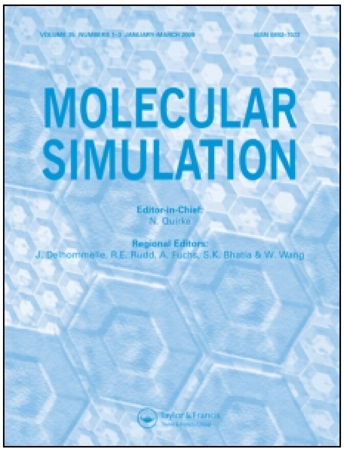

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Molecular Dynamics Simulation of Limiting Conductance for Li^+ Ion in Supercritical Water using Polarizable Models

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We report results of molecular dynamics simulations of the limiting conductance of Li^+ ion in ambient water and in supercritical water using polarizable models for water and Li^+. The limiting conductances of Li^+ in ambient water calculated from mean square displacement (MSD) using four points transferable intermolecular potential model (TIP4P), extended simple point charge model (SPC/E), and revised polarizable model 1 (RPOL1) are larger than the experimental value. The behavior of the limiting conductance of Li^+ in supercritical water using the RPOL models results in good agreement with experimental results for the limiting conductance of LiCl. The agreement of the RPOL1 model with the experimental results is much better than the RPOL2 model in the higher-density regime, whereas that of the RPOL2 model is much better than the RPOL1 model in the lower-density regime. Using the RPOL models (in contrast to the SPC/E model), the number of hydration water molecules around Li^+ is the dominating contributor to the limiting conductance in the higher-density regime. In agreement with the SPC/E model, the interaction strength between Li^+ and the hydration water molecules is a non-factor in the lower-density region since the potential energy per hydration water molecule decreases with decreasing water density at the lowest water densities.

Keywords: Molecular dynamics simulation; Li^+ ion; Polarizable models; Supercritical conditions

INTRODUCTION

In the previous work [1,2], we reported molecular dynamics (MD) simulations of NaCl, LiCl, NaBr, and CsBr in supercritical water aimed at explaining experimental observations of limiting conductance as a function of the density of water at supercritical state points using the extended simple point charge model (SPC/E) [3] for water and literature-derived ion–water potential parameters. We explained the experimental observations in terms of a changing balance between two 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. The number of hydration water molecules around ions was the dominating factor 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 evident 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. In the cases of Cs^+ and Br^-, however, in the lower-density region the ion-hydration water interaction was not as dominant as in the cases of Na^+ and Cl^- since a clear difference between the potential energy per hydration water molecule at densities about and below $0.45\ \mathrm{g\ cc^{-1}}$ was not clearly observed in the cases.

Similar considerations of the residence time explain the dependence of ion mobility on ion size at ambient conditions, as reported in MD simulations of the mobilities of the alkali metal ions (Li^+, Na^+, K^+, Rb^+, and Cs^+) and the halides (F^-, Cl^-, Br^-, and I^-) at 298 K [4–6] using the SPC/E model [3] for water and ion–water potential parameters. The residence times of water in hydration shells around an ion were found to decrease dramatically with its size. The classical Solventberg model describes the mobility of Li^+ ion in water adequately but not those of the other ions. For large ions, the steric effect due to large ion size and the large number of hydration water molecules restrict ionic mobility. As the size of an ion decreases, it should diffuse more easily due to the smaller steric

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effect and the decreasing number of the hydration water molecules. But for the small ions, the increase in the interaction between an ion and the hydrated water, reflected in the average potential energy per hydration water molecule [5], strongly decreases ionic mobility. This effect is seen in the residence time of the water in the first hydration shell around the ion.

Good agreement with limiting conductance experiments at supercritical conditions was found for all salts except LiCl. Since the limiting conductance of other chloride salts was well predicted, the poor results for LiCl was clearly a reflection of the poor prediction of that of Li^+. The limiting conductance of Li^+ over the whole range of water density calculated underestimated the experimental results [7] and exhibited almost linear dependence for the limiting conductance on the water density. The hydration number for Li^+ was nearly unchanged over the whole range of water density, and 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 monotonically decreased with decreasing water density. This was consistent with the linear increase of the limiting conductance for Li^+ ion with decreasing water density. The slope of the residence time (versus density) for Li^+ in the lower-density region was smaller than in the higher-density region, which was also consistent with the behavior of the limiting conductance for Li^+.

A possible explanation for the failure to predict the limiting conductance of Li^+ accurately may be the strong polarizing effect of Li^+ due to its small size. It is now widely accepted that many-body or nonadditive interactions are important if one wishes to quantitatively describe ionic interactions [8–17]. The interaction of Li^+ with water is stronger than the interaction of Na^+ with water and thus nonadditive intermolecular effects for water–water and ion–water can be expected to be more pronounced in this system. A polarizable potential model that explicitly includes the electronic polarization energy by the use of MD simulation method is the revised polarizable (RPOL) model of Caldwell *et al.* [8].

In this paper, we extend our MD simulations of Li^+ in supercritical water at 673 K to the RPOL model with and without three-body interactions. In the following section, we describe the technical details of MD simulation. We present our results in the third section and the concluding remarks in the fourth section.

MOLECULAR MODELS AND MOLECULAR DYNAMICS SIMULATION DETAILS

The RPOL model [8] consists of the Lennard–Jones (LJ) and electrostatic interactions, plus a nonadditive polarization energy. The ion is represented by a point-charge model including the polarizability placed on the LJ center. The total potential of the system, which includes the three-body term, is given by

$$U_{\text{tot}} = U_{\text{pair}} + U_{\text{pol}} + U_{\text{3-body}}. \tag{1}$$

The pair-additive potential is

$$U_{\text{pair}} = \sum_i \sum_j 4\varepsilon_{ij} \left[\frac{\sigma_{ij}}{r_{ij}^{12}} - \frac{\sigma_{ij}}{r_{ij}^{6}} \right] + \frac{q_i q_j}{r_{ij}}, \tag{2}$$

and the potential energy is

$$U_{\text{pol}} = -\frac{1}{2} \sum_i \mu_i E_i^0, \tag{3}$$

where μ_i is the induced dipole moment, and E_i^0 is the electrostatic field at atom i. The potential function which describes the short-range repulsive three-body interactions in the ion–water trimer is given as

$$U_{\text{3-body}} = A \exp(-\beta r_{12}) \exp(-\beta r_{13}) \exp(-\gamma r_{23}), \tag{4}$$

where r_{12} and r_{13} are the ion–oxygen distances, r_{23} is the oxygen–oxygen distance for the two water molecules involved in the ion–water trimer, and A, β, and γ are the empirical parameters. During the MD simulation, the induced dipole moment μ_i and the total electrostatic field E_i at the polarizable center are evaluated by the self-consistent-field method using following expressions:

$$\mu_i = \alpha_i E_i, \tag{5}$$

$$E_i = E_i^0 + \sum_{j \neq i} T_{ij} \mu_j, \tag{6}$$

$$E_i^0 = \sum_{j \neq i} \frac{q_j \mathbf{r}_{ij}}{r_{ij}^3}, \tag{7}$$

and

$$T_{ij} = \frac{1}{r_{ij}^3} \left(\frac{3 \mathbf{r}_{ij} \mathbf{r}_{ij}}{r_{ij}^2} - 1 \right), \tag{8}$$

where T_{ij} is the dipole tensor, α_i the polarizability of atom i, $\mathbf{r}_{ij}$ the vector from atom j to i, and q_j is the charge at atom j. To solve Eqs. (5) and (6), the traditional iterative approach was used with the iteration continuing until the root mean square of the difference in the induced dipole moment between successive iterations was less than 0.01 D/atom. The self-consistency was usually achieved within five iterative steps.

The potential parameters of RPOL models for water and Li^+ with and without three-body interactions are compared with transferable intermolecular potential model (TIP4P) [18] and SPC/E [3] models in Table I, and those for the three-body

TABLE I Comparison of potential parameters for TIP4P, SPC/E, and RPOL models with and without three-body interactions

Model	*Atom type*	σ (Å)	ϵ (kJ mol^{-1})	q (e)	α (Å)
TIP4P	O	3.154	0.6487	–	–
	H	–	–	+0.52	–
	M	–	–	−1.04	–
	Li^+	1.260	26.14	+1.0	–
SPC/E	O	3.169	0.6502	− 0.8476	–
	H	–	–	+0.4238	–
	Li^+	1.505	0.6904	+1.0	–
RPOL1: with 3-body interaction	O	3.169	0.6485	− 0.730	0.465
	H	–	–	+0.365	0.135
	Li^+	1.506	0.6904	+1.0	0.029
RPOL2: without 3-body interaction	O	3.196	0.6694	− 0.730	0.528
	H	–	–	+0.365	0.170
	Li^+	1.700	0.6904	+1.0	0.029

interactions are the same as those used in Ref. [15]: $A = 3.975 \times 10^6\,\mathrm{kJ\,mol^{-1}}$, $\beta = 3.20\,\mathrm{Å^{-1}}$ and $\gamma = 0.10\,\mathrm{Å^{-1}}$. We specify the RPOL model with the three-body interactions as RPOL1 and that without the three-body interactions as RPOL2. The Lennard–Jones parameters for water and Li^+ ion and the polarizability parameter for water of the RPOL1 model [9,15] are slightly different from those of the RPOL2 [16,17]. 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 interaction for water containing a single ion was shown by Perera *et al.* [19] to be comparable in accuracy to the use of Ewald summation or reaction field methods for the non-polarizable SPC and TIP4P models. Although Perera *et al.* did not explicitly consider the case of polarizable models, the total dipole moment (permanent + induced) of the RPOL models at the ambient and supercritical state conditions considered here is comparable to or less than that of SPC or TIP4P. Thus, the conclusion that a large spherical truncation is comparable in accuracy to the Ewald sum method should be valid for the present study. We compared the average dipole moments of water and Li^+ ion and other quantities with and without Ewald summation [20,21] in Tables II and IV. The differences are acceptably small.

The experimental critical properties of water are $T_c = 647.13\,\mathrm{K}$, $\rho_c = 0.322\,\mathrm{g\,cc^{-1}}$, and $P_c = 160\,\mathrm{bar}$ [22]. We chose the simulation state points for the calculation of the limiting conductance of Li^+, $T_r = T/T_c = 1.05(673\,\mathrm{K})$ 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 densities of about 0.22, 0.31, 0.40, 0.48, 0.61, and $0.74\,\mathrm{g\,cc^{-1}}$ for the RPOL models; this spans the range of densities around $0.45\,\mathrm{g\,cc^{-1}}$ where the clear change of slope from the assumed linear dependence of limiting equivalent conductances of LiCl [7].

We used Gaussian isokinetics [23–26] to keep the temperature of the system constant and the quaternion formulation [27,28] of the equations of rotational motion about the center of mass of the RPOL water molecules. For the integration over time, we adopted Gear's fifth order predictor–corrector algorithm [29,30] with a time step $0.5 \times 10^{-15}\,\mathrm{s}$ (0.5 fs). Each MD simulation of a single ion system with 215 RPOL water were carried out for Li^+ ion for 600 ps after equilibration of 300 ps. The equilibrium properties are averaged over six 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 the gas constant, F the Faraday constant, z_i 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 $\lambda_i^0 = u_i z_i F$. The total limiting conductance of LiCl is the sum of each ion: $\lambda^0 = \lambda_+^0 + \lambda_-^0$.

RESULTS AND DISCUSSION

First, we compare our results for Li^+ at 298 K and 1 atm using TIP4P, SPC/E, RPOL1, and RPLO2 models in Table II. The results for SPC/E model is the same as Ref. [5] but those for TIP4P model were recalculated using the simple truncation for all the pair interactions since the previous result [4] had an artifact effect due to the use of Steinhauser switching function [31].

TABLE II Average molar conductance λ^0 (S cm^2 mol^{-1}) of Li$^+$ at infinite dilution calculated from mean square displacement (MSD), water–water potential energy (kJ mol − 1), ionic potential energy, polarization energies (Eq. (3)) of water and Li$^+$ ion, dipole moments (Debye) of water and Li$^+$ ion, three-body interaction energy, hydration number, ion–water potential energy divided by hydration number n, and residence time τ (ps) of water molecules in hydration shell of an ion at 298 K using SPC/E, RPOL1, and RPOL2 models. The set of results in parentheses are obtained using Ewald summation method. U_{w-w} and U_{pol} (H_2O) are divided by the number of water molecules ($N = 215$) and $U_{ion} = U_{i-w}+U_{pol}(Li^+)+U_{3\text{-body}}$

Model	λ^0	$-U_{w-w}$	$-U_{i-w}$	$-U_{pol}$ (H_2O)	$-U_{pol}$ (Li^+)	μ (H_2O)	μ (Li^+)	$U_{3\text{-body}}$	n	$-U_{ion}/n$	τ
TIP4P	43.3 ± 3.8	38.3	847	–	–	–	–	–	5.87	144	57.3
SPC/E	44.3 ± 3.4	39.6	912	–	–	–	–	–	4.10	222	~400
RPOL1	68.1 ± 5.9	30.2	711	10.3 (8.90)	0.049 (0.052)	0.535 (0.491)	0.0073 (0.0082)	29.4 (28.5)	4.11 (4.17)	166	27.4
RPOL2	32.8 ± 6.3	30.0	693	15.6 (10.6)	0.043 (0.041)	0.742 (0.592)	0.0070 (0.0071)	–	4.08 (4.15)	170	66.8

The hydration number n is found by integrating the water number density from the inner to the outer boundary of the first solvation shell [32]:

$$n = 4\pi\rho\int_a^b g_{io}(r)r^2\,\mathrm{d}r, \tag{9}$$

where ρ is the bulk water number density, a the point at which the ion–oxygen radial distribution function $g_{io}(r)$ first rises from zero, and b is the point at which the first minimum in $g_{io}(r)$ occurs. The residence time of the hydrated water is a useful quantity to elucidate the environment around the ion. The residence time correlation function is defined by [4,5]

$$R(r,t) = \frac{1}{N_r}\sum_{i=1}^{N_r}[\theta_i(r,t)\theta_i(r,0)], \tag{10}$$

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 $\langle R(r,t)\rangle = \exp(-t/\tau)$, which is useful particularly when τ is large.

The introduction of the polarization into the water and ion models changes dramatically the energetics of the ion–water system. The average water–water potential energies in the RPOL models are smaller than that of the SPC/E model (-39.6 kJ mol^{-1}) but are compensated by the average polarization energies of water to give -40.5 and -45.6 kJ mol^{-1}, respectively, for RPOL1 and RPOL2. The experimental water–water potential energy is pure water is -41.5 kJ mol^{-1} [33] and the calculated water–water potential energy in pure water using the SPC/E model is -41.5 kJ mol^{-1} [5]. The average polarization energies of Li$^+$ in the RPOL models are too small due to its small polarizability. The effect of the average three-body interaction energy on the behavior of the Li$^+$ ion in the RPOL1 model is larger than the simple sum (-682 kJ mol^{-1}) of the average three-body interaction energy and average ion–water potential energy when compared with the average ion–water interaction energy (-693 kJ mol^{-1}) in the RPOL2 model, since the average ion–water interaction energy is considered for the interactions between the ion and all the water molecules while the three-body interaction is for those between the ion and a few nearest water molecules. This is consistent with the smaller residence time of the hydration water and the larger limiting conductance of Li$^+$ in the RPOL1 model than in the RPOL2 model.

The limiting conductances of Li$^+$ in ambient water calculated from MSD using the TIP4P, SPC/E,

TABLE III Diffusion coefficient D and molar conductance λ^0 of Li^+ at infinite dilution in supercritical water at 673 K calculated from mean square displacement (MSD) and velocity autocorrelation function (VAC) using SPC/E, RPOL1, and RPOL2 models

Model	ρ (g cc^{-1})	D (10^{-5} cm^2 s^{-1})		λ^0 (S cm^2 mol^{-1})	
		MSD	*VAC*	*MSD*	*VAC*
SPC/E	0.22	31.6 ± 4.9	31.9 ± 5.0	526 ± 82	531 ± 83
SPC/E	0.31	30.2 ± 1.6	30.9 ± 2.1	502 ± 27	514 ± 35
SPC/E	0.40	28.1 ± 5.6	28.4 ± 5.5	468 ± 93	472 ± 92
SPC/E	0.48	25.4 ± 3.1	25.1 ± 2.9	423 ± 52	418 ± 48
SPC/E	0.61	22.5 ± 3.8	22.6 ± 4.4	374 ± 63	376 ± 73
SPC/E	0.74	18.3 ± 3.0	18.4 ± 3.3	305 ± 50	306 ± 55
RPOL1	0.22	42.5 ± 3.8	43.4 ± 3.5	707 ± 63	722 ± 58
RPOL1	0.31	41.8 ± 1.8	42.6 ± 1.8	695 ± 30	709 ± 30
RPOL1	0.40	41.1 ± 3.2	41.4 ± 2.9	684 ± 53	689 ± 48
RPOL1	0.48	37.5 ± 1.6	37.8 ± 1.3	624 ± 27	629 ± 22
RPOL1	0.61	29.6 ± 2.5	29.5 ± 2.5	492 ± 42	491 ± 42
RPOL1	0.74	25.9 ± 1.9	26.1 ± 2.2	431 ± 32	434 ± 37
RPOL2	0.22	35.9 ± 3.6	36.3 ± 3.8	597 ± 60	604 ± 63
RPOL2	0.31	34.9 ± 2.9	35.1 ± 3.2	581 ± 48	584 ± 53
RPOL2	0.40	34.1 ± 4.4	34.2 ± 4.4	567 ± 73	569 ± 73
RPOL2	0.48	29.9 ± 1.5	29.9 ± 1.8	497 ± 25	497 ± 30
RPOL2	0.61	26.1 ± 2.2	25.9 ± 2.3	434 ± 37	431 ± 38
RPOL2	0.74	21.3 ± 2.0	21.1 ± 2.0	354 ± 33	351 ± 33

and RPOL1 models are larger than the experimental value (38.7 S cm^2 mol^{-1}), whereas that using the RPOL2 model is smaller than the experimental value. TIP4P water has a large hydration number as discussed in the previous paper [2] and the hydration numbers around the Li^+ ion in the other three water models are almost the same. The Li^+ ion in the TIP4P water is more restricted than in the SPC/E water which reflects that the water number effect dominates in the TIP4P model as the hydration number indicates while the interaction effect dominates in the SPC/E model as the potential energy per hydration water molecules and the residence time indicate. The average ionic potential energies of the RPOL models become smaller than that of the SPC/E model due to the polarization. The polarization of water rather than that of Li^+ ion has the direct effect of decreasing the average ion–water potential energy and the residence time of the hydration water. The repulsive three-body interaction decreases the residence time of the hydration water further and increases the molar conductance of Li^+ ion.

The diffusion coefficients D_{i} and the molar conductances λ_i^0 of Li^+ calculated from MSD and VAC at infinite dilution in supercritical water at 673 K using the SPC/E. RPOL1, and RPOL2 models are listed in Table III. The limiting conductances of Li^+ calculated from the MSD are compared in Fig. 1. The limiting conductances of LiCl calculated using

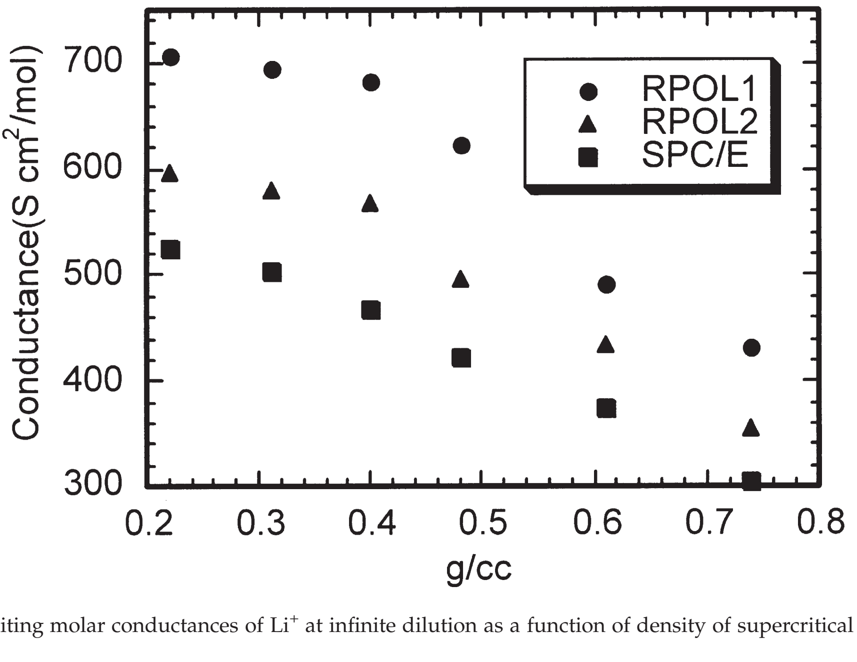

FIGURE 1 Limiting molar conductances of Li^+ at infinite dilution as a function of density of supercritical water at 673 K.

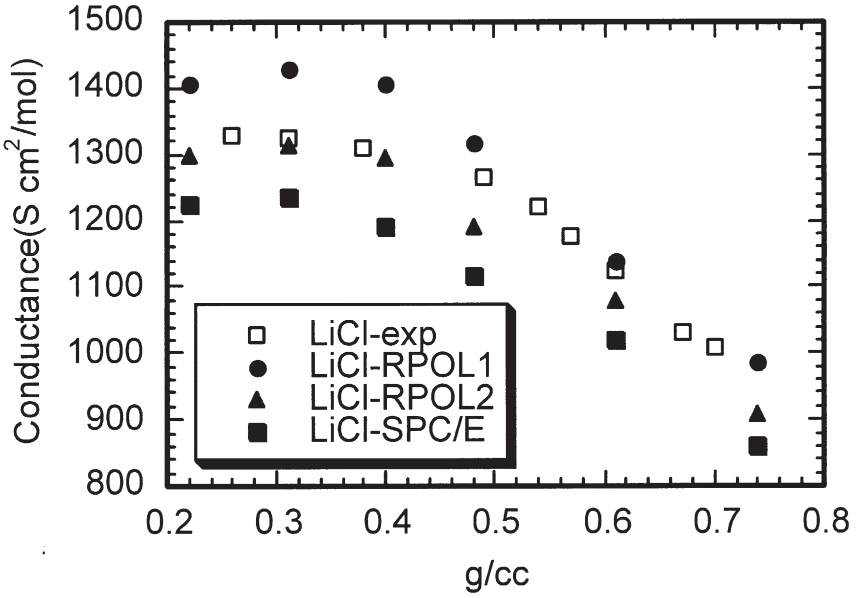

FIGURE 2 Limiting molar conductances of LiCl at infinite dilution as a function of density of supercritical water at 673 K.

the three different models are compared with the experimental result in Fig. 2, in which the limiting conductances of Cl^- are obtained from our previously study [1].

In Fig. 1, the behavior of the limiting conductances of Li^+ using the RPOL models show two different slopes as a function of water density, respectively, in the higher- and in the lower-density regime (above and below $0.45\,g\,cc^{-1}$). This is very similar to the behavior of the limiting conductance of Cs^+ using the SPC/E model [2]. But the limiting conductance of Li^+ using the SPC/E model shows almost a linear behavior over the whole range of water density except at $0.22\,g\,cc^{-1}$. This behavior of the limiting conductances of Li^+ using the RPOL models results is in good agreement of the limiting conductances of LiCl with the experimental results as shown in Fig. 2. The agreement of the RPOL1 model with the experimental results is much better than the RPOL2 model in the higher-density regime, whereas that of the RPOL2 model is much better than the RPOL1 model in the lower-density regime. This suggests that the three-body interaction plays an important role in the higher-density regime. The calculated limiting conductance of Li^+ using the RPOL1 model in the lower-density regime overestimated the experimental results [7] but exhibited a clear change of slope from the assumed linear dependence of limiting conductances as a function of the water density like the RPOL2 model. This suggests the importance of the polarization effect in explaining the behavior of Li^+.

Several thermodynamic, structural, and dynamic quantities have been calculated and listed in Table IV. Figure 3 shows that the average ionic potential energies ($U_{\text{ion}} = U_{\text{i-w}} + U_{\text{pol}}(\text{Li}^+) + U_{\text{3-body}}$) for Li^+ ion using the three models decrease nearly linearly with decreasing water density except for a relatively sudden decrement at the lower water densities. Table IV also lists the hydration number of water in the first solvation shell around Li^+ ion using the three models. Figure 4 shows that the hydration numbers for Li^+ ion using the three models are monotonically decreasing with decreasing water density, but the slopes for Li^+ using the RPOL models are very different from that for Li^+ using the SPC/E model. The change in the hydration number for Li^+ using the SPC/E model (4.1–4.2) and using the RPOL models (4.0–4.5) is very small when compared with that for Na^+ (4.7–5.7) or for Cs^+ (6.2–8.7) using the SPC/E model.

The ionic potential energy per hydration water molecule, defined as the average ionic potential energy divided by the hydration number, for Li^+ using the three models is also listed in Table IV. The previous studies [1,2] showed that in the cases of Na^+ and Cl^- using the SPC/E model, the difference between these potential energies at densities above and below $0.45\,g\,cc^{-1}$ was clearly observed. These potential energies for Cs^+ and Br^+ using the SPC/E model increased linearly with decreasing water density over the whole range of water density and, moreover, the slopes were the same in the ranges of density above and below $0.45\,g\,cc^{-1}$. This is largely due to the slopes of the hydration numbers for these four ions in the ranges of density above and below $0.45\,g\,cc^{-1}$. In the case of Li^+ using the SPC/E model, the average ionic potential energy decreased linearly with decreasing water density as shown in Fig. 3 and the hydration number is nearly unchanged in

TABLE IV Average water–water potential energy (kJ mol^{-1}), ion–water potential energy, polarization energies (Eq. (3)) of water and Li$^+$ ion, dipole moments (Debye) of water and Li$^+$ ion, three-body interaction energy, hydration number *n*, ionic potential energy divided by hydration number, and residence time τ (ps) of water molecules in hydration shell of an ion at 673 K using SPC/E, RPOL1, and RPOL2 models. The set of results in parentheses are obtained using Ewald summation method. U_{w-w} and U_{pol} (H_2O) are divided by the number of water molecules ($N = 215$) and $U_{ion} = U_{i-w} + U_{pol}(Li^+) + U_{3\text{-body}}$

Model	ρ (g cc^{-1})	$-U_{w-w}$	$-U_{i-w}$	$-U_{pol}$ (H_2O)	$-U_{pol}$ (Li^+)	μ (H_2O)	μ (ion)	$U_{3\text{-body}}$	n	$-U_{ion}/n$	τ
SPC/E	0.22	14.9	744	–	–	–	–	–	4.12	180	3.45
SPC/E	0.31	17.6	761	–	–	–	–	–	4.18	182	3.41
SPC/E	0.40	19.8	773	–	–	–	–	–	4.19	184	3.36
SPC/E	0.48	21.6	776	–	–	–	–	–	4.20	185	3.26
SPC/E	0.61	24.9	789	–	–	–	–	–	4.23	187	3.06
SPC/E	0.74	27.1	797	–	–	–	–	–	4.24	188	2.79
RPOL1	0.22	8.29	609	1.64	0.103	0.166	0.0106	18.9	3.97	149	2.27
RPOL1	0.31	10.4	625	2.09	0.102	0.198	0.0106	19.2	4.05	150	2.30
RPOL1	0.40	12.1	639	2.53	0.101	0.224	0.0105	19.8	4.13	150	2.20
RPOL1	0.48	13.6	642	2.90 (2.67)	0.099 (0.097)	0.245 (0.233)	0.0104 (0.0101)	20.1 (20.3)	4.16 (4.25)	150	2.11
RPOL1	0.61	15.7	652	3.54	0.097	0.278	0.0103	20.5	4.28	148	1.94
RPOL1	0.74	17.6	659	4.25	0.096	0.312	0.0102	21.1	4.45	143	1.83
RPOL2	0.22	8.74	613	2.26	0.091	0.216	0.0097	–	4.00	153	3.17
RPOL2	0.31	10.9	628	2.91	0.088	0.257	0.0098	–	4.02	156	3.22
RPOL2	0.40	12.6	636	3.50	0.088	0.291	0.0098	–	4.09	156	3.13
RPOL2	0.48	14.0	643	4.01 (3.10)	0.086 (0.083)	0.319 (0.275)	0.0097 (0.0094)	–	4.15 (4.30)	155	2.94
RPOL2	0.61	16.1	649	4.91	0.086	0.363	0.0097	–	4.25	153	2.69
RPOL2	0.74	17.9	655	5.88	0.083	0.406	0.0095	–	4.36	150	2.40

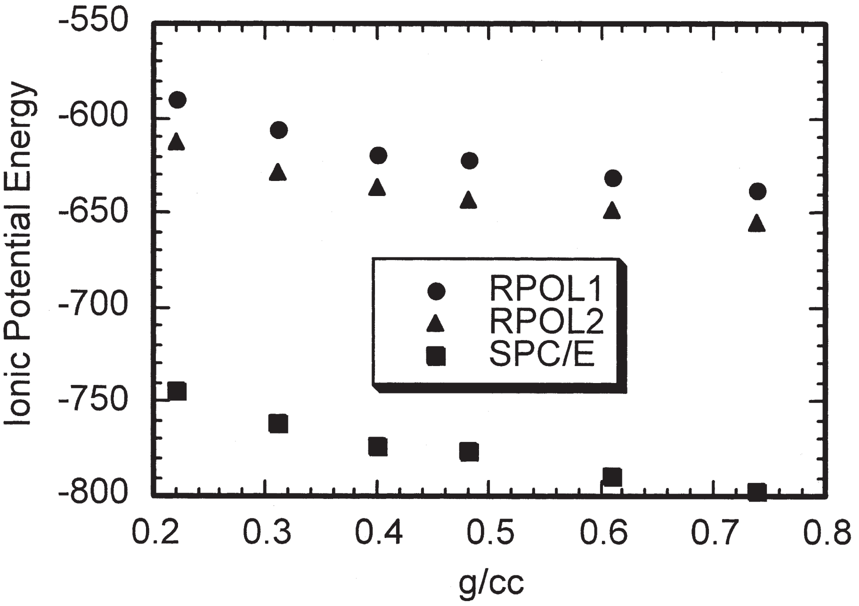

FIGURE 3 Ionic potential energy for Li^+, $U_{\text{ion}} = U_{\text{i-w}} + U_{\text{pol}}(Li^+) + U_{\text{3-body}}$.

the whole range of water density as shown in Fig. 4. As a result, ionic potential energy per hydration water molecule decreased linearly with decreasing water density over the whole range of water density as shown in Fig. 5. The ionic potential energy per hydration water for Li^+ using the RPOL models increases and then decreases with decreasing water density. The linear increase of the ionic potential energy per hydration water molecule with decreasing water density deviates at the lowest water densities. This is mainly due to the sudden decrease of the ionic potential energy at these water densities as shown in Fig. 3 since the hydration number decreased nearly linearly with decreasing water density over the whole range of water density as shown in Fig. 4. The energetics of the RPOL models is more complicated than that of the SPC/E model. The polarization energy of water (divided by the number of water) and the three-body interaction energy decrease with decreasing water density, while the polarization energy of Li^+ increases with decreasing water density even though its magnitude is very small compared with the polarization energy of water.

There were two important competing factors in the explanation of the limiting conductance of NaCl in

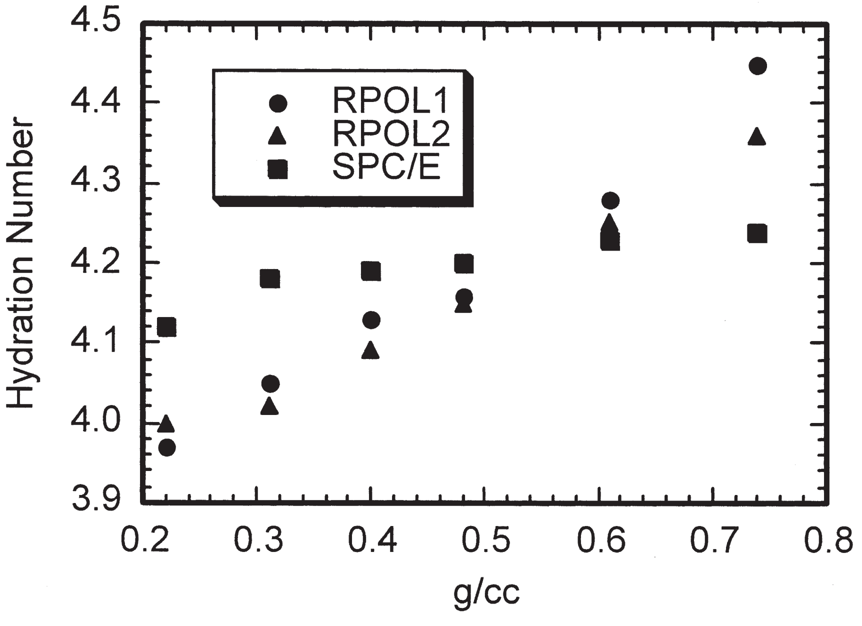

FIGURE 4 Hydration number for Li^+.

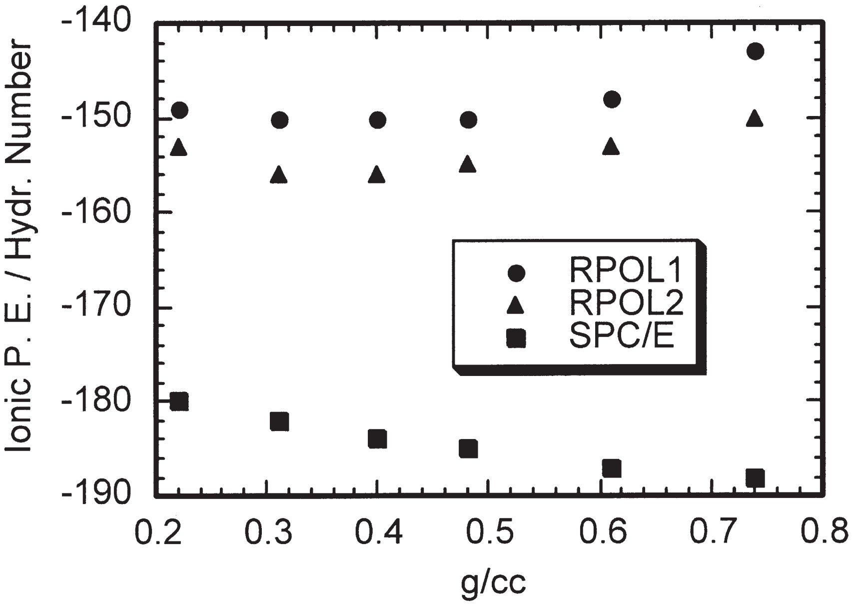

FIGURE 5 The ionic potential energy per hydration water molecule, defined as the ionic potential energy divided by hydration number for Li$^+$.

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 [1] of Na$^+$ and Cl$^-$ using the SPC/E model, 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 dominated in the lower-density region. The same explanation appears to apply for the limiting conductances [2] of Cs$^+$ and Br$^-$. In the case of Li$^+$ using the SPC/E model, the interaction strength between Li$^+$ and the hydration water molecules in the lower-density region is almost a non-factor since the potential energy per hydration water molecule monotonically decreasing with decreasing water density. In the case of Li$^+$ using the RPOL models, the effect of the number of hydration water molecules around Li$^+$ dominates in the higher-density region as was observed in the cases for Na$^+$, Cs$^+$, Cl$^-$, and Br$^-$ ions, but the effect of the interaction strength between Li$^+$ and the hydration water molecules is again a non-factor as is in the case for Li$^+$ using SPC/E model in the lower-density region since

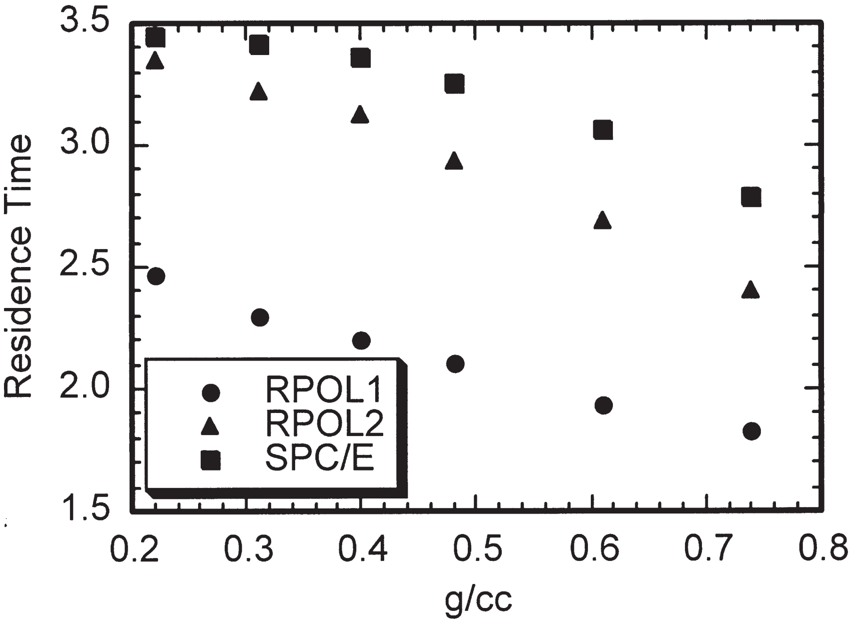

FIGURE 6 Residence time for Li$^+$.

the potential energy per hydration water molecule rather decrease with decreasing water density at the lowest water densities.

The residence times for Li^+ using the three models are also listed in Table IV and plotted in Fig. 6. The sudden decrement of the calculated residence times for Li^+ using the RPOL model at the lowest water density coincides with the sudden decrement of the average ionic potential energies per hydration water as shown in Fig. 5.

CONCLUDING REMARKS

In this study, we have recalculated the limiting conductances of Li^+ in ambient water and in supercritical water using polarizable models [8] for water and the Li^+ ion. The introduction of the polarization into the water and ion models changes dramatically the energetics of the ion–water system and the limiting conductances of Li^+ calculated from MSD in ambient water using TIP4P, SPC/E and RPOL1 models are larger than the experimental values. The polarization of water rather than that of Li^+ ion has the direct effect to decrease the average ion–water potential energy and the residence time of the hydration water. The repulsive three-body interaction decreases the residence time of the hydration water further and increases the molar conductance of Li^+ ion. The behavior of the limiting conductances of Li^+ in supercritical water using the RPOL models [8] results in good agreement between the simulated limiting conductances of LiCl and the experimental results. The agreement of the RPOL1 model with the experimental results is much better in the higher-density regime but that of the RPOL2 model is much better in the lower-density regime. This suggests that the three-body interaction plays an important role in the higher-density regime. From the analyses of the hydration number of water in the first solvation shell around Li^+ ion and the average ionic potential energy per water molecule, the effect of the number of hydration water molecules around Li^+ dominates in the higher-density region as is the case for Na^+, Cs^+, Cl^-, and Br^- ions, but the effect of the interaction strength between Li^+ and the hydration water molecules is again a non-factor as is the case for Li^+ using SPC/E model in the lower-density region since the potential energy per hydration water molecule decreases with decreasing water density at the lowest densities.

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