

An extended Stokes-Einstein model for condensed ionic water structures with topological complexity

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Abstract: “What is the structure of water?” This has been a perplexing question for a long time and water structure with various phases is a great topic of research interest. Topological complexity generally occurs because hydrophilic ions strongly influence the size and shape of condensed water structures owing to their kosmotropic and chaotropic transitions. In this study, an extended Stokes-Einstein model incorporating Flory–Huggins free energy equation is proposed to describe the constitutive relationship between dynamic diffusion and condensed water structure with a topological complexity. The newly developed model provides a geometrical strategy of end-to-end distance and explores the constitutive relationship between condensed ionic water structures and their dynamic diffusion behaviors. A free-energy function is then formulated to study thermodynamics in electrolyte aqueous solution, in which the condensed ionic water structures undergo topologically complex changes. Finally, effectiveness of the proposed model is verified using both molecular dynamics simulations and experimental results reported in literature.

Keywords: Condensed water structure; ionic water; Stokes-Einstein model; topology

1. Introduction

Water, the most abundant liquid on the earth and one of the most mysterious systems, shows many interesting and anomalous properties which are generally believed to be related to its extensive hydrogen bonds [1-4]. Therefore, the water is assumed to have condensed structures, similar to those of polymer macromolecules [1-4]. Both experimental and theoretical works have been carried out to study the condensed water structures [5-9]. For examples, X-ray absorption and Raman spectroscopy technologies have been used to probe the local structures and arrangement of molecules in condensed water structures [5-9], revealing the existence of multiple local structures. Statistical mechanics and molecular dynamics (MD) simulation have also been employed to study this topic [10]. Tanaka et al studied multiple local environments in water [11], and reported that there were two overlapped peaks of pure water being associated with the tetrahedral water structure owing to the tetrahedral asymmetry of its local structure [11].

Diffusion behaviors of various aqueous solutions were also investigated using theoretical models and experimental measurements [12-15]. For example, Chremos et al. [12] studied the influences of salts on the viscosity and water diffusion coefficient, both of which play essential roles to determine thermodynamic properties of electrolyte solutions. Yethiraj et al. [13] investigated effects of concentration and temperature on diffusion for the electrolyte aqueous solutions using MD simulations and nuclear magnetic resonance (NMR) technique. These results revealed that “structure-making” salts cause decreases of the diffusion coefficients of the water

molecules with increasing the salt concentrations, whereas “structure-breaking” salts cause increases of the diffusion coefficients of the water molecules. Müller and Hertz [14] proposed a parameter to describe water–water association, which is a complicated function of the salt concentration. Novotny and Sohnel [15] also developed a model which shows that the density of aqueous solutions is a function of salt concentration. However, so far there is no any theoretical framework developed to describe the effects of “structure-making” and “structure-breaking” salts on the condensed ionic water structure.

On the other matter, as water is a solvent extensively applied in biology, chemistry and engineering [16,17], dynamics of water structure have recently also been investigated experimentally [17-19] and theoretically [20,21]. However, effect of ion on the condensed water structure in electrolyte aqueous solution is still not well understood. Previously experimental studies showed that the ions can promote liquid-liquid phase transitions of two structures of water, which is closely related to the anomalous density property of water [11,22]. Both kosmotropic (structure-making) and chaotropic (structure-breaking) interactions between the water structures and ions have been reported in an ordered manner [23,24]. Many macroscopic properties, including diffusion coefficient, surface tension and chromatographic selectivity all show similar ordered manners [25-29]. The combined kosmotropic and chaotropic transitions of condensed water structure has also been verified from the MD simulation results [30,31].

In this study, based on Flory–Huggins free energy equation [32], the

Stokes-Einstein model [33,34] is modified to explore the effect of ions on the condensed water structures in electrolyte aqueous solutions. Diffusion coefficient, density and surface tension of electrolyte aqueous solutions are investigated using this newly proposed model, to understand the constitutive relationship between dynamic diffusion and condensed water structure undergoing electrostatic topology changes. A constitutive relationship between the condensed ionic water structures and their geometrical end-to-end distances has been formulated to explore the topological complexity. Finally, effectiveness of the proposed model is verified using both MD simulations and experimental results reported in literature. Our proposed model has a great advantage in the fast calculation of the diffusion coefficient, density and other properties for electrolyte aqueous solutions.

2. Theoretical analyses

Water has recently been recognized as a condensed matter, whose structure plays an essential role to determine the diffusion, density, dynamic relaxation of water, although all these have not still been fully understood [25,35-38]. Herein the pure water structures are simplified as spheres based on the Stokes-Einstein model [33]. Figure 1 shows a schematic diagram of condensed water structures with NaCl ions, of which the electrostatic charges achieve the geometry of condensed water structures transformed from a sphere shape into an ellipsoidal one, due to the actions of asymmetric ionic and hydrogen bonds [17,23,35]. These ions have electrostatic effects on the water molecules, leading to their increased cooperative movements [17]. Based on Flory–Huggins free energy theory [32], there is a repulsive free energy during

mixing between pure water and ions, and the repulsive effect of charges is expected to influence the condensed ionic water structure [4,18-23,25]. Therefore, non-Euclidean geometry model has been used to describe the condensed ionic water structure, of which the geometrical sizes and shapes of sphere and ellipsoid have been well characterized [39]. A self-consistent geometry model has further been developed to investigate the effect of polyatomic cation on topologic structures of condensed polymer networks, which cause the changes in non-Euclidean shapes of spheres and ellipsoids [39]. Due to the repulsive effect of charges, it is expected that the water structure is changed from a sphere shape into an ellipsoidal one based on the non-Euclidean geometry approach, and the end-to-end distances (h_0 and h_e) of the ellipsoids are essentially determined by the ions, as illustrated in Figure 1.

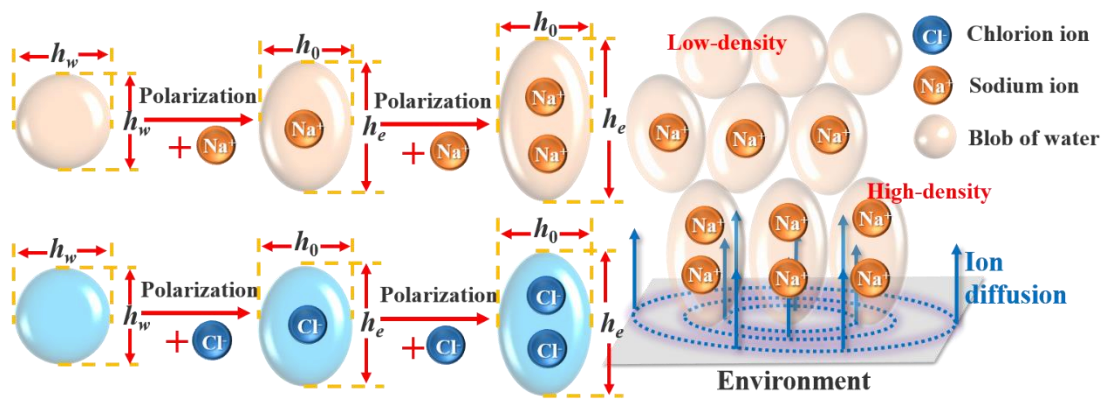


Figure 1. Schematic diagrams for the topological structures of condensed ionic water structure using end-to-end distances (h_0 and h_e). The water structure is changed from a sphere shape into an ellipsoidal one due to the repulsive free energy based on the Flory–Huggins free energy theory [32] and non-Euclidean geometry model [39].

2.1 Extended Stokes-Einstein model

The Stokes-Einstein model is often used to describe the constitutive relationship

between the diffusion coefficient (D) and end-to-end distance (h) [33]. For the water with condensed sphere structures, the diffusion coefficient (D_w) takes the form of [33,34],

$$D_w = \frac{k_B T}{6\pi\eta h_w} \quad (1)$$

where $k_B=1.38\times 10^{-23}$ J/K is the Boltzmann constant, T is the temperature, h_w is the end-to-end distance, and η is the viscosity of the condensed pure water.

On the other hand, for the ionic water with a condensed ellipsoidal structure, the diffusion coefficient (D_{ion}) can be expressed as [33],

$$D_{ion} = \frac{k_B T \ln \left[\frac{1 + (1 - h_0^2 / h_e^2)^{1/2}}{h_0 / h_e} \right]}{6\pi\eta h_e (1 - h_0^2 / h_e^2)^{1/2}} \quad (2)$$

where h_e and h_0 are the end-to-end distances along the longitudinal and latitudinal directions of the condensed ionic water with an ellipsoidal structure.

The parameters ϕ and $(1 - \phi)$ are the volume fractions of ionic water and pure water in an electrolyte aqueous solution. The diffusion coefficient of electrolyte aqueous solution (D) can be obtained as [40],

$$\ln D = \phi \ln D_{ion} + (1 - \phi) \ln D_w \quad (3)$$

By inserting equations (1) and (2) into (3), the ratio of diffusion coefficient for the electrolyte aqueous solution (D/D_w) can be written as,

$$\ln \left(\frac{D}{D_w} \right) = \phi \cdot \ln \left[\frac{h_w \ln \left(h_e / h_0 + (h_e^2 / h_0^2 - 1)^{1/2} \right)}{h_e (1 - h_0^2 / h_e^2)^{1/2}} \right] + (1 - \phi) \quad (4)$$

Figure 2 shows the analytical results of the diffusion coefficients (D) of electrolyte

aqueous solution as functions of the end-to-end distance ratio (h_e/h_0) and volume fraction of ionic water (ϕ). In Figure 2(a), the ratio h_0/h_w has been set to be 0.75. When h_e/h_0 is set to be 1.0 and 1.5 (where $h_e/h_w=0.75$ and 1.125), the increase in volume fraction of ionic water (ϕ) results in an increased ratio of diffusion coefficients (D/D_w), because the ions enable a chaotropic transition of the water structure [12,13,16,17,23]. When the values of h_e/h_0 are 3.5 and 5.0 (where h_e/h_w values are 2.625 and 3.75), an increase in volume fraction of ionic water (ϕ) results in a decrease in the diffusion coefficient ratio (D/D_w), mainly because the ions enable a kosmotropic transition of the water structure [12,13,16,17,23].

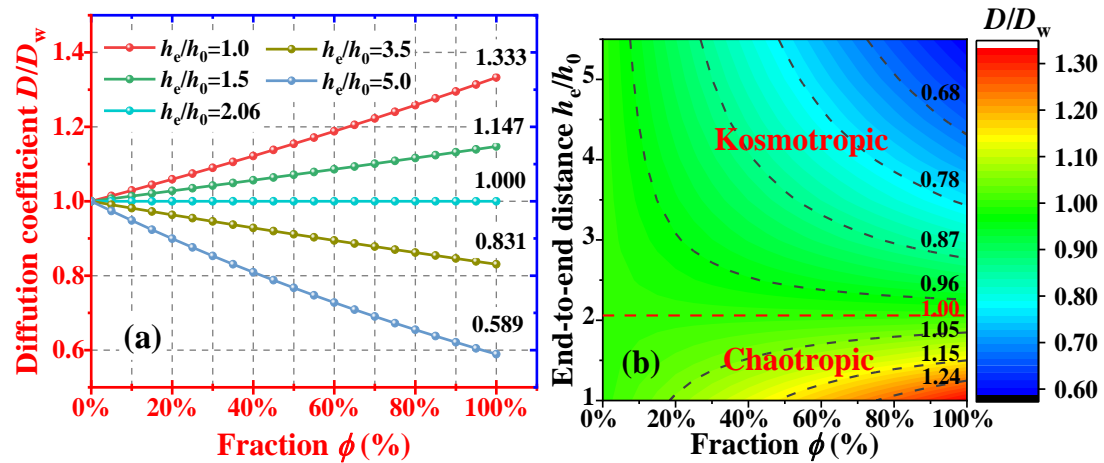


Figure 2. Diffusion coefficient ratio (D/D_w) as functions of the end-to-end distance ratio (h_e/h_0) and volume fraction of ionic water (ϕ). (a) Constitutive relationship between diffusion coefficient ratio (D/D_w) and volume fraction of ionic water (ϕ), at $h_e/h_0 = 1.0, 1.5, 2.06, 3.5$ and 5.0 . (b) 2D heatmap chart of diffusion coefficient ratio (D/D_w) as functions of the end-to-end distance ratio (h_e/h_0) and volume fraction of ionic water (ϕ).

Figure 2(b) plots a 2D heatmap chart for the diffusion coefficient ratio (D/D_w) as functions of the end-to-end distance ratio (h_e/h_0) and volume fraction of ionic water

(ϕ). It is revealed that the diffusion coefficient of electrolyte aqueous solution is essentially determined by volume fraction of the ionic water (ϕ) and the end-to-end distance ratio (h_e/h_0), both of which describe the topological geometries of the condensed ionic water structures. A larger value of h_e determines a lower diffusion coefficient. Under the combined effects of h_e and ϕ , there is a kosmotropic or chaotropic transition of condensed ionic water structure as illustrated in Figure 2(b).

2.2 Free-energy equation

Ionic free energy (F_{ion}) of electrolyte aqueous solution is further incorporated into the conformational free energy (F_{conf}) and electrostatically repulsive free energy (F_{electr}). The relationship among them can be described using [41],

$$\frac{F_{ion}(h_e)}{k_B T} = \frac{F_{conf}(h_e)}{k_B T} + \frac{F_{electr}(h_e)}{k_B T} \quad (5)$$

The conformational free energy of the condensed ionic water is written as [41,42],

$$\frac{F_{conf}(h_e)}{k_B T} \approx \frac{h_e^2}{N b^2} \quad (6)$$

where N is the number of water molecules and $b = \frac{h_0}{N^{1/2}}$ is the length of condensed water structure [42].

The electrostatically repulsive free energy (F_{electr}) of the condensed ionic water can be scaled using [41,42],

$$\frac{F_{electr}(h_e)}{k_B T} \approx \frac{l_B (fN)^2}{h_e} \quad (7)$$

where $f=f_0 c/\phi$ is the charge density, c is the ion concentration, f_0 is a given constant

and $l_B = \frac{e^2}{\epsilon k_B T}$ is the Bjerrum length [41,42]. Here the end-to-end distance (h_e) can

be expressed as [41],

$$\frac{\partial F_{ion}(h_e)}{\partial h_e} = 0 \Rightarrow h_e \approx Nl_B^{1/3} b^{2/3} f^{2/3} \quad (8)$$

By combining equations (6), (7) and (8) into (5), the free energy of the electrolyte aqueous solution (F_{ion}) can be expressed as,

$$\frac{F_{ion}(h_e)}{k_B T} \approx \frac{[Nl_B^{1/3} b^{2/3} (f_0 c / \phi)^{2/3}]^2}{Nb^2} + \frac{l_B^{2/3} (Nf_0 c / \phi)^2}{Nb^{2/3} (f_0 c / \phi)^{2/3}} \quad (9)$$

With respect to the Flory-Huggins model, Staverman-Guggenheim combinatorial term can be applied to describe the entropic contribution to the different sizes and shapes of polyatomic cation and anion solutions, in terms of the two geometrical parameters, i.e., volume and area [43,44]. Based on the Flory-Huggins theory, free energy of mixing (F_{mix}) can be written in the following form [45-47],

$$F_{mix} = k_B T \chi \phi (1 - \phi) \quad (10)$$

where χ is the Flory-Huggins interaction parameter, which is determined by the temperature (T) and volume fraction of ionic water (ϕ) [48],

$$\chi_{mix} = \frac{A}{T} + B\phi + C \quad (11)$$

where A , B and C are the given constants [48].

By inserting equation (10) into (11), the free energy of mixing (F_{mix}) can be obtained as,

$$F_{mix} = k_B T \left(\frac{A}{T} + B\phi + C \right) \phi (1 - \phi) \quad (12)$$

Combining equations (5), (9) and (12), the total free energy (F) of electrolyte aqueous solution can be obtained,

$$\begin{aligned}
F &= F_{conf} + F_{electr} + F_{mix} \\
&\approx \frac{2k_B N^{4/3} l_B^{2/3} f_0^{4/3} c^{4/3} T}{h_0^{2/3} \phi^{1/3}} + k_B T \left(\frac{A}{T} + B\phi + C \right) \phi(1-\phi)
\end{aligned} \tag{13}$$

Finally, a constitutive relationship between volume fraction (ϕ) and ion concentration (c) of electrolyte aqueous solution can be obtained,

$$\frac{\partial F}{\partial \phi} = 0 \Rightarrow \left[\left(\frac{A}{T} + C \right) (1-2\phi) - B(3\phi^2 - 2\phi) \right] \phi^{4/3} = c^{4/3} \tag{14}$$

3. Experimental verifications

3.1 Effect of ion concentration

According to the proposed model based on the equations (4) and (8), the ratio of diffusion coefficient (D/D_w) of an electrolyte aqueous solution can be expressed as,

$$\ln\left(\frac{D}{D_w}\right) = \phi \ln \left[\frac{h_w \ln \left(\frac{N^{2/3} l_B^{1/3} f_0^{2/3} c^{2/3}}{h_0^{1/3} \phi^{2/3}} + \left(\frac{N^{4/3} l_B^{2/3} f_0^{4/3} c^{4/3}}{h_0^{2/3} \phi^{4/3}} - 1 \right)^{1/2} \right)}{\left(h_0^{4/3} N^{4/3} l_B^{2/3} f_0^{4/3} c^{4/3} / \phi^{4/3} - h_0^2 N^2 \right)^{1/2}} \right] + (1-\phi) \tag{15}$$

where η is the viscosity [13] and D_w is the diffusion coefficient of pure water [13,14].

To verify the proposed model of equation (15), the analytical results have been plotted to reveal the effects of ion concentrations (c) on diffusion coefficients of the electrolyte aqueous solutions with NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr and CsI [14]. Analytical results of equation (15) are fitted using the experimental data reported by Müller et al. [14] and the obtained parameters are listed in Table 1. Diffusion coefficient of pure water ($D_w \approx 6.31 \times 10^{-10}$ m²/s) was obtained from Ref. [13,14]. The end-to-end distance of the water structure ($h_w \approx 1.2 \times 10^{-10}$ m) was determined by the D_w . The viscosity ($\eta = 5.62 \times 10^{-4}$ kg/(ms)) of the electrolyte aqueous solution was obtained from Ref. [13]. By numerically fitting equation (15) using the

experimental data reported in Ref. [14], the end-to-end distance (h_0) and number of water molecules (N) were obtained by fitting equation (15) with the experimental data. The Bjerrum length (l_B) and charge density constant (f_0) were determined using the equation of $l_B^{1/2}/f_0 = \frac{e}{k_B^{1/2} T^{1/2} \epsilon^{1/2} f_0}$, where $k_B=1.38 \times 10^{-23}$ J/K is the Boltzmann constant, $e=1.6 \times 10^{-19}$ C is the unit charge, and $\epsilon=40\sim 80$ F/m is the dielectric constant [4]. The parameters A , B and C are given constants at $T=298$ K in equation (11) [48].

Effect of ion concentration (c) was firstly investigated by comparing experimental and analytical obtained results using equation (15), as shown in Figures 3(a), 3(b) and 3(c). It is revealed that these analytical results obtained using the proposed model fit well with the experimental results [14]. Figure 3(d) shows the calculated correlation index R^2 between the analytical and experimental results which are 99.95%, 99.89%, 99.84%, 89.94%, 92.66% , 98.05%, 93.51%, 99.71% and 99.72% for the electrolyte aqueous solutions with NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr and CsI, respectively.

Table 1. Values of parameters used in equation (15) for various electrolyte aqueous solutions.

	NaCl	NaBr	NaI	KCl	KBr	KI	CsCl	CsBr	CsI
h_0/h_w	1.386	1.196	0.919	0.709	0.636	0.534	0.570	0.541	0.481
N	12.04	11.19	10.91	10.19	10.83	10.17	10.55	10.3	9.98
$l_B^{1/2}/f_0$ (cm/s ²)	0.69	0.34	0.17	0.16	0.17	0.12	0.13	0.15	0.12
$A/T+C$	0.74								
B	10.86	10.89	9.75	19.93	9.90	9.80	14.91	10.18	10.12

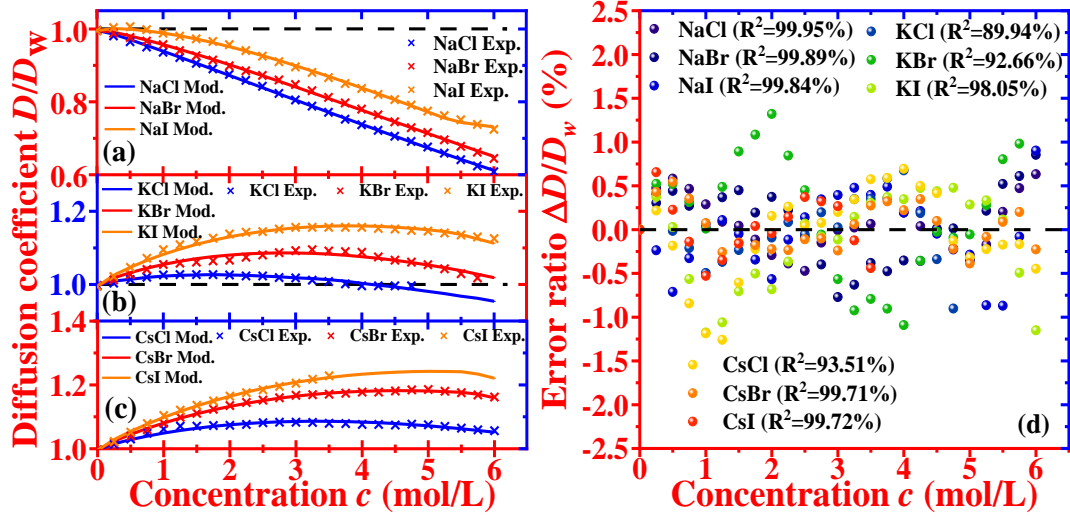


Figure 3. Effect of ion concentration (c) on the diffusion coefficient of the electrolyte aqueous solutions at atmospheric pressure and $T=298$ K. (a) Comparisons between analytical results obtained using equation (15) and the experimental data reported in Ref. [14] for electrolyte aqueous solutions with NaCl, NaBr, NaI, KCl, KBr, KI, CsCl, CsBr and CsI. (d) Divergences of analytical and experimental results of diffusion coefficient ratio (D/D_w).

According to the equation (13), end-to-end distance (h_e), which is used to describe the geometrical size and shape of condensed ionic water structure owing to the existence of conformational free energy (F_{conf}) and electrostatically repulsive free energy (F_{electr}), plays a critical role to determine the ionic free energy (F_{ion}) and total free energy (F) of electrolyte aqueous solution. Figure 4(a) shows the obtained results for the effects of ion concentrations (c) on the end-to-end distances (h_e) of condensed ionic water structures. All the parameters used in the equation (15) are presented in Table 1. As can be seen from the obtained analytical results, the end-to-end distance ratio (h_e/h_w) is gradually increased with an increase in the ion concentration (c). Therefore, the topology geometry of condensed water ionic structure is significantly influenced by the ion concentration (c), which plays an essential role to influence the

end-to-end distance ratio (h_e/h_w) in comparison with that of the pure water.

Figure 4(b) shows the results for the effects of ion concentrations (c) on the diffusion coefficients (D/D_w) of the condensed ionic water structures. With an increase in ion concentration (c), the end-to-end distance ratio (h_e/h_w) is increased, resulting in a decreased diffusion coefficient (D_{ion}) of ions. As presented in equation (9), the ionic free energy (F_{ion}) is gradually increased with an increase in the ion concentration (c), thus resulting in the increase of the geometrical size and shape (h_e/h_0). Therefore, the diffusion coefficient (D/D_w) is decreased because the diffusion of condensed ionic water structure becomes difficult with an increase in the geometrical size and shape (h_e/h_0). That is to say, the diffusion behavior of sphere structure is easier than that of the ellipsoidal structure [32,33].

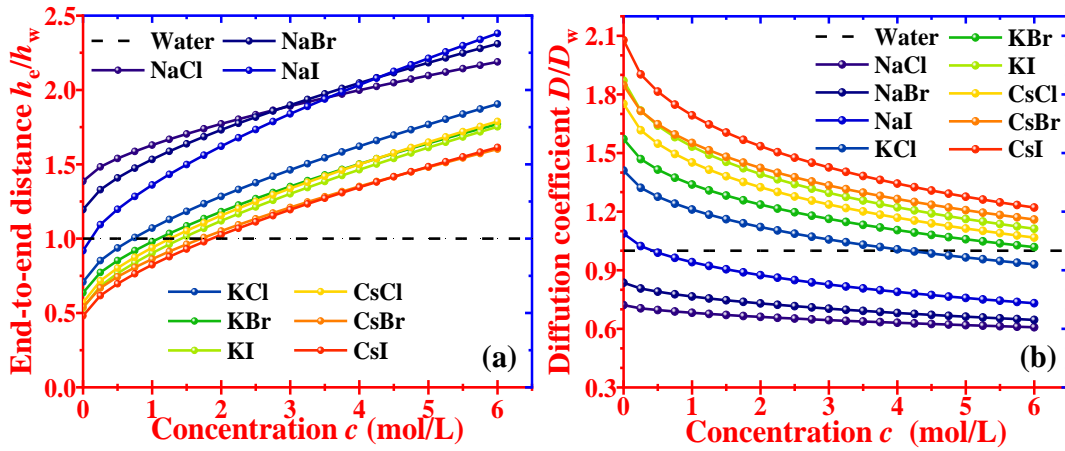


Figure 4. Effect of ion concentration (c) on the end-to-end distance ratio (h_e/h_w) and diffusion coefficient ratio (D/D_w) at atmospheric pressure and $T=298$ K. (a) A constitutive relationship between ion concentration (c) and end-to-end distance ratio (h_e/h_w). (b) A constitutive relationship between ion concentration (c) and diffusion coefficient ratio (D/D_w).

Furthermore, effect of ion concentration (c) on the density of condensed ionic water structure is also investigated, where the density parameter plays a critical role to

determine the viscosity and diffusion coefficient. According to the free volume theory [48], the volume of electrolyte aqueous solution is incorporated in three components, i.e., pure water (V_w), ionic water (V_{ion}) and free volume (V_f), the last of which is used to present the unoccupied space in solution. Thus, the total volume (V) of the electrolyte aqueous solution can be written as,

$$V = V_0 + V_f = \phi V_{ion} + (1 - \phi)V_w + V_f \quad (16)$$

where $V_{ion} = \frac{4}{3}\pi h_e h_0^2$ and $V_w = \frac{4}{3}\pi h_w^3$

According to the Cohen-Turnbull model [49], a constitutive relationship among the diffusion coefficient (D), V_0 and V_f is expressed as,

$$D = D_0 \exp\left(-\alpha \frac{V_0}{V_f}\right) \quad (17)$$

where D_0 is the initial diffusion coefficient and α is the thermal expansion coefficient.

By inserting equation (17) into (16), we can obtain,

$$V/V_w = \left(\phi \frac{h_e}{h_w} + (1 - \phi)\right) \left(1 - \frac{\alpha}{\ln(D/D_w) - \ln(D_0/D_w)}\right) \quad (18)$$

The density of the electrolyte aqueous solution can be further written as

$\rho = \frac{m}{V} = \frac{m_w + m_i}{V}$ [15,22], where m_w and m_i are the masses of pure water and ionic

water, respectively. Here the density of electrolyte aqueous solution is expressed as,

$$\rho = M_i c + \frac{\rho_w V_w}{V} = M_i c + \frac{\rho_w}{\left(\phi \frac{h_e}{h_w} + (1 - \phi)\right) \left(1 - \frac{\alpha}{\ln(D/D_w) - \ln(D_0/D_w)}\right)} \quad (19)$$

where M_i is the mass per mol of ions and ρ_w is the density of pure water.

Meanwhile, the apparent density (ρ_A) of electrolyte aqueous solution is written as

[22],

$$\rho_A = \frac{m_w}{V_w} = \frac{m - m_{ion}}{V - V_{ion}} = \frac{\rho V - M_i c}{V - v_i c} \quad (20)$$

where v_i is the volume per mole of ion. The apparent density (ρ_A) is used to characterize the hydrogen bond strength of ionic water. The higher the value of the apparent density is, the weaker the hydrogen bond strength of the ionic water becomes.

Table 2. Values of parameters used in equation (19) for various electrolyte aqueous solutions.

	NaCl	NaBr	NaI	KCl	KBr	KI	CsCl	CsBr	CsI
α	48.15	34.49	69.57	85.68	76.69	61.98	60.61	68.72	63.52
D_0/D_w	0.033	0.036	0.043	0.063	0.132	0.231	0.162	0.189	0.253

To verify the proposed model based on the equations (19) and (20), a group of experimental data reported in Ref. [15] were employed to compare with the analytical results. The analytical results of density (ρ) and apparent density (ρ_A) as a function of ion concentration (c) are plotted in Figures 5(a) and 5(b), respectively. All the parameters used in the equations (19) and (20) are listed in Table 2. The obtained analytical results reveal that the density (ρ) is gradually increased with an increase in the ion concentration (c), thus resulting in the decreased apparent density (ρ_A). The working principles are originated from the changes of chaotropic and kosmotropic structures in the condensed ionic water [16]. A decrease in the apparent density is corresponding to a larger hydrogen bond length between ionic water molecules. This means that with the introduction of ions and the increase in their concentrations, the end-to-end distance of condensed ionic water structure is decreased to trigger the

chaotropic transition [16].

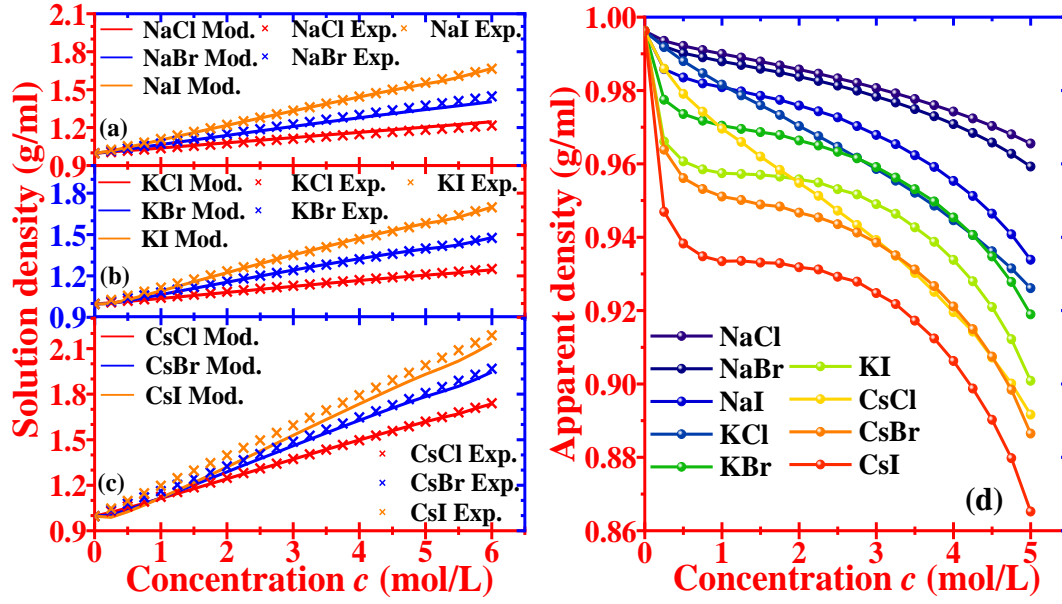


Figure 5. Effect of ion concentration (c) on the density (ρ) and apparent density (ρ_A) of electrolyte aqueous solutions at atmospheric pressure and $T=298$ K. (a) A constitutive relationship between ion concentration (c) and density (ρ). (b) A constitutive relationship between ion concentration (c) and apparent density (ρ_A).

Surface tension (γ) is another key parameter to determine the total free energy (F) of electrolyte aqueous solution. The relationship between the surface tension (γ) and total free energy (F) can be obtained using $dF=\gamma dA$ [50], where the interfacial area (A) is calculated for the condensed water with a sphere structure,

$$dA = \frac{4}{(4/3)^{2/3}} \frac{2}{3} V^{-1/3} dV \quad (21)$$

The surface tension (γ) can be obtained as,

$$\gamma = \frac{dF}{dV} \frac{dV}{dA} \approx V^{1/3} \frac{dF}{dV} \quad (22)$$

Based on the equations (9), (13) and (18), both the free energy (F) and volume (V) can be expressed as a function of the end-to-end distance (h_e), and accordingly, the

term of dF/dV can be rewritten as,

$$\frac{dF}{dV} = \frac{dF}{dh_e} \bigg/ \frac{dV}{dh_e} = \left[\frac{4\phi h_e}{Nb^2} \right] \bigg/ \left[\frac{\phi}{b_w} V_w \left(1 - \frac{\alpha}{\ln(D/D_0)} \right) \right] \quad (23)$$

By inserting equation (23) into (22), the normalized surface tension (γ/γ_w) is obtained as,

$$\frac{\gamma}{\gamma_w} = \left(\frac{V}{V_w} \right)^{1/3} \left(\frac{h_e}{h_w} \right) \left[1 - \frac{\alpha}{\ln(D_w/D_0)} \right] \bigg/ \left[1 - \frac{\alpha}{\ln(D/D_0)} \right] \quad (24)$$

where γ_w represents the surface tension of pure water.

Analytical results using equation (24) are plotted in Figure 6(a), and they are also been compared with the MD simulation ones [12] for the electrolyte aqueous solutions with NaCl, KCl, CsBr and CsI. The corresponding parameters used in the calculation based on the equation (24) are listed in Tables 1 and 2. The analytical results fit well with the MD simulation ones. For the electrolyte aqueous solutions with KCl and NaCl, the normalized surface tensions (γ/γ_w) are gradually increased from 1.000, 1.028 to 1.049, at the same ion concentration of $c=3$ mol/L. Whereas those of the electrolyte aqueous solutions with CsBr and CsI are decreased from 1.000, 0.981 to 0.964. Moreover, the divergences between the analytical and MD simulation results are calculated based on their correlation index (R^2), and the obtained values are 98.30%, 80.02%, 82.34% and 87.08% for the electrolyte aqueous solutions with NaCl, KCl, CsBr and CsI, respectively, as shown in Figure 6(b). These results indicate that a good agreement between the analytical results and MD simulation ones ($|\gamma/\gamma_w| \leq 1.5\%$).

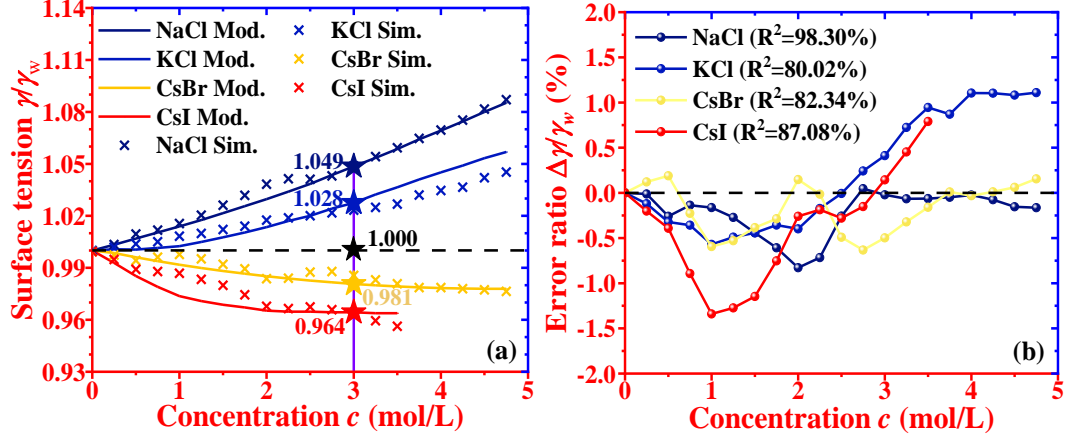


Figure 6. Comparisons between analytical results using equation (24) and MD simulation results [28] for the electrolyte aqueous solutions at atmospheric pressure and $T=298$ K. (a) Surface tensions (γ/γ_w) as a function of ion concentration (c) of electrolyte aqueous solutions with NaCl, KCl, CsBr and CsI. (b) Divergences of the analytical and MD simulation results.

3.2 Thermodynamic diffusion coefficient

Apart from density (ρ) and surface tension (γ) parameters, thermodynamic parameters have also played essential roles to determine the diffusion coefficient (D) of condensed ionic water structure. For example, it is necessary to investigate the effect of temperature on the hydrogen bond strength and conformational free energy (F_{conf}), both of which determine the diffusion behavior and topological geometry of the condensed ionic water structure [13]. A constitutive relationship between the diffusion coefficient (D) and temperature (T) is written as [13],

$$D = D_0 + \frac{k_B T}{6\pi\eta} \exp \left\{ \phi \ln \left[\frac{\ln \left(\frac{N^{\frac{2}{3}} L_B^{\frac{1}{3}} f_0^{\frac{2}{3}} c^{\frac{2}{3}}}{h_0^{\frac{1}{3}} \phi^{\frac{2}{3}}} + \left(\frac{N^{\frac{4}{3}} L_B^{\frac{2}{3}} f_0^{\frac{4}{3}} c^{\frac{4}{3}}}{h_0^{\frac{2}{3}} \phi^{\frac{4}{3}}} - 1 \right)^{\frac{1}{2}} \right)}{\left(\frac{h_0^{\frac{4}{3}} N^{\frac{4}{3}} L_B^{\frac{2}{3}} f_0^{\frac{4}{3}} c^{\frac{4}{3}}}{\phi^{\frac{4}{3}} - h_0^2 N^2} \right)^{\frac{1}{2}}} \right] + (1-\phi) \ln \left(\frac{1}{h_w} \right) \right\} \quad (25)$$

To verify the proposed model of equation (25), the analytical results have been obtained and then compared with the MD simulation results [15], to explore the constitutive relationship between diffusion coefficient (D) and temperature (T) of the electrolyte aqueous solutions. The results are shown in Figures 7(a-e). It is found that the proposed model can well predict the MD simulation results. Moreover, the values of their correlation index (R^2) are 97.79%, 98.60%, 97.45%, 99.06%, 96.76% for 1.4 mol/L CsI, 1.5 mol/L CsI, 1.0 mol/L NaCl, 1.5 mol/L NaCl and 2.9 mol/L NaCl, as shown in Figure 7(f). The error ratios are limited in $\pm 10\%$ approximately, showing a good agreement between the analytical and MD simulation results.

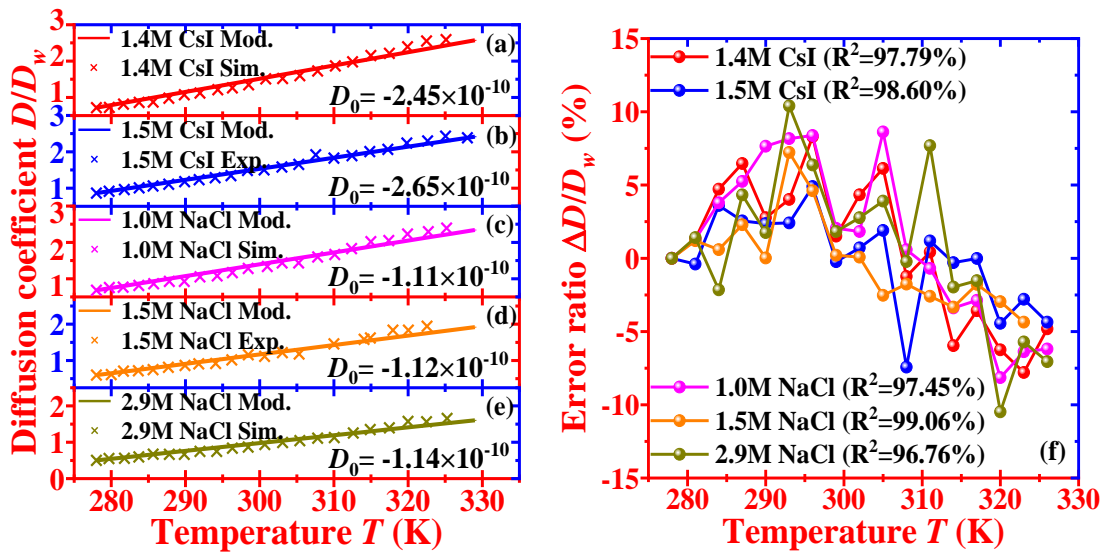


Figure 7. Comparisons between analytical results using equation (25) and MD simulation results [15] for the electrolyte aqueous solutions at atmospheric pressure. (a-e) Diffusion coefficient ratio (D/D_w) as a function of temperature (T) of electrolyte aqueous solutions with 1.4 mol/L CsI, 1.5 mol/L CsI, 1.0 mol/L NaCl, 1.5 mol/L NaCl and 2.9 mol/L NaCl. $D_w \approx 6.02 \times 10^{-9}$ m²/s is the diffusion coefficient of pure water at 278 K. (f) Divergences of the analytical and MD simulation results.

A heatmap of diffusion coefficient ratio (D/D_w) as functions of the ion concentration (c) and temperature (T) for KBr aqueous solution is plotted in Figure 8, in which coupling effect of ion concentration (c) and temperature (T) on the diffusion coefficient ratio (D/D_w) is clearly presented. At the same ion concentration of $c=2.5$ mol/L, the diffusion coefficient ratio (D/D_w) is gradually increased from 1.061, 1.096, 1.135, 1.174, 1.213 to 1.252 with an increased in temperature from 280 K, 290 K, 300 K, 310 K, 320 K to 330 K. The results show that a higher diffusion coefficient ratio (D/D_w) of the condensed water can be achieved at a higher temperature (T).

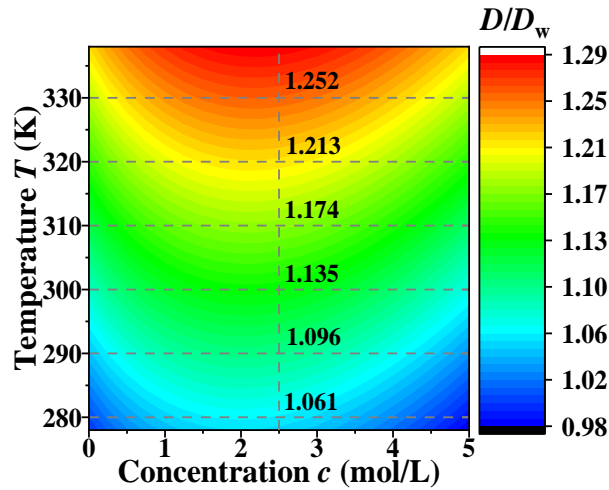


Figure 8. The 2D heatmap chart of diffusion coefficient ratio (D/D_w) for KBr aqueous solution as functions of the ion concentration (c) and temperature (T), at the atmospheric pressure.

4. Conclusion

In this study, a topological geometry strategy has been proposed to investigate the condensed ionic water structures based on the end-to-end distances (h_e/h_0 and h_w) of electrolyte aqueous solutions. Based on the Flory–Huggins theory, a free-energy function is initially formulated to describe the effects of ion concentration (c), density (ρ), apparent density (ρ_A), surface tension (γ) and temperature on the diffusion

coefficient, of which the constitutive relationship using the end-to-end distances (h_e/h_0 and h_w) is obtained based on the extended Stokes-Einstein model. Furthermore, the effects of geometrical end-to-end distance on electrostatic and thermodynamic diffusion behaviors have been explored and discussed for the electrolyte aqueous solutions. A thermodynamic model of diffusion coefficient is formulated to characterize the water structure using parameters of geometrical end-to-end distances (h_e and h_0). The functions of salts are considered in analysis, and their ionic bond strengths are associated with the “structure-making” and “structure-breaking” in the electrolyte aqueous solutions. The analytical and experimental results reveal that the diffusion coefficients are in an order of $\text{NaCl} > \text{NaBr} > \text{NaI} > \text{KCl} > \text{KBr} > \text{CsCl} > \text{CsBr} > \text{KI} > \text{CsI}$, which is attributed to the increased local structure of end-to-end distance (h_e). Meanwhile, the end-to-end distance (h_0) has been used to describe the ionic water structure from a sphere shape into an ellipsoidal one, whose geometrical shapes are governed by the non-Euclidean geometry model. Analytical results reveal that the diffusion coefficient is decreased with the increases of end-to-end distance (h_e) and end-to-end distance ratio (h_e/h_0). Finally, effectiveness of the proposed model is verified using both MD simulations and experimental results reported in literature, and good agreements of analytical, simulation and experimental results have been achieved.

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