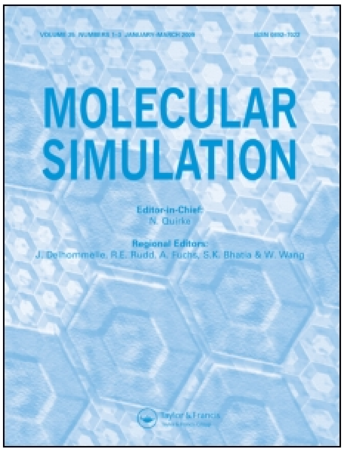

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Molecular Dynamics Simulation of Limiting Conductance for Na^2, Cl^{2-}, Na°, and Cl° in Supercritical Water

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MOLECULAR DYNAMICS SIMULATION OF LIMITING CONDUCTANCE FOR Na^{2+}, Cl^{2-}, Na°, AND Cl° IN SUPERCRITICAL WATER

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We report results of molecular dynamics simulations of the limiting conductance of Na^{2+}, Cl^{2-}, Na°, and Cl° in supercritical water using the SPC/E model for water in conjuction with our previous study (Lee *et al.*, Chem. Phys. Lett. **293**, 289 (1998)). The behavior of the limiting conductances of Na^{2+} and Cl^{2-} in the whole range of water density shows almost the same trend as those of Na^{+} and Cl^{-}, but the deviation from the assumed linear dependence of limiting conductances of Na^{2+} and Cl^{2-} on the water density is smaller than that of Na^{+} and Cl^{-}. The ratio of the limiting conductance of the divalent ions to that of the corresponding monovalent ions over the whole range of water density is almost constant. In the cases of Na^{2+} and Cl^{2-}, the dominating factor of the number of hydration water molecules around ions in the higher-density region and the dominating factor of the interaction strength between the ions and the hydration water molecules in the lower-density region are also found as was the cases for Na^{+} and Cl^{-}. These factors, however, are not so strong as for the corresponding monovalent ions because the change in the energetics, structure, and dynamics are very small mainly due to the strong Coulomb interaction of the divalent ions with the hydration water molecules. The diffusion coefficient of Na° and Cl° monotonically increases with decreasing water density over the whole range of water density. The increase of the diffusion coefficient with decreasing water density is attributed only to the dramatic decrease of the hydration number of water in the first solvation shell around the uncharged species. Among the two important competing factors in the limiting conductance of Na^{+} and Cl^{-}, the effect of the number of hydration water molecules around the uncharged species is the only existing factor over the whole range of water density since the interaction strength between the uncharged species and the hydration water molecules very small through the LJ interaction. This result has confirmed the dominating factor of the number of hydration water molecules around ions in the higher-density region in the explanation of the limiting conductance of Na^{+} and Cl^{-} in supercritical water at 673 K.

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Keywords: Molecular dynamics; Simulation; Limiting conductance

I. INTRODUCTION

Recently three experimental results of the limiting molar conductances as a function of water density at high temperatures (supercritical points) showed two different trends [1–3]. Wood *et al.* [1] reported a clear change of slope from the assumed linear dependence of limiting equivalent conductances of LiCl, NaCl, NaBr, and CsBr on the water density, and the others had clear maxima in limiting equivalent conductances of NaOH reported by Ho and Palmer [2] and in those of $CaCl_2$ and $MgCl_2$ at 400 C reported by Frantz and Marshall [3]. In the case of NaOH, the phenomenon is expected to closely relate to the structure of water around an ion and to the Grotthuss mechanism, not to the shape of the anion, OH^-. This system is presently under study.

Lee and Cummings [4, 5] reported molecular dynamics (MD) simulations of LiCl, NaCl, NaBr, and CsBr in supercritical water in order to explain the experimental observations of the limiting conductances as a function of the density of water supercritical state points, using SPC/E (extended simple point charge) model [6] for water. They found two important competing factors – the effect of the number of hydration water molecules around ions and the interaction strength between the ions and the hydration water molecules. In the cases of Na^+, Cs^+, Br^-, and Cl^-, the number of hydration water molecules around ions dominated in the higher-density region while the interaction between the ions and the hydration water molecules dominated in the lower-density region. The competition between these two factors was seen in the residence time of water in the first hydration shell around the ions. The different effects in the lower- and higher-density regimes led to different slopes for the limiting conductances as a function of density in the two regimes. Similar considerations explain the dependence of ion mobility on ion size at ambient conditions [7–9].

In the case of Li^+, the interaction between the ions and the hydration water in the lower-density region was almost a non-factor since the potential energy per hydration water molecule was monotonically decreased with decreasing water density, which was consistent with the linear increase of the limiting conductance for Li^+ ion with decreasing water density. The behavior of the limiting conductances of Li^+ in supercritical water using the revised polarized (RPOL) models [10, 11] for water and Li^+ ion resulted in a good agreement of the limiting conductances of LiCl with the experimental results [12]. The agreement of the RPOL1 model with the experimental results was much better in the higher-density regime but that of the RPOL2 model was slightly better in the lower-density regime. In the case of Li^+ using the RPOL models, the effect of the number of hydration water molecules around ions dominated in the higher-density region as was the case for Na^+, Cs^+, Cl^-, and Br^- ions but the effect of the interaction strength between the ions and the hydration water molecules was again a non-factor as was the case for Li^+ using the SPC/E model in the lower-density region since the potential energy per hydration water molecule rather decreased with decreasing water density at the lowest water densities.

Frantz and Marshall [3] measured electrical conductances of $CaCl_2$ and $MgCl_2$ in dilute aqueous solutions from 25 to 600 C at pressures up to 4000 bars. Solution compositions of the salts used were between 0.001 and 0.005 molal. The results showed that in $CaCl_2$ and $MgCl_2$ solutions with compositions less than 0.005 molar the salts exist primarily as Ca^{2+}, Mg^{2+}, and Cl^- ions at temperatures below 400 C and densities greater than 0.75 g/cc. They computed limiting equivalent conductance in this temperature-density range. Figure 2 shows clear maxima of the limiting equivalent conductances of both $CaCl_2$(0.001 molal) and $MgCl_2$(0.001 molal) as functions of water density at 400 C. The maxima in the limiting equivalent conductances of $CaCl_2$ and $MgCl_2$ are located around 0.75 g/cc, while the maximum in the limiting equivalent conductance [2] of NaOH is located around 0.55 g/cc and the clear change of slope from the assumed linear dependence of limiting equivalent conductances of LiCl, NaCl, NaBr, and CsBr [1] on water density is located around 0.45 g/cc. They also pointed out significant ion-pairings at temperatures greater than 400 C.

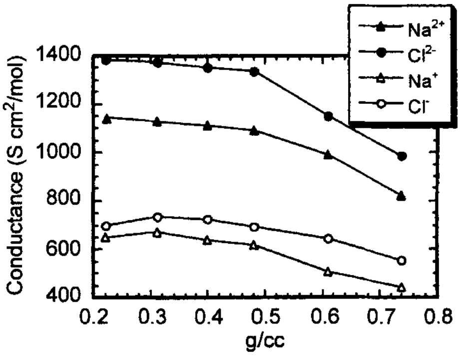

FIGURE 1 Limiting molar conductances of Na^{2+}, Cl^{2-}, Na^+, and Cl^- at infinite dilution calculated from MSD as a function of density of supercritical water at 673 K.

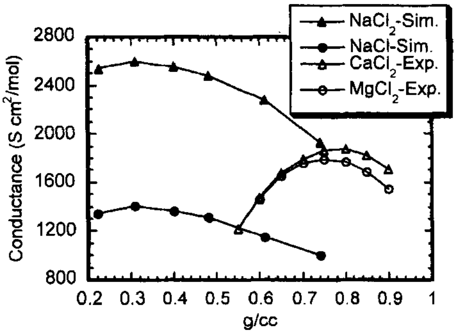

FIGURE 2 Limiting molar conductances of $NaCl_2$ and NaCl at infinite dilution as a function of density of supercritical water at 673 K obtained from MSD, and experimental results of $CaCl_2$ and $MgCl_2$.

Elimination of the charge on an ion makes the dielectric effect of the solvent on the ion a nonfactor and the dynamics of uncharged species is governed by the Stokes' law. The distinct maxima on separate curves of cation and anion mobilities as functions of ion size at ambient conditions [7, 8] disappear upon elimination of the charges on ions [9]. The comparison of dynamics of an ion and the corresponding uncharged species provides a useful information in understanding the dielectric effect of the solvent on the ion. The study of the fictitious species such as Na^{2+}, Cl^{2-}, Na°, and Cl° is possible only by the use of computer simulation methods. Recently an MD simulation study for the aqueous solution of Cl^{2-} at 298 K was reported by Guardia and Padro [10]. The influence of ionic charge as well as flexibility, molecular dipole moment, charge distribution and molecular geometry of water on the properties of the ion and the hydration water was discussed.

In this paper, we extend our MD simulations of the systems to Na^{2+}, Cl^{2-}, Na°, and Cl° in supercritical water at 673 K using the SPC/E model for water. The study for these systems is in conjuction with our previous study [4] of NaCl to delineate the effect of charge doubling and charge neutralization. The work for the systems of in $CaCl_2$ and $MgCl_2$ with considering the use of the revised polarized (RPOL) models [11,12] for water and the ions will be the next subject in our series of studies on ionic systems [4, 5, 7–9, 13]. In the following section, we describe the technical details of MD simulation. We present our results in Section III and the concluding remarks in Section IV.

II. MOLECULAR MODELS AND MOLECULAR DYNAMICS SIMULATION DETAILS

The SPC/E (extended simple point charge) model [6] was adopted for the water molecule. All ions were represented by a point charge having a Lennard–Jones (LJ) center. Na^{2+}, and Na° have the same ion-water potential parameters as Na^+ and Cl^{2-} and Cl° as Cl^-. The ion-oxygen σ_{io} is 2.876 and 3.875 A, respectively, and $\varepsilon_{io} = 0.5216$ kJ/mol for Na^+ and Cl^- ions [4, 8]. A spherical cutoff r_c of half the simulation box length was employed for all the pair interactions. This is a simple truncation in which two molecules are considered as interacting if the distance between their centers is less than the cutoff radius r_c and the interaction is neglected if the distance is larger than r_c. This simple truncation of all interactions for water containing a single ion was shown by Perera *et al.* [14] to be comparable in accuracy to the use of Ewald summation or reaction field methods.

The experimental critical properties of water are $T_c = 647.13$ K, $\rho_c = 0.322$ g/cc, and $P_c = 220.55$ bar [15] and the critical properties of SPC/E water are $T_c = 640$ K, $\rho_c = 0.29$ g/cc, and $P_c = 160$ bar [16]. We chose the simulation state points for the calculation of the limiting conductance of Na^{2+}, Cl^{2-}, Na°, and Cl°, $T_r = T/T_c = 1.05$ (673 K) and at the reduced densities, $\rho_r = \rho/\rho_c = 0.76$, 1.07, 1.38, 1.66, 2.10, and 2.55, corresponding to real densities of about 0.22, 0.31, 0.40, 0.48, 0.61, and 0.74 g/cc for the SPC/E model; this spans the range of densities around 0.45 g/cc where the clear change of slope from the assumed linear dependence of limiting equivalent conductances of NaCl [1].

We used Gaussian isokinetics [17–20] to keep the temperature of the system constant and the quaternion formulation [21, 22] of the equations of rotational motion about the center of mass of the SPC/E water molecules. For the integration over time, we adopted Gear's fifth-order predictor-corrector algorithm [23, 24] with a time step of 0.5×10^{-15} s (0.5 fs). Each MD simulation of a single ion system with 215 SPC/E water were carried out for Na^{2+}, Cl^{2-}, Na°, and Cl° for 1,200,000 time steps after equilibration of 600,000 time steps. The equilibrium properties are averaged over 6 blocks of 200,000 time steps and the configurations of water molecules and an ion are stored every 10 time steps for further analysis.

The diffusion coefficient, D_i, of each ion is calculated from the mean square displacement (MSD) and from the velocity auto-correlation function (VAC), and the ion mobility is obtained by $u_i = D_i z_i e/k_B T = D_i z_i F/RT$ (Einstein relation) where k_B is the Boltzmann constant, R is the gas constant, F is the Faraday constant, z_i is the charge on the ion in units of the electronic charge e, T is the absolute temperature, and $i = +$and$-$. The limiting conductance of each ion can be calculated from

$$\lambda_i^\circ = u_i z_i F = D_i z_i^2 F^2/RT. \tag{1}$$

The total limiting conductance of a salt is the sum of each ion: $\lambda^\circ = \lambda_+^\circ + \lambda_-^\circ$. For the uncharged species, $z_i \pm 1$ is assumed.

III. RESULTS AND DISCUSSION

The diffusion coefficients D_i of Na^{2+} and Cl^{2-}, calculated from the mean square displacement (MSD) and from the velocity auto-correlation function (VAC), are listed in Table I. The limiting conductances λ° determined from these diffusion coefficients are also listed in the same table. The limiting conductances of Na^{2+} and Cl^{2-} calculated from the MSD are compared, in Figure 1, with those of Na^+ and Cl^-[4].

In Figure 1, the behavior of the limiting conductances of Na^{2+} and Cl^{2-} in the whole range of water density shows almost the same trend as those of Na^+ and Cl^- except at the lowest density. The ratio of the diffusion coefficient of the divalent ions to that of the corresponding monovalent ions over the whole range of water density is almost constant (0.42 ~ 0.49 for cations and 0.44 ~ 0.49 for anions). The ratio of the limiting conductance is four times of that of the diffusion coefficient according to Eq. (1) (1.7 ~ 2.0 for cations and 1.8 ~ 2.0 for anions). Charge doubling of Na^+ and Cl^- gives

TABLE I Diffusion coefficient D and molar conductance λ° of Na^{2+} and Cl^{2-} at infinite dilution in supercritical water at 673 K calculated from mean square displacement (MSD) and velocity autocorrelation function (VAC)

		D ($\times 10^{-5}$ cm^2/s)		λ° ($\times$ $S\,cm^2/mol$)	
Ion	*Density (g/cc)*	*MSD*	*VAC*	*MSD*	*VAC*
Na^{2+}	0.22	17.2 ± 2.2	17.6 ± 2.4	1145 ± 146	1171 ± 160
Na^{2+}	0.31	17.0 ± 2.2	17.2 ± 2.3	1131 ± 146	1145 ± 153
Na^{2+}	0.40	16.7 ± 2.6	16.8 ± 2.9	1111 ± 173	1118 ± 193
Na^{2+}	0.48	16.4 ± 1.6	16.5 ± 1.6	1091 ± 106	1098 ± 106
Na^{2+}	0.61	14.9 ± 2.2	14.9 ± 2.5	991.6 ± 146	991.6 ± 166
Na^{2+}	0.74	12.3 ± 0.7	12.2 ± 0.6	818.5 ± 46.6	811.8 ± 39.9
Cl^{2-}	0.22	20.8 ± 4.2	21.3 ± 4.3	1384 ± 279	1417 ± 286
Cl^{2-}	0.31	20.6 ± 2.4	21.1 ± 2.6	1371 ± 160	1404 ± 173
Cl^{2-}	0.40	20.3 ± 2.4	20.8 ± 2.3	1351 ± 160	1384 ± 153
Cl^{2-}	0.48	20.1 ± 3.4	20.4 ± 3.7	1338 ± 226	1358 ± 246
Cl^{2-}	0.61	17.3 ± 3.8	17.5 ± 4.1	1151 ± 253	1165 ± 273
Cl^{2-}	0.74	14.8 ± 1.7	14.9 ± 2.1	984.9 ± 113.1	991.6 ± 140.0

merely a constant effect on the diffusion coefficient and hence the limiting conductance at supercritical conditions. A possible explanation for this may be the strong Coulomb interaction of the divalent ions with the hydration water molecules as discussed below. The deviation from the assumed linear dependence of limiting conductances of Na^{2+} and Cl^{2-} on the water density, as a measure of the slope, is smaller than that of Na^+ and Cl^-.

The limiting conductance of $NaCl_2$ calculated from those of the individual ions by $\lambda^\circ = \lambda^\circ_{2+} + 2\lambda^\circ_-$ are compared, in Figure 2, with that of NaCl and with experimental results of $CaCl_2$ and $MgCl_2$, in which the limiting conductances of Na^+ and Cl^- used are obtained from our previous study [4]. Again the ratio of the limiting conductance of $NaCl_2$ to that of NaCl over the whole range of water density is almost constant (1.8 ~ 2.0). Since the same calculated limiting conductances of Cl^- are used, this reflects again that the behavior of the limiting conductances of Na^{2+} in the whole range of water density has almost the same trend as that of Na^+. The dependence of the limiting conductances of $NaCl_2$ on the water density is rather ambiguous for the obtained results – a clear change of slope from the assumed linear dependence of limiting conductances or a clear maximum in limiting conductances. But the experimental limiting equivalent conductances of both $CaCl_2$ and $MgCl_2$ as functions of water density show clear maxima located around 0.75 g/cc. This suggests that the chemical circumstances around Na^{2+} is completely different from that around Ca^{2+} or Mg^{2+}. Or one may need to consider the use of the revised polarized (RPOL) models [11, 12] for water and the ions due to the strong polarizing effect of Ca^{2+} and Mg^{2+} with their divalent charges.

Several thermodynamic, structural, and dynamic quantities have been calculated and listed in Table II. Some MD simulation results for Cl^{2-} at 298 K are available in a recent report [10]. The average ion-water potential energies for Na^{2+} and Cl^{2-} ions increase nearly linearly with decreasing water as was observed in the cases of Na^+ and Cl^- but the change in this energy for the given water densities is very small (90/2300 and 70/1950) when compared with that for Na^+(50/600), Cl^-(50/450)^4, Cs^+(40/440), and Br^-(50/420)^5. This can be seen in Figure 3.

The hydration number n is found by integrating the water number density from the inner to the outer boundary of the first solvation shell [25]:

$$n = 4\pi\rho \int_a^b g_{\mathrm{io}}(r) r^2 dr \qquad (2)$$

where ρ is the bulk water number density, a is the point at which the ion-oxygen radial distribution function $g_{\mathrm{io}}(r)$ first rises from zero, and b is the

TABLE II Average ion-water potential energy, hydration number, ion-water potential energy divided by hydration number, and residence time of water molecules in hydration shell of an ion at 673 K

Ion	*Density (g/cc)*	*Ion-water p. e. (kJ/mol)*	*Hydration number (n)*	*Ion-water p. e./n*	*Residence time of water (ps)*
Na^{2+}	0.22	– 2246 ± 3	6.71 ± 0.06	– 334.7 ± 0.4	7.45 ± 0.47
Na^{2+}	0.31	– 2273 ± 2	6.75 ± 0.07	– 336.7 ± 0.3	7.35 ± 0.33
Na^{2+}	0.40	– 2290 ± 6	6.77 ± 0.02	– 338.3 ± 0.9	7.29 ± 0.62
Na^{2+}	0.48	– 2294 ± 9	6.80 ± 0.04	– 337.4 ± 1.3	7.17 ± 1.05
Na^{2+}	0.61	– 2317 ± 4	6.86 ± 0.07	– 337.8 ± 0.6	7.07 ± 0.70
Na^{2+}	0.74	– 2335 ± 5	6.91 ± 0.07	– 337.9 ± 0.7	6.91 ± 0.47
Cl^{2-}	0.22	– 1911 ± 6	10.48 ± 0.39	– 182.3 ± 0.6	3.57 ± 0.29
Cl^{2-}	0.31	– 1928 ± 5	10.53 ± 0.42	– 183.1 ± 0.5	3.51 ± 0.11
Cl^{2-}	0.40	– 1944 ± 7	10.56 ± 0.18	– 184.1 ± 0.7	3.48 ± 0.12
Cl^{2-}	0.48	– 1948 ± 5	10.62 ± 0.22	– 183.4 ± 0.5	3.45 ± 0.12
Cl^{2-}	0.61	– 1967 ± 1	10.69 ± 0.16	– 184.0 ± 0.1	3.43 ± 0.09
Cl^{2-}	0.74	– 1980 ± 6	10.78 ± 0.24	– 183.7 ± 0.6	3.41 ± 0.15

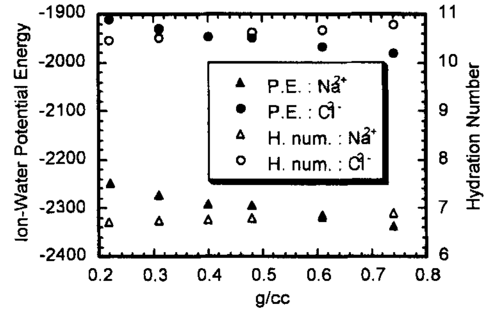

FIGURE 3 Ion-water potential energy for Na^{2+} (filled triangles) and Cl^{2-} (filled circles) and residence time for Na^{2+} (filled triangles) and Cl^{2-} (filled circles).

point at which the first minimum in $g_{io}(r)$ occurs. Table II lists the hydration number of water in the first solvation shell around Na^{2+} and Cl^{2-} ions. The number of hydration water molecules around these ions are larger than that of the corresponding monovalent ions (4.7 ~ 5.7 and 6.8 ~ 8.6)[4] but are comparable with that of Cs^+ and Br^- ions (6.2 ~ 8.7 and 7.3 ~ 9.5)[5]. Figure 3 shows that the hydration numbers for these ions are monotonically decreasing with decreasing water density, but the slopes for these ions are not very different in the ranges of density above and below 0.45 g/cc like those of Cs^+ and Br^-[5] but unlike those of Na^+ and Cl^-[4]. The change in this number for the given water densities is very small (0.2/6.8 and 0.3/10.6) when compared with that for Na^+(1.0/5.2), Cl^-(1.8/7.7)[4], Cs^+(2.5/7.5), and Br^-(2.2/8.4)[5] in which the numerator is the difference in the numbers and the denominator is the average of the numbers for the given water densities.

The potential energy per hydration water molecule, defined as the average ion-water potential energy divided by the hydration number, for Na^{2+} and Cl^{2-} ions is also listed in Table II. In the cases of Na^+ and Cl^-, the difference between these potential energies at densities above and below 0.45 g/cc was clearly observed, and these potential energies for Cs^+ and Br^- decreased nearly linearly with decreasing water density over the whole range of water density and the slopes were the same in the ranges of density above and below 0.45 g/cc. In the cases of Na^{2+} and Cl^{2-}, however, these energies are almost constant over the whole range of water density. This is largely due to the small changes in the average ion-water potential energies and the hydration numbers number of water in the first solvation shell around these ions over the whole range of water density. The small change in the energetics of Na^{2+} and Cl^{2-} and the structure of water around these ions suggests that the chemical circumstances around these ions is almost invariate for the given water densities, and this is mainly due to the strong Coulomb interaction of the divalent ion with the hydration water molecules unlike that of monovalent ion. The small change in the dynamics of Na^{2+} and Cl^{2-} is also expected as can be seen in residence times of hydration water molecules around ions.

The residence time correlation function is defined by [7, 8]

$$R(r,t) = \frac{1}{N_r}\sum_{i=1}^{N_r}[\theta_i(r,t)\theta_i(r,0)] \tag{3}$$

where $\theta(r, t)$ is the Heaviside unit function, which is 1 if a water molecule i is within a spherical region of radius r within the first hydration shell of the ion and 0 otherwise, and N_r is the average number of water molecules in this region r at $t=0$. The characteristic decay time (residence time), τ, is obtained by fitting the time correlation function to an exponential decay $\langle R(r,t)\rangle \approx \exp(-t/\tau)$, which is useful particularly when τ is large. The residence times for Na^{2+} and Cl^{2-} are listed in Table II and plotted in Figure 4. The residence time for these ions are larger than that of monovalent ions – $Na^+(1.7 \sim 2.4)$, $Cl^-(1.5 \sim 1.9)^4$, $Cs^+(1.6 \sim 2.1)$, and $Br^-(1.7 \sim 2.1)^5$ due to the strong Coulomb interaction of the divalent ions with the hydration water molecules. Figure 4 shows, however, that the change in this number for the given water densities is very small (0.5/7.2 and 0.2/3.5) when compared with that for $Na^+(0.8/2.1)$, $Cl^-(0.4/1.7)^4$, $Cs^+(0.5/1.8)$, and $Br^-(0.4/1.9)^5$.

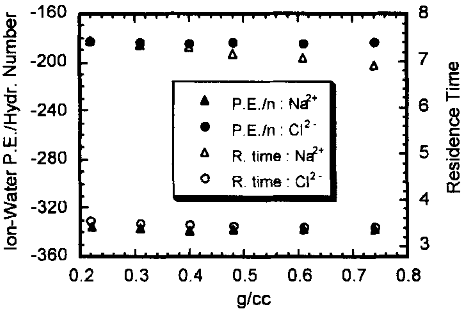

FIGURE 4 Ion-water potential energy divided by hydration number for Na^{2+}(filled triangles) and Cl^{2-}(filled circles) and residence time for Na^{2+}(filled triangles) and Cl^{2-}(filled circles).

There were two important competing factors in the explanation of the limiting conductance of LiCl, NaCl, NaBr, and CsBr in supercritical water at 673 K – the number of hydration water molecules around ions and the interaction between the ions and the hydration water molecules. In the cases of Na^+ and Cl^-, the effect of the number of hydration water molecules around ions dominated in the higher-density region while the interaction strength between the ions and the hydration water molecules was dominating factor in the lower-density region. The same explanation appeared to apply for the limiting conductances of Cs^+ and Br^-, but the latter factor in the lower-density region was not very dominant as in the cases of Na^+ and Cl^-; that is, a difference between the potential energy per hydration water molecule at densities above and below 0.45 g/cc was not clearly observed in the cases of Cs^+ and Br^-. In the cases of Na^{2+} and Cl^{2-}, the dominating factor of the number of hydration water molecules around ions in the higher-density region and the dominating factor of the interaction strength between the ions and the hydration water molecules in the lower-density region are also found as was the cases for Na^+ and Cl^-. These factors, however, are not so strong as for the corresponding monovalent ions because the change in the energetics, structure, and dynamics are very small mainly due to the strong Coulomb interaction of the divalent ions with the hydration water molecules. That is why the behavior of the limiting conductances of Na^{2+} and Cl^{2-} in the whole range of water density shows almost the same trend as those of Na^+ and Cl^- as shown in Figure 1, but the deviation from the assumed linear dependence of limiting conductances of Na^{2+} and Cl^{2-} on the water density is smaller than that of Na^+ and Cl^-.

TABLE III Diffusion coefficient D and molar conductance λ° of Na° and Cl° at infinite dilution in supercritical water at 673 K calculated from mean square displacement (MSD), and hydration number and residence time of water molecules in hydration shell of an ion at 673 K

Ion	*Density* *(g/cc)*	D $(\times 10^{-5} cm^2/s)$	λ° $(\times S cm^2/mol)$	*Hydration number(n)*	*Residence time of water(ps)*
Na°	0.22	293 ± 12	4870 ± 200	1.36 ± 0.04	0.93 ± 0.01
Na°	0.31	226 ± 10	3760 ± 170	2.71 ± 0.06	1.14 ± 0.03
Na°	0.40	184 ± 30	3060 ± 490	3.86 ± 0.07	1.35 ± 0.02
Na°	048	127 ± 13	2110 ± 220	4.12 ± 0.05	1.31 ± 0.06
Na°	0.61	83.0 ± 9.4	1380 ± 160	7.04 ± 0.11	1.40 ± 0.05
Na°	0.74	66.6 ± 12.8	1110 ± 210	8.16 ± 0.14	1.46 ± 0.05
Cl°	0.22	180 ± 9	2990 ± 150	2.65 ± 0.09	1.03 ± 0.04
Cl°	0.31	125 ± 8	2080 ± 130	3.57 ± 0.08	1.20 ± 0.06
Cl°	0.40	101 ± 5	1680 ± 80	5.05 ± 0.12	1.26 ± 0.05
Cl°	0.48	73.7 ± 11.7	1230 ± 190	6.35 ± 0.16	1.38 ± 0.07
Cl°	0.61	50.8 ± 10.4	845 ± 170	9.53 ± 0.17	1.61 ± 0.09
Cl°	0.74	34.4 ± 3.7	572 ± 60	14.12 ± 0.22	1.75 ± 0.07

We now turn our attention to the systems of uncharged species. Table III contains diffusion coefficient and limiting conductance of Na° and Cl° at infinite dilution in supercritical water at 673 K calculated from mean square displacement (MSD), and hydration number and residence time of water molecules in the first solvation shell of uncharged species at 673 K. In the calculation of limiting conductance of Na° and Cl°, $z_i = \pm 1$ is assumed. Figure 5 shows diffusion coefficients of Na° and Cl° as a function of water density. The only difference between Na° and Cl° is the ion-oxygen LJ parameter, σ_{io} (2.876 and 3.875 A). The diffusion coefficients of Na° for the given water densities are larger than those of Cl° according to the Stokes–Einstein relation, $D = kT/6\pi\eta a$, where η is the viscosity of water and a is the radius of particle.

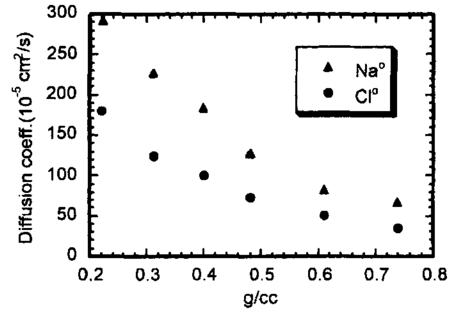

FIGURE 5 Diffusion coefficients of Na° and Cl° at infinite dilution calculated from MSD as a function of density of supercritical water at 673 K.

The diffusion coefficient monotonically increases with decreasing water density over the whole range of water density. The increase of the diffusion coefficient with decreasing water density is attributed only to the dramatic decrease of the hydration number of water in the first solvation shell around the uncharged species. Among the two important competing factors in the limiting conductance of Na^+ and Cl^- – the number of hydration water molecules around ions and the interaction between the ions and the hydration water molecules, the effect of the number of hydration water molecules around the uncharged species is the only existing factor over the whole range of water density as dominated in the higher-density region in the cases of Na^+ and Cl^- since the interaction strength between the uncharged species and the hydration water molecules very small through the LJ interaction when compared with the Coulomb interaction. This result has confirmed the dominating factor of the number of hydration water molecules around ions in the higher-density region in the explanation of the limiting conductance of Na^+ and Cl^- in supercritical water at 673 K.

The residence time of water molecules in the first solvation shell around uncharged species decreases with decreasing water density unlike in the cases of Na^+ and Cl^-, which is consistent with the monotonic increase of the limiting conductance of uncharged species with decreasing water density. This also reflects the null effect for the factor of the interaction between the uncharged species and the hydration water molecules. It is interesting to compare the hydration number and residence time of water molecules in the first solvation shell of Na° and Cl° at 673 K with those (13 and $9 \sim 13$ for Na°, and 23 and $18 \sim 22$ for Cl°)[9] at 298 K. The difference of the hydration number is reasonable but that of the residence time is remarkable.

IV. CONCLUDING REMARKS

In this study, we have extended our MD simulations of the systems to Na^{2+}, Cl^{2-}, Na°, and Cl° in supercritical water at 673 K using the SPC/E model for water in conjuction with our previous study [4] of NaCl to delineate the effect of charge doubling and charge neutralization. The behavior of the limiting conductances of Na^{2+} and Cl^{2-} in the whole range of water density shows almost the same trend as those of Na^+ and Cl^- except the lowest density, but the deviation from the assumed linear dependence of limiting conductances of Na^{2+} and Cl^{2-} on the water density is smaller than that of Na^+ and Cl^-. The ratio of the diffusion coefficient of the monovalent ions to that of the corresponding divalent ions over the whole range of water density is almost constant. Charge doubling of Na^+ and Cl^- gives merely a constant effect on the diffusion coefficient and hence the limiting conductance at supercritical conditions. In the cases of Na^{2+} and Cl^{2-}, the dominating factor of the number of hydration water molecules around ions in the higher-density region and the dominating factor of the interaction strength between the ions and the hydration water molecules in the lower-density region are also found as was the cases for Na^+ and Cl^-. These factors, however, are not so strong as for the corresponding monovalent ions because the change in the energetics, structure, and dynamics are very small mainly due to the strong Coulomb interaction of the divalent ions with the hydration water molecules.

The diffusion coefficients of Na° for the given water densities are larger than those of Cl° according to the Stokes–Einstein relation, $D = kT/6\pi\eta a$, since the only difference between Na° and Cl° is the ion-oxygen LJ parameter, σ_{io}. The diffusion coefficient of Na° and Cl° monotonically increases with decreasing water density over the whole range of water density. The increase of the diffusion coefficient with decreasing water density is attributed only to the dramatic decrease of the hydration number of water in the first solvation shell around the uncharged species. Among the two important competing factors in the limiting conductance of Na^+ and Cl^-, the effect of the number of hydration water molecules around the uncharged species is the only existing factor over the whole range of water density since the interaction strength between the uncharged species and the hydration water molecules very small through the LJ interaction. This result has confirmed the dominating factor of the number of hydration water molecules around ions in the higher-density region in the explanation of the limiting conductance of Na^+ and Cl^- in supercritical water at 673 K. The residence time of water molecules in the first solvation shell around uncharged species decreases with decreasing water density unlike in the cases of Na^+ and Cl^-, reflects the null effect for the factor of the interaction between the uncharged species and the hydration water molecules.

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