velocity Verlet algorithm obtained from MSDs of our MD simulations with the experimental data [23].

that the MD results \(D\) for all the Ewald sum parameter \(\kappa\) overestimate the experimental data \((\bigtriangledown)\) except those \((\bigcirc)\) with \(\kappa = 0.10\) Å\(^{-1}\) at 3.0 and 4.0 mol/L and those \((\blacktriangle)\) with \(\kappa = 0.05\) Å\(^{-1}\) at 2.0, 3.0, and 4.0 mol/L.

When compared with the experimental data, the best MD results for \(D\) are obtained at 0.0278–0.50 mol/L with \(\kappa = 0.25\) Å\(^{-1}\) (\(\bigtriangledown\)), at 1.0 M with \(\kappa = 0.05\) Å\(^{-1}\) (\(\bigcirc\)), and at 2.0–4.0 mol/L with \(\kappa = 0.10\) Å\(^{-1}\) (\(\blacktriangle\)). This best result set of \(D\) is also listed in Table 3. In our previous MD study [8], the Ewald sum parameter \(\kappa = 0.20–0.30\) Å\(^{-1}\) gives the best result for the ionic mobility \(\mu_{Na^+}\) and \(\mu_{Cl^-}\) at 25°C in single-ion systems in 1023 SPC/E water molecules. However, in the current work for multi-ion systems, the numbers of SPC/E water molecules are in the range of \(N_w = 1800–2000\). Note that the best results of \(D\) for \(N_{NaCl} = 1, 2, 4, 8, \) and 18 (the A1 – A5 MD systems) are obtained with \(\kappa = 0.25\) Å\(^{-1}\) which also gives the best result for \(\mu_{Na^+}\) and \(\mu_{Cl^-}\) in single-ion systems in 1023 SPC/E water molecules. [2].

In Figure 2, we have compared the best obtained \(D\) \((\bigtriangleup)\) and \(D\) with \(\kappa = 0.10\) Å\(^{-1}\) \((\bigcirc)\) as a function of \(c\) with the experimental data \((\bigtriangledown)\). However, the obtained structural and dynamic properties of the MD systems are totally different for the different values of the Ewald sum parameter \(\kappa\), which is discussed in the following sections. Instead of choosing the MD systems for the best obtained \(D\) to the experimental data with different \(\kappa\), we have chosen those of the same \(\kappa = 0.10\) Å\(^{-1}\) which give \(D\) \((\bigcirc)\) closest to the experimental data among those with the same \(\kappa\), but less closer to the best obtained \(D\) with different \(\kappa\). Figure 2 also shows \(D_{Na^+}\) and \(D_{Cl^-}\) as a function of \(c\). \(D_{Cl^-}\) at all the \(c\) (mol/L) is greater than \(D_{Na^+}\), and these two values become equal as \(c\) increases.

At very low concentrations, the \(D\) values of NaCl are much higher than the experimental data, the values at 0.222 and 0.5 mol/L are slightly higher than the experimental data, and the values at 1.0 and 2.0 mol/L are similar to the experimental data. At 3.0 and 4.0 mol/L, it is slightly lower than the experimental data. This result can be highly dependent on the choice of the Ewald sum parameter, \(\kappa\), as discussed above.

3.2. Molar Conductivity. We plotted molecular conductivity \(\Lambda_m = (\lambda_{Na^+} + \lambda_{Cl^-})\) of NaCl as a function of \(c^{1/2}\) obtained from \(D\) in our MD simulations in the inset of Figure 2, where \(\lambda_i = D_iz_i^2F^2/RT\), where \(z_i\) is the charge on the ion in units of the electronic charge \(e\), \(F\) is the Faraday constant, \(R\) is the gas constant, and \(T\) is the absolute temperature. Both the experimental data and the MD results for \(\Lambda_m\) of NaCl show two linear dependences (Ex1 and Ex2) as a function of \(c^{1/2}\). The value of the first slope for the first 4 experimental points (Exp. Ex1) and that of the second slope for the rest 6 points (Exp. Ex2) are \(-8.83\) and \(-2.94\) mSm\(^{-1}\)mol\(^{-1/2}\)/(molL\(^{-1}\))\(^{1/2}\), respectively. Those for the first 3 MD results (MD Ex1) and the rest 6 results (MD Ex2) are \(-34.73\) and \(-4.47\) mSm\(^{-2}\)mol\(^{-1/2}\)/(molL\(^{-1}\))\(^{1/2}\), respectively. According to the Debye–Hückel–Onsager (DHO) theory, equation (3), the slope \((A + B\Lambda_m^o)\) is equal to \(-8.91\) mSm\(^{-2}\)mol\(^{-1/2}\)/(molL\(^{-1}\))\(^{1/2}\) with the numerical values of \(A\) and \(B\) in water, 6.02 mSm\(^{-2}\)mol\(^{-1/2}\)/(molL\(^{-1}\))\(^{1/2}\) and 0.229 (molL\(^{-1}\))\(^{1/2}\), and \(\Lambda_m^o\) of NaCl, 12.64 mSm\(^{-2}\)mol\(^{-1}\) [1].
conclusion, the MD results for \( \Lambda_n \) of NaCl show two linear dependences like the experimental result, but the value of the first slope is too large for the DHO theory and the value of the second slope is similar to the experimental result.

### 3.3. Radial Distribution Functions \( g_{jn} (r) \) and Running Hydration Numbers \( n_{jn} (r) \)

The radial distribution functions, \( g_{io} (r) \) and \( g_{oi} (r) \), and the running hydration numbers, \( n_{jo}(r) \), for the ions (Na\(^+\) or Cl\(^-\)) and the O or H atoms of SPC/E water molecules are shown in Figure 3 for the A6 MD system (\( c = 1.0 \) mol/L, each Na\(^+\)(Cl\(^-\)) 36 ions with 1956 water molecules) with \( \kappa = 0.10 \) Å\(^{-1}\) as a function of distance. The running hydration number is defined as

\[
n_{ij}(r) = \int_0^r g_{ij}(r') 4\pi r'^2 dr'. \tag{11}
\]

Figure 3 shows the typical \( g_{io} (r) \) functions with positions of \( g_{ClO} (r) \) at the first maximum 3.25 Å and the first minimum 3.95 Å, of \( g_{Cl-H} (r) \) at the first maximum 2.30 Å and the first minimum 3.10 Å, \( g_{NaO} (r) \) at the first maximum 2.35 Å and the first minimum 3.15 Å and \( g_{Na-H} (r) \) at the first maximum 3.00 Å and the first minimum 3.75 Å. The positions of the first maxima and minima of \( g_{io} (r) \) and \( g_{oi} (r) \) are almost the same for all the values of \( c \) and \( \kappa \) considered in this study and the magnitudes of those maxima and minima are very slightly different for all \( c \) and \( \kappa \). These radial distribution functions \( g_{io} (r) \) of multi-ion systems are almost the same to those of single-ion systems [2].

The hydration number \( n_{io}(R_i) \) in the first shell is defined through equation (11) from the ion-oxygen distribution functions \( g_{io} (r) \) where the upper limit of integration \( R_i \) is the radius of the first hydration sphere, which corresponds to the first minimum in \( g_{io} (r) \). That is, \( R_i = 3.95 \) Å for \( g_{ClO} (r) \) and 3.15 Å for \( g_{NaO} (r) \) (and \( g_{ClO} (r) \)). We have listed the average hydration numbers \( n_{NaO} (R_i) \) and \( n_{ClO} (R_i) \) for the values of \( \kappa = 0.05, 0.10 \) and 0.25 Å\(^{-1}\) in the first hydration shells of Na\(^+\) and Cl\(^-\) in SPC/E water at 25°C in Table 4. The values of \( n_{NaO} (R_i) \) and \( n_{ClO} (R_i) \) are almost the same for \( \kappa = 0.05 \) Å\(^{-1}\) (5.64–5.85 and 7.55–7.62), \( \kappa = 0.10 \) Å\(^{-1}\) (5.67–5.90 and 7.65–7.82), and \( \kappa = 0.25 \) Å\(^{-1}\) (5.47–5.69 and 7.51–7.68).

### 3.4. Radial Distribution Functions \( g_{ri} (r) \) and Running Coordination Numbers \( n_{ri} (r) \)

The MD systems of small numbers of ion(s) – the A1 [each Na\(^+\)(Cl\(^-\)) 1 ion] and the A2 [each Na\(^+\)(Cl\(^-\)) 2 ions] show unstructured \( g_{ri} (r) \) functions due to the very small numbers of ion(s). The radial distribution functions, \( g_{NaNa} (r) \), \( g_{NaCl} (r) \), and \( g_{ClCl} (r) \), and the running coordination numbers, \( n_{NaNa} (r) \), \( n_{NaCl} (r) \), and \( n_{ClCl} (r) \) at 25°C for the A6 MD system \( [c = 1.0 \text{ mol/L}, \text{each Na}\(^+\)(Cl\(^-\)) 36 ions with 1956 water molecules] \) with \( \kappa = 0.25 \) Å\(^{-1}\) and \( \kappa = 0.10 \) Å\(^{-1}\) are shown in Figures 4 and 5, respectively. The radial distribution functions \( g_{ri} (r) \) of other MD systems (the A3 ~ A5 and the A7 ~ A9) with the same \( \kappa = 0.25 \) Å\(^{-1}\) are very similar to those of the A6 (Figure 4) with slightly different magnitudes of peaks, which are rather similar to the ordinary \( g_{io} (r) \) functions (Figure 3). However, the \( g_{ri} (r) \) functions with different \( \kappa \) are totally different. For comparison, we show the \( g_{ri} (r) \) and \( n_{ri} (r) \) functions of the A6 MD system with \( \kappa = 0.10 \) Å\(^{-1}\) in Figure 5, in which a dramatic change occurs with a very deep minimum of \( g_{NaCl}(r) \) and, as a result, sharp maxima of \( g_{NaNa}(r) \) and \( g_{ClCl}(r) \) at the distance 9.95 Å. Which is closer to nature, \( \kappa = 0.10 \) Å\(^{-1}\) or 0.25 Å\(^{-1}\)?

Other MD systems (the A3 ~ A5 and the A7 ~ A9) with the same \( \kappa = 0.10 \) Å\(^{-1}\) have also almost the same \( g_{ri} (r) \) to those of the A6 (Figure 5) with slightly different magnitudes of peaks. Also, the \( g_{ri} (r) \) functions for the A3 ~ A9 MD systems with \( \kappa = 0.0 \) (no Ewald sum), 0.05 Å\(^{-1}\), and 0.15 Å\(^{-1}\) are similar to those for those MD system with \( \kappa = 0.10 \) Å\(^{-1}\) (Figure 5), but the running coordination numbers \( n_{ri} (r) \) are different, while those \( g_{ri} (r) \) for the A3 ~ A9 MD systems with \( \kappa = 0.20 \) Å\(^{-1}\) are similar to those with \( \kappa = 0.25 \) Å\(^{-1}\) (Figure 4).

In Figure 5, \( g_{NaNa} (r) \) and \( g_{ClCl} (r) \) at short distances are nonzero but the corresponding average \( n_{NaNa} (r) \) at 5.0 Å and \( n_{ClCl} (r) \) at 6.5 Å are very small, 0.17 and 0.21, respectively, but \( n_{NaCl} (r) \) at 5.0 Å and 6.5 Å are already 0.28 and 1.20. As the distance \( r \) increases, \( n_{NaNa} (r) \) and \( n_{ClCl} (r) \) increase slowly, then suddenly reaching 2.04 and 2.10 at 9.95 Å, while the corresponding average \( n_{NaCl} (r) \) is 2.73 at 8.0 Å and slowly reaches about 3.80 at 9.95 Å.

### 3.5. Ionic Atmosphere

We have also listed the average coordination numbers \( n_{NaNa} (R_i) \), \( n_{ClCl} (R_i) \), and \( n_{NaCl} (R_i) \) (\( \sim n_{NaNa} (R_i) \)) for the A3 ~ A9 MD systems with \( \kappa = 0.10 \) Å\(^{-1}\) in the coordination shells around Na\(^+\) and Cl\(^-\) at 25°C with \( R_i = 9.95 \) Å in Table 5, while the coordination numbers \( n_{ii} \)
For the A3~A9 MD systems with $\kappa = 0.25 \text{Å}^{-1}$ are not defined since $g_{\text{NaO}} (r)$ for $\kappa = 0.25 \text{Å}^{-1}$ show neither any clear maxima for $g_{\text{ClCl}} (r)$ and $g_{\text{NaNa}} (r)$ at $R_1 = 9.95 \text{ Å}$ nor a clear minimum for $g_{\text{NaCl}} (r)$ at $R_1 = 9.95 \text{ Å}$. For the A3 (each Na$^+$ (Cl$^-$) 4 ions) and the A4 (each Na$^+$ (Cl$^-$) 8 ions), $n_{\text{NaNa}} (R_1)$ and $n_{\text{ClCl}} (R_1)$ are less than 1. The ratios of $n_{\text{NaCl}} (R_1) / (n_{\text{NaNa}} (R_1) + 1)$ and $n_{\text{ClNa}} (R_1) / (n_{\text{ClCl}} (R_1) + 1)$ for the A5~A9 MD systems are greater than 1 which indicates a characteristic of ionic atmosphere: Averaged over time, counterions are more likely to be found by any given ion. The time averaged, spherical haze, in which counterions outnumber ions of the same charge as the central ion, has a net charge opposite in sign to that on the central ion.

Relating to the running coordination numbers, $n_{\text{NaNa}} (r)$, $n_{\text{NaCl}} (r)$, and $n_{\text{ClCl}} (r)$ as seen in Table 5, we can imagine an imaginary sphere with Na$^+$ at the origin and 9.95 Å from it, filled with water molecules, with more number of Cl$^-$ inside the sphere and less number of Na$^+$ near the surface of the sphere. Figure 6 shows a snapshot of the ionic atmosphere with Na$^+$ at the origin and 9.95 Å from it, obtained from our MD simulation. Since an electric field is not applied to a solution of ions in this study, an asymmetric ionic atmosphere, the relaxation and the electrophoretic effects are not observed, but it is currently under studying by applying an electric field to a solution of ion.

### 3.6 Residence Time Correlation Functions and Residence times

The residence times are calculated from time correlation functions [8–10, 24] defined by

$$ R(r, t) = \frac{1}{N_h} \sum_{i=1}^{N_h} [\theta_i (r, 0) \cdot \theta_i (r, t)], $$

where $\theta_i (r, t)$ is the Heaviside unit step function, which is 1 if a water molecule $i$ is in a region $r$ within the coordination sphere.

![Figure 3: Radial distribution functions $g_{\text{io}} (r)$ and $g_{\text{ih}} (r)$ and the running hydration numbers $n_{\text{io}} (r)$ and $n_{\text{ih}} (r)$ of SPC/E water molecules for the A6 MD system at 25°C as a function of the distance $r$ (Å) between the ion (i) and the oxygen (O) and hydrogen atom (H) of a water molecule using Ewald sum with $\kappa = 0.10 \text{Å}^{-1}$.](image)

### Table 4: The average hydration numbers ($n_{\text{io}} (R_1)$) and residence times ($\tau_{\text{io}}$, ps) of water molecules in the first hydration shells of Na$^+$ and Cl$^-$ in SPC/E water at 25°C employing a velocity Verlet algorithm where $R_1 = 3.15 \text{ Å}$ for Na$^+$ and $R_1 = 3.95 \text{ Å}$ for Cl$^-$.  

<table>
<thead>
<tr>
<th>System</th>
<th>$\kappa = 0.05 \text{ Å}^{-1}$</th>
<th>$\kappa = 0.10 \text{ Å}^{-1}$</th>
<th>$\kappa = 0.25 \text{ Å}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$n_{\text{NaO}} (R_1)$</td>
<td>$\tau_{\text{NaO}} (R_1)$</td>
<td>$n_{\text{ClO}} (R_1)$</td>
</tr>
<tr>
<td>A2</td>
<td>5.65</td>
<td>12.9</td>
<td>7.62</td>
</tr>
<tr>
<td>A3</td>
<td>5.66</td>
<td>15.6</td>
<td>7.63</td>
</tr>
<tr>
<td>A4</td>
<td>5.66</td>
<td>16.7</td>
<td>7.63</td>
</tr>
<tr>
<td>A5</td>
<td>5.66</td>
<td>16.3</td>
<td>7.59</td>
</tr>
<tr>
<td>A6</td>
<td>5.64</td>
<td>14.3</td>
<td>7.57</td>
</tr>
<tr>
<td>A7</td>
<td>5.78</td>
<td>13.8</td>
<td>7.55</td>
</tr>
<tr>
<td>A8</td>
<td>5.85</td>
<td>14.0</td>
<td>7.62</td>
</tr>
<tr>
<td>A9</td>
<td>5.94</td>
<td>13.9</td>
<td>7.65</td>
</tr>
</tbody>
</table>
ions with \( R_i = 3.95 \text{ Å} \) for \( g_{CIO} (r) \) and \( 3.15 \text{ Å} \) for \( g_{NaO} (r) \) and that for \( \text{Na}^+ \) or \( \text{Cl}^- \) in the coordination shell around the \( \text{Cl}^- \) or \( \text{Na}^+ \) with \( R_i = 9.95 \text{ Å} \) at 25°C calculated from our MD simulations. The residence time \( t \) is obtained by fitting the time correlation function to an exponential decay \( \exp (-t/\tau) \), which is useful particularly when \( t \) is large. Table 4 shows the average residence times of water in the first hydration shell of the \( \text{Na}^+ \) and \( \text{Cl}^- \) ions for all the MD systems with \( \kappa = 0.05 \text{ Å}^{-1} \), 0.10 \text{ Å}^{-1} , and 0.25 \text{ Å}^{-1} .

In Table 4, the values of \( \tau_{NaO} \) and \( \tau_{CIO} \) for the A1 MD system are exceptionally smaller than those for the other MD systems. \( \tau_{NaO} \) are always greater than \( \tau_{CIO} \) with given values of \( \kappa \) and both the residence times increase with \( \kappa \) for all the systems. Roughly saying, \( \tau_{NaO} \) with \( \kappa = 0.05 \text{ Å}^{-1} \) increases and decreases with the concentration of NaCl, \( c \), and \( \tau_{CIO} \) increases monotonically with \( c \), while \( \tau_{NaO} \) and \( \tau_{CIO} \) with \( \kappa = 0.10 \) and 0.25 \text{ Å}^{-1} increase with \( c \). Generally, both residence times for all the MD systems with \( \kappa = 0.05 \text{ Å}^{-1} \) are too low, those with \( \kappa = 0.25 \text{ Å}^{-1} \) are too high, and those with \( \kappa = 0.10 \text{ Å}^{-1} \) are moderate.

Table 5 shows the average residence times of \( \text{Na}^+ \) and \( \text{Cl}^- \) in the coordination shell around \( \text{Na}^+ \) and \( \text{Cl}^- \) with \( R_i = 9.95 \text{ Å} \) for the A3 \( \sim \) A9 systems with \( \kappa = 0.10 \text{ Å}^{-1} \). Approximately, the values of \( \tau_{NaNa} \) and \( \tau_{ClCl} \) are in the range of 20–50 ps, while \( \tau_{NaCl} \) and \( \tau_{ClNa} \) are in that of 110 and 115 ps. Also, \( \tau_{NaNa} \) and \( \tau_{ClCl} \) increase with \( c \), while \( \tau_{NaCl} \) and \( \tau_{ClNa} \) are independent of \( c \). The ratios of \( \tau_{NaCl}/\tau_{NaNa} \) and \( \tau_{ClNa}/\tau_{ClCl} \) for the A5 \( \sim \) A9 MD systems are greater than 1 which indicates that oppositely charged ions attract each other. Also, the increase of \( \tau_{NaNa} \) and \( \tau_{ClCl} \) and, as a result, the decrease of the ratios of \( \tau_{NaCl}/\tau_{NaNa} \) and \( \tau_{ClNa}/\tau_{ClCl} \) with \( c \) means that the migration of \( \text{Na}^+ \) (or \( \text{Cl}^- \)) occurs hardly due to the increasing numbers of \( \text{Na}^+(or \text{Cl}^-) \).

3.7. Water Diffusion. We have listed diffusion coefficients \( D_w \) of SPC/E water at 25°C for the all MD systems with \( \kappa = 0.05 \), 0.10, and 0.25 \text{ Å}^{-1} \) in Table 6. For the pure water system, a recent MD simulation study [25] of 1024 SPC/E water molecules using Ewald with \( \kappa = 0.20 \text{ Å}^{-1} \) employing the vV algorithm reported \( 2.78 \times 10^{-9} \text{ m}^2/\text{s} \) obtained from MSD (mean square displacement, equation (9)) and \( 2.75 \times 10^{-9} \text{ m}^2/\text{s} \) from VAC (velocity autocorrelation, equation (10)) function at 300 K, which overestimate the experimental data at the same temperature \( (2.39 \times 10^{-9} \text{ m}^2/\text{s}) \) [26, 27] and \( 2.49 \times 10^{-9} \text{ m}^2/\text{s} \) [26–28]. However, TIP4P/2005 water model [29] gives an excellent agreement, \( 2.39 \times 10^{-9} \text{ m}^2/\text{s} \), obtained from both the MSD and VAC in our previous study [25] with the experiment one.

\( D_w \) obtained from our recent MD simulations [8] as a function of RFC (reaction field correction), ST (simple truncation), and Ewald sum parameter employing the Gear algorithm overestimates the experimental data, while \( D_w \) employing the vV algorithm underestimates except for ST and Ewald with \( \kappa > 0.45 \text{ Å}^{-1} \). These MD simulations [8] reported that \( D_w \) is \( 3.03 \times 10^{-9} \text{ m}^2/\text{s} \) in the \( \text{Na}^+ \)-water system and \( 3.09 \times 10^{-9} \text{ m}^2/\text{s} \) in the \( \text{Cl}^- \)-water system using ST employing the Gear algorithm with \( N_w = 215 \) of SPC/E water. An MD simulation for alkali Earth metal cations (Mg?²)
Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, and Ba\textsuperscript{2+}) in an aqueous solution at 25°C of SPC/E water potential (\(N_w\) = 215) using Ewald employing the Gear algorithm reported that \(D_w\) is in the range of \(2.46–2.62 \times 10^{-9} \text{m}^2/\text{s}\) [17].

In Table 6, roughly speaking, \(D_w\) with \(\kappa = 0.05 \text{Å}^{-1}\) increases up to the A7 MD system with slow decreases as \(c\) increases, while \(D_w\) with \(\kappa = 0.10 \text{Å}^{-1}\) has almost the same values up to the A6 MD system with sudden decreases, and \(D_w\) with \(\kappa = 0.25 \text{Å}^{-1}\) decreases monotonically up to the A6 MD system with sudden decreases. The behavior of \(D_w\) with \(\kappa = 0.10 \text{Å}^{-1}\) seems to be the most reasonable one; \(D_w\) has almost the same values up to \(n = 36\) Na\textsuperscript{+} (Cl\textsuperscript{−}) ions and decreases suddenly for \(n = 72, 108, \text{and} 144\).

In a study of the system-size dependence of translational diffusion coefficients and viscosities of pure water in molecular dynamics simulations under periodic boundary conditions [30], for a cubic simulation box of length \(L\), the diffusion coefficient is corrected for system-size effects as \(D_0 = D_{\text{PBC}} + 2.837297 \ k_B T/(6\eta L)\), where \(D_{\text{PBC}}\) is the diffusion coefficient calculated in the simulation, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(\eta\) is the shear viscosity of the solvent. Using \(T = 298.15 \text{K}\) and \(L = 39.1009 \text{ Å}\) for our systems and \(\eta = 0.854 \text{ cP}\) at 300 K, \(D_0 - D_{\text{PBC}} = 0.1856 \times 10^{-9} \text{ m}^2/\text{s}\) which is quite small, compared to our calculated \(D_w = 2.02–2.84 \times 10^{-9} \text{ m}^2/\text{s}\) with \(\kappa = 0.10 \text{Å}^{-1}\) (Table 6). This correction for \(D_w\) is not included in this study.

A recent study [31] reported that the effect of salt on the dynamics of water molecules follows the Hofmeister series. For some structure-making salts, the self-diffusion coefficient of the water molecules, \(D_w\), decreases with increasing salt concentration and for other structure-breaking salts, \(D_w\) increases with increasing salt concentration \(c\). Both ratios of experimental and simulation \(D_w\) (NaCl)/\(D_0\) (bulk) almost linearly decrease with \(c\) up to 0.75 and 0.5 at \(c = 4\text{M}\).

A more recent study [32] reported that when used with a good-quality water model, e.g., TIP4P/2005 [29] or E3B [33],
3.8. Energetics. Equations (7) and (8) have 18 potential energies, which are (1) water-water, (2) water-Na\(^{+}\), (3) water-Cl\(^{-}\), (4) Na\(^{+}\)-Na\(^{+}\), (5) Cl\(^{-}\)-Cl\(^{-}\), and (6) Na\(^{+}\)-Cl\(^{-}\) LJ potential energy and the corresponding electrostatic (Coulomb) energy in real and reciprocal spaces for the Ewald sum. The important potential energy that determines the molar conductivity of an electrolyte can be the electrostatic energy of ion-ion in real space and reciprocal spaces for the Ewald sum. In Table 7, we compared the average electrostatic energies of the electrolytic system obtained using the Ewald sum of \(\kappa = 0.10\ \text{Å}^{-1}\) and the velocity Verlet algorithm. Na\(^{+}\)-Na\(^{+}\) and Cl\(^{-}\)-Cl\(^{-}\) electrostatic energies in real space increase monotonically as the number of Na\(^{+}\)(Cl\(^{-}\)) ions increases and the corresponding Na\(^{+}\)-Cl\(^{-}\) energy also increases negatively, whereas the corresponding electrostatic energies in reciprocal space increase and decrease with the number of Na\(^{+}\)(Cl\(^{-}\)) ions. The ion-ion electrostatic energy in real space seems to be more important than in reciprocal space when determining the molar conductivity of an electrolyte. Ion-ion electrostatic energy, which increases monotonically in real space with the number of Na\(^{+}\)(Cl\(^{-}\)) ions, positively or negatively, retards the diffusion of ions. In conclusion, the molar conductivity of the electrolyte decreases with the concentration of the electrolyte.

The molar conductivity of an electrolyte is found to vary with the concentration. One reason for this variation is that the number of ions in the solution might not be proportional to the concentration of the electrolyte (that is, a strong or a weak electrolyte). Second, because ions interact with each other strongly, the conductivity of a solution is not exactly proportional to the number of ions present. Figure 8 shows the sum of diffusion coefficients (\(\mathcal{D}\)) of all ions multiplied by \(n\) in \(D_{A1}\) to \(D_{A9}\) in Table 3 for systems A1 to A9 for \(\kappa = 0.10\ \text{Å}^{-1}\). The sum of the "ideal" diffusion coefficients (---) of all ions obtained from \(D_{A1}\) multiplied by \(n\) in Table 3 for all identical systems is also shown. Here, of course, the molar conductivity of a solution is exactly proportional to the number of ions

### Table 6: Water diffusion coefficients (\(10^{-9}\ \text{m}^2/\text{s}\)) at 25°C employing a velocity Verlet algorithm, where \(n\) is the number of (Na\(^{+}\) + Cl\(^{-}\)) ions.

<table>
<thead>
<tr>
<th>System ((n))</th>
<th>(\kappa = 0.05\ \text{Å}^{-1})</th>
<th>(\kappa = 0.10\ \text{Å}^{-1})</th>
<th>(\kappa = 0.25\ \text{Å}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (2)</td>
<td>2.74</td>
<td>2.81</td>
<td>2.68</td>
</tr>
<tr>
<td>A2 (4)</td>
<td>2.76</td>
<td>2.79</td>
<td>2.66</td>
</tr>
<tr>
<td>A3 (8)</td>
<td>2.80</td>
<td>2.82</td>
<td>2.64</td>
</tr>
<tr>
<td>A4 (16)</td>
<td>2.87</td>
<td>2.82</td>
<td>2.62</td>
</tr>
<tr>
<td>A5 (36)</td>
<td>3.01</td>
<td>2.84</td>
<td>2.52</td>
</tr>
<tr>
<td>A6 (72)</td>
<td>3.15</td>
<td>2.80</td>
<td>2.38</td>
</tr>
<tr>
<td>A7 (144)</td>
<td>3.25</td>
<td>2.58</td>
<td>2.05</td>
</tr>
<tr>
<td>A8 (216)</td>
<td>3.14</td>
<td>2.32</td>
<td>1.76</td>
</tr>
<tr>
<td>A9 (288)</td>
<td>2.94</td>
<td>2.02</td>
<td>1.51</td>
</tr>
</tbody>
</table>

### Table 7: The average electrostatic energies (kJ/mol) per ion of the electrolyte systems using Ewald sum with \(\kappa = 0.10\ \text{Å}^{-1}\) employing a velocity Verlet algorithm, where \(n\) is the number of (Na\(^{+}\) or Cl\(^{-}\)) ion(s).

<table>
<thead>
<tr>
<th>System ((n))</th>
<th>Na(^{+})-Na(^{+}) Real reciprocal</th>
<th>Cl(^{-})-Cl(^{-}) Real reciprocal</th>
<th>Na(^{+})-Cl(^{-}) Real reciprocal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (1)</td>
<td>10.00</td>
<td>13.41</td>
<td>-0.29</td>
</tr>
<tr>
<td>A2 (2)</td>
<td>1.70</td>
<td>30.90</td>
<td>-1.10</td>
</tr>
<tr>
<td>A3 (4)</td>
<td>6.86</td>
<td>33.20</td>
<td>-23.3</td>
</tr>
<tr>
<td>A4 (8)</td>
<td>34.1</td>
<td>38.00</td>
<td>-48.2</td>
</tr>
<tr>
<td>A5 (18)</td>
<td>52.8</td>
<td>34.50</td>
<td>-131.0</td>
</tr>
<tr>
<td>A6 (36)</td>
<td>107.0</td>
<td>15.90</td>
<td>-272.0</td>
</tr>
<tr>
<td>A7 (72)</td>
<td>182.0</td>
<td>14.40</td>
<td>-347.0</td>
</tr>
<tr>
<td>A8 (108)</td>
<td>257.0</td>
<td>4.910</td>
<td>-405.0</td>
</tr>
</tbody>
</table>

### Figure 8: Sum of diffusion coefficients of all the ions in the systems. MD result: multiplied by \(n\) in \(D_{A1}\) to \(D_{A9}\) in Table 3 for systems A1 to A9 for \(\kappa = 0.10\ \text{Å}^{-1}\) and ideal: obtained from \(D_{A1}\) multiplied by \(n\) in Table 3 for all identical systems.
present. The deviation of the sum (O) of the diffusion coefficients from the “Ideal” diffusion coefficient (---) is due to the delay of the moving ions due to the strong ion-ion electrostatic interaction in real space as described above.

4. Conclusions

We have carried out molecular dynamics (MD) simulations of NaCl in SPC/E water at 25°C to calculate the molar conductivity \( \Lambda_m \) of NaCl as a function of NaCl concentration (c) using Ewald sums employing a velocity Verlet algorithm.

It is found that the structural properties of the MD systems with different \( \kappa \) are totally different. The obtained ion-ion radial distribution functions \( g_{ii}(r) \) with \( \kappa = 0.25 \) Å\(^{-1}\) show the ordinary behavior similar to the ion-water radial distribution functions \( g_{iw}(r) \). However, those functions \( g_{il}(r) \) with \( \kappa = 0.10 \) Å\(^{-1}\) give a dramatic change with a very deep minimum of \( g_{NaCl}(r) \) and, as a result, sharp maxima of \( g_{NaNa}(r) \) and \( g_{ClCl}(r) \) at the distance \( R_1 = 9.95 \) Å. The ratio of \( n_{NaCl}(R_1)/n_{NaNa}(R_1) + 1 \) and \( n_{ClCl}(R_1)/n_{ClCl}(R_1) + 1 \) for the A5~A9 MD systems with \( \kappa = 0.10 \) Å\(^{-1}\) are greater than 1 which indicates a characteristic of ionic atmosphere. This is the actual evidence of the basis of the Debye–Hückel theory of ionic solutions.

It is also found that the MD result for \( \Lambda_m \) of NaCl with Ewald sum parameter \( \kappa = 0.10 \) Å\(^{-1}\) gives the closest one to the experimental data. The behavior of \( \Lambda_m \) is close to the experimental date except at very low concentrations which are much higher than the experimental data. The analysis of radial distribution functions, hydration numbers, coordination numbers around Na\(^+\) and Cl\(^-\), residence times of water around Na\(^+\) and Cl\(^-\), water diffusion, and ion-ion electrostatic energies support this finding. It has been found that the ion-ion electrostatic energy in real space plays an important role in explaining that the molar conductivity of the electrolyte decreases with concentration.

Compared with the experimental data, the best MD results of \( D_{Na^+} \) and \( D_{Cl^-} \) for \( \Lambda_{NaCl} = 1, 2, 4, 8, \) and \( 18 \) are obtained with \( \kappa = 0.25 \) Å\(^{-1}\). This is consistent with the best result for \( \mu_{Na^+} \) and \( \mu_{Cl^-} \) in single-ion systems in 1023 SPC/E water molecules. [2] This indicates that the Ewald sum parameter \( \kappa = 0.25 \) Å\(^{-1}\) is suitable for systems with a small number of ions and 1000 to 2000 water molecules. However, as the number of ions increases without significant fluctuations in the number of water molecules, \( \kappa \) changes for the best MD results of \( D_{Na^+} \) and \( D_{Cl^-} \). We conclude that the appropriate value of \( \kappa \) is determined by the number of ions rather than the water molecule.

Data Availability

The data used in this study are given in the manuscript.

Conflicts of Interest

The author declares no conflicts of interest.

References


