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Shimizu, Seishi orcid.org/0000-0002-7853-1683 and Matubayasi, Nobuyuki (2018) Ion hydration::Linking self-diffusion and reorientational motion to water structure. Physical Chemistry Chemical Physics. pp. 5909-5917. ISSN 1463-9084

https://doi.org/10.1039/c7cp07309g

Ion hydration: Linking self-diffusion and reorientational motion to water structure

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ABBREVIATIONS

KB, Kirkwood-Buff; TS: transition state; TST, transition state theory; EJ, extended jump; EJM, extended jump model

ABSTRACT

Ions affect water's self-diffusion and relaxation. Such ion-induced changes of water dynamics have long been rationalized in terms of the change of water structure around the ions. The aim of this paper is to establish a link between dynamics and the "water structure" on the basis of the extended jump (EJ) model for the reorientational motion of water, Eyring's transition state theory of the self-diffusion of water, and the statistical thermodynamic preferential solvation theory developed from the Kirkwood-Buff (KB) theory. Through the synthesis of the above three, we formulate a scheme to correlate the ion-induced water dynamics changes to the water structure. With this new formulation, it is shown that chaotropic or negatively hydrated ions preferentially bind the transition state of water motion thereby stabilizing the transition state, whereas the exclusion of kosmotropes or positively hydrated ions suppresses the formation of the transition state. The ion effects on water dynamics are thus analyzed in a unified manner in terms of KB integrals, which represent the (averaged) "structures" of water.

1. Introduction

The dynamics of water (such as self-diffusion, reorientational motion and viscosity) is affected strongly by the presence of ions.[1–17] This observation has long been rationalized by the change in the hydrogen bond network of water (commonly referred to as "water structure") induced by ions.[1–17] However, this presumed link between the dynamics and structure of water has long remained intuitive and purely speculative;[8,11] there was no consensus with regards to which distribution function or which of the well-defined quantities in statistical thermodynamics is referred to by this "water structure".[1–17]

Here we aim to fill this gap between the structure and dynamics of water by virtue of the following advancements:

- The extended jump model (EJM) of water dynamics,[18–22] which identified the structural basis of water dynamics as large-amplitude angular-jump that takes place when a water OH group trades HB acceptors.[18–22] The presence of ions affect this extended jump (EJ) process.[21,22]
- The transition state (TS) theory by Eyring and coworkers, which attributed the self-diffusion of water, as well as the effect of ions thereupon, to the activation process connecting two basins.[23,24]
- The rigorous Kirkwood-Buff (KB) theory of preferential solvation,[25–38] which has made it possible to evaluate solute-cosolvent and solute-solvent interactions from experimental data alone.[25–38]

Consequently, the effect of ions on water dynamics, through the transition state (TS) theory,[23,24] can be translated into the change of activation free energy in the presence of ions, which, in turn, be converted through the KB theory into the TS-water and TS-ion interactions.[25–38] (Note that the TS here does not refer to any distinct chemical species. Rather it is an unstable state of a water molecule, which is identified by its mode of interaction with the surroundings.[21–24]) The combination of KB with EJM or Eyring's classical treatment thus leads to the rationalisation of ion-induced water dynamics change based upon the ion-water and ion-TS interactions, which will be demonstrated in this paper.

Based upon this theoretical approach, we will re-examine the following classical hypotheses on the effect of salts on the dynamics of water.

(1) **"Positive hydration" and "negative hydration" of Samoilov.**[4,6,7,11,12] Self-diffusion coefficient of water is reduced in the presence of ions by "positive hydration", i.e., the reduced mobility of water around ions; self-diffusion is enhanced by "negative hydration", i.e., enhanced mobility of water around ions.

(2) "**Kosmotropes" and "Chaotropes".**[3,5–17] Kosmotropic ions enhance the water structure, namely the hydrogen bond network of water around them, making the water molecules less mobile, thereby reducing water dynamics;[6,7,11,12] chaotropic ions break the water structure, i.e., the hydrogen bond network of water around them, increasing the mobility, hence dynamics, of water molecules.[6,7,11,12]

In the present work, we express the water structure in terms of the KB integrals and correlate them to the ion-induced changes of water dynamics. Since the KB integral is defined as integrated molecular distribution function over the whole space,[25–38] it is accessible from molecular simulations, and serves further as a basis for bridging between the intermolecular interactions on a microscopic scale and observable effects on a laboratory scale. However, the chief aim of our theory is to explain and quantify, directly from experimental data, how ions affect the dynamics of water, rather than to help analyze molecular dynamics simulations. Through extensive molecular dynamics simulations, Laage, Hynes and coworkers have already provided a strong support for the applicability of the transition-state theory to the dynamics of water around ions.[18–22] Building on such support from simulation, our theory aims to clarify the structural basis of ion hydration dynamics, facing directly to experiments.

2. A Kirkwood-Buff transition state theory

Consider a solution which consists of water and solute molecules. Following our previous papers,[26,27] we adopt the following indexing scheme: $i = 1$ for water, $i = 2$ for solute. Let us now focus on one water molecule, and consider its change from its equilibrium state (indexed as $i = 1$) to the transition state (indexed as $i = t$), just like a chemical reaction.[18–24] Such a treatment of water dynamics, which was pioneered by Eyring,[23] has been adopted by EJM.[18–22]

Let $\Delta\mu^{\ddagger}$ be the activation free energy, namely the change of Gibbs free energy which accompanies the move of a water molecule from its equilibrium state to the transition state. Let us now apply the KB theory of preferential solvation,[25–38] so that $\Delta\mu^{\ddagger}$ can be linked to the structure of aqueous solution. $\Delta\mu^{\ddagger}$ is in fact the difference in pseudo chemical potential between $i = t$ and

$i = 1$. Consequently, the following relationship on the solute concentration (n_2) dependence arise from the KB theory:[25–38]

$$\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial n_2}\right)_{T,P;n_2\to 0} = -RT(\Delta\mathrm{G}_2 - \Delta\mathrm{G}_1) \tag{1}$$

where R is the gas constant, T is the temperature, and

$$\Delta G_j = G_{tj} - G_{1j} \tag{2}$$

is the change of the KB integral, which accompanies the move of an equilibrium water molecule to the transition state. At each state ($i = 1$ or t), G_{ij} represents the KB integral between the species i and j, defined as[25–38]

$$G_{ij} = \int dr\, 4\pi r^2 \left[g_{ij}(r) - 1\right] \tag{3}$$

where $g_{ij}(r)$ is the radial distribution function between the i and j at the separation r. The KB integral, as is clear from Eq. (3), signifies the overall increment of the concentration of j around i from its bulk value The change of solution structure that accompanies the reaction can therefore be captured quantitatively through the KB integrals. The classical concepts of kosmotropes, chaotropes, positive hydration, and negative hydration will then be founded on KB integrals.

Kosmotropes are known to slow down the dynamics of water (positive hydration).[6–11,39–43] This, according to the TS theory, is achieved by the increase of $\Delta\mu^{\ddagger}$ upon the addition of kosmotropes, i.e., $\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial n_2}\right)_{T,P;n_2\to 0} > 0$. This, according to Eq. (1), corresponds to $\Delta\mathrm{G}_2 < \Delta\mathrm{G}_1$, and hence to $\Delta G_2 < 0$ and $G_{t2} < G_{12}$ (because of $|\Delta G_1| \ll |\Delta G_2|$ as will be shown later in this paper; our argument will be done in terms of ΔG_2 and is valid within an allowance of ΔG_1). This means that the ions bind a water molecule at equilibrium more strongly than a water at the transition state. The unfavourable TS-ion interaction, i.e., the exclusion of ions from TS, is the cause of the slowdown of water dynamics. Taking advantage of the symmetry ($G_{ij} = G_{ij}$), $G_{2t} < G_{21}$ also means that the equilibrium water molecules tend to accumulate around the ion more than the water at TS.

Chaotropes,[6–11,39–43] on the other hand, accelerate the dynamics of water (negative hydration) by lowering $\Delta\mu^{\ddagger}$, namely $\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial n_2}\right)_{T,P;n_2\to 0} < 0$. This, according to Eq. (1) and the small magnitude of ΔG_1 as will later be shown, means $\Delta G_2 > 0$ and $G_{2t} > G_{21}$. Hence the ions bind the transition state water more strongly than the water at equilibrium state. The favourable TS-ion interaction is the cause of water dynamic acceleration. Using the symmetry of the KB parameters, $G_{2t} > G_{21}$ also signifies that TS-water tend to accumulate more around the ion than equilibrium water.

What is useful here is that both ΔG_1 and ΔG_2 can be determined from experimental data, when Eq. (1) is supplemented by the activation volume $\Delta V^{\ddagger}$:[25–38]

$$\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial P}\right)_{T,n_2=0} = \Delta V^{\ddagger} = -\Delta \mathrm{G}_1 \qquad (4)$$

ΔG_1 and ΔG_2 can thus be evaluated by solving simultaneous equations (Eqs. (1) and (4)).

It should be emphasized that the “transition state” employed in the present work does not refer to any distinct, chemical species.[18–22] Instead, it is an unstable state of a water molecule, which is identified by its mode of interaction with the surroundings.[18–22] The corresponding statistical quantities, such as the KB integrals, should be understood to involve the “transition state” water molecule defined as above.

3. Water structure and extended jump motion

3.1 A transition state theory approach to the extended jump motion of water

According to EJM, ion-water hydrogen bonding is the crucial factor that affects the EJ time of water.[21,22] This observation will be translated into the distribution of water and ions around the TS by the help of the KB theory.

Here we focus on the reorientation correlation time, τ_2, determined from measurement of the NMR spin-lattice relaxation time T_1.[18–22,39–43] For small molecules, τ_2 decreases when T_1 increases. The relationship between these two quantities are simple for D_2O, unlike the case of H_2O.[39–43] While T_1 of H_2O reflects both the intra- and intermolecular effects in a rather complicated manner, the following relationship holds for D_2O: [39–43]

$$\frac{1}{T_1} = \frac{3\pi^2}{2}(\mathrm{QCC})^2\tau_2 \tag{5}$$

where QCC is the quadrupolar coupling constant, which can be considered invariant as far as aqueous solutions are concerned. Thus, in the following, we will focus on the τ_2 of D_2O in a variety of aqueous electrolyte solutions, and analyse the NMR "B coefficient" introduced as[18–22,39–43]

$$\frac{\tau_2}{\tau_2^0} = 1 + B_{NMR}n_2 \tag{6}$$

where τ_2^0 is τ_2 in the absence of solutes ($n_2 = 0$). Note that B_{NMR}, i.e., the coefficients for the first-order dependence on the concentration, have been determined from τ_2 measurements over the dilute ionic concentration range and pertaining to the gradient at infinite dilution. This means that they do not contain the effect of ion-ion correlation, including the overlap of hydration shells that belong to different ions; the lack of the overlap has been the foundation for the calculation of the widely-available individual ionic B_{NMR} parameters.[8,11]

Let us now formulate a TST for the NMR B coefficient. Following Laage and Hynes,[18–22] we apply TST to analyse the solute concentration dependence of the relaxation time. In the absence of solutes, τ_2^0 of $\mathrm{D_2O}$ has the following TST expression:[18–23]

$$\frac{1}{\tau_2^0} = \frac{kT}{h} e^{-\frac{\Delta\mu^{\ddagger 0}}{kT}} \tag{7}$$

where k is the Boltzmann constant and h is the Planck constant. When the solute molecules are introduced into the system, it affects τ_2 not only though the change of activation free energy $\Delta\mu^{\ddagger}$ but also through the steric restriction on the jump direction. Hence Eq. (7) in the presence of the solute is expressed as[18–22]

$$\frac{1}{\tau_2} = \frac{kT}{h} f(n_2) e^{-\frac{\Delta\mu^{\ddagger}}{kT}} \tag{8}$$

where $f(n_2)$ is the contribution of steric exclusion, whose mathematical form will be determined below. (Note, first of all, that $f(n_2) = 1$ at $n_2 = 0$ so that Eq. (8) reduces to Eq. (7) at this limit.)

An approximate expression for $f(n_2)$ can be derived based upon a simple geometric argument on the restriction of possible jump direction in the vicinity of solute molecules (Appendix A). In the absence of the solute, there is no restriction to water's possible jump direction; the solid angle available for the jump is therefore 4π. When the water molecule is located in the first coordination shell of $g_{21}(r)$, the possible jump direction is geometrically restricted. Since $g_{21}(r)$ exhibits a sharp peak at the water-ion contact distance, here we consider that a solute affects the angular jump direction of N_h water molecules (=solute hydration number) at water-solute contact distance R_{21}.

Appendix A shows that the solid angle available for hydrating water molecules is $2\pi\left(1+\frac{R_{11}}{2R_{21}}\right)$, where R_{11} is the nearest-neighbor distance between two water molecules. In this setup, $f(n_2)$ can be approximated as the average solid angle fraction available for a water molecule and is given at $n_2 \to 0$ as

$$f(n_2) = \frac{(n_1 - n_2 N_h) + n_2 N_h\left(\frac{1}{2}+\frac{R_{11}}{4R_{21}}\right)}{n_1} \simeq 1 + \frac{n_2 N_h V_1^0}{4}\left(\frac{R_{11}}{R_{21}} - 2\right) \tag{9}$$

where n_1 is the molar concentration of water and V_1^0 is the partial molar volume of pure water.

We emphasize here the geometrical restriction, quantified by Eq. (9), contributes to slow down the jump motion in an entropic manner by limiting the available space for the hydrogen bond jump motion due to the presence of the ion. This explains why there is EJ slow down for weakly-hydrated ions. Eq. (9) is thus crucial for determining the free energy of activation $\Delta\mu^{\ddagger}$.

3.2 KB theory of NMR B coefficient (extended jump motion)

Here we aim is to evaluate the changes in the KB integrals that accompanies the formation of the extended-jump transition state. To this end, we apply Eqs. (1) and (4) to the extended jump model of water, as has been reformulated in the framework of the transition state theory (Section 3.1).

n_2 dependence. NMR B coefficient can be linked to the KB theory (Eq. (2)). Combining Eqs. (1), (7), (8), and (9), we obtain

$$\frac{1}{RT}\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial n_2}\right)_{T,P;n_2\to 0} = -(\Delta \mathrm{G}_2 - \Delta \mathrm{G}_1) = B_{NMR} + \frac{N_h V_1^0}{4}\left(\frac{R_{11}}{R_{21}} - 2\right) \tag{10}$$

***P* dependence.** In order to calculate ΔG_1, we need the pressure-dependence of $\Delta\mu^{\ddagger}$ in the absence of solutes. A straightforward application of Eqs. (4) and (7) yields

$$\Delta G_1 = -\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial P}\right)_{T,N_2=0} = RT\left(\frac{\partial \ln\frac{1}{\tau_2^0}}{\partial P}\right)_T = -RT\left(\frac{\partial \ln\frac{1}{T_1^0}}{\partial P}\right)_T \tag{11}$$

Using the data of Jonas et al. at 30 °C,we obtain $RT\left(\frac{\partial \ln\frac{1}{T_1^0}}{\partial P}\right)_T \simeq 2.45$ cm^3 mol^{-1}.[40] As will be shown in the following, this value is much smaller than the NMR B coefficient, which should therefore be neglected.

KB theory of the extended jump motion. KB integral changes that accompany the extended jump motion of water can be summarized in the following manner:

$$\Delta G_1 \simeq 0 \tag{12}$$

$$\Delta \mathrm{G}_2 = -B_{NMR} - \frac{N_h V_1^0}{4}\left(\frac{R_{11}}{R_{21}} - 2\right) \tag{13}$$

Here, as shown in Table 1, the second term of Eq. (13) can be evaluated for each ion through the ionic radius and the hydration number estimated from scattering experiments. B_{NMR} has been calculated from the salt concentration dependence of T_1 measured by Müller and Hertz.[43] As shown in Table 2, $\frac{N_h V_1^0}{4}\left(2 - \frac{R_{11}}{R_{21}}\right)$ for salts can be calculated from the sum of individual ionic values tabulated in Table 1.[44–46] The resultant $\Delta\mathrm{G}_2$ based upon such experimental data[43–48] are summarized in Table 2.

3.3 A KB perspective on the extended jump time and water-ion interaction

Here we aim to clarify how, on a molecular scale, ions affect the extended jump time. This can be achieved by translating the observation of Laage and Hynes,[20,22] that there is a correlation between extended jump rate and ion-water interaction, into the language of the KB theory.[25–38]

In the framework of KB-TST, the fundamental relationship for the solute-induced change of EJ rate is Eq. (1), which employs the activation free energy. Consequently, what we seek here is an expression analogous to Eq. (1), which involves the ion-water interaction. The following formula, derived in Appendix B, fits the bill:

$$\left(\frac{\partial \mu_1^*}{\partial n_2}\right)_{T,P;n_2\to 0} = -RT(G_{21} - G_{11}) \tag{14}$$

where μ_1^* is the pseudo chemical potential of water, which expresses the binding free energy of water to the aqueous solution and can be obtained from the vapour pressure of water.

Thus, KB-TST transforms the parallel between the EJ time and the ion-water binding proposed by EJM[21,22] into the parallel between μ_1^* (binding free energy of water) and $\Delta\mu_1^\ddagger$ (activation free energy). This, by virtue of Eqs. (10) and (14), can further be converted to a correlation between $\Delta G_2 - \Delta G_1 \approx \Delta G_2$ and $G_{21} - G_{11}$. The former has been evaluated in Table 2; the latter can be obtained directly from partial molar volumes (V_i, of species i) data[45,47,48] thanks to the following rigorous relationship derived in Appendix B:

$$G_{12} - G_{11} = V_1 - V_2 \tag{15}$$

In Table 2, V_2^0 is the value of V_2 at infinite dilution and its value for each solute has been taken from literatures and summarized. Note that V_1^0 is simply the molar volume of pure water and is independent of the solute species.

Figure 1 shows that there is a good correlation between $G_{t2} - G_{12}$ and $G_{21} - G_{11}$. Moreover, the stronger the preferential ion-water interaction (i.e., $G_{21} - G_{11}$ towards positive), the weaker TS-ion interaction compared to water-ion interaction becomes (i.e $G_{t2} - G_{12}$ towards negative). Indeed, when $G_{t2} - G_{12}$ is large and negative, this is driven by a large negative G_{t2}, as is clear from the relatively small magnitude of $G_{21} - G_{11}$. Hence the preferential ion-water interaction drives the exclusion of ions from TS water, suppressing the formation of TS via preferential exclusion, thereby slowing down the relaxation process of water.

The opposite is true when ion-water interaction is weaker than water-water (i.e., $G_{21} - G_{11}$ towards negative), when TS-ion interaction is stronger compared to water-ion interaction ($G_{t2} - G_{12}$ towards positive). In this case, the ions bind stronger to TS water than to the bulk water, hence the presence of ions promote the formation of TS, thereby facilitating the relaxation of water.

$G_{21} - G_{11}$ corresponds to the ion-induced change of the fugacity of water at the equilibrium state, while $G_{t2} - G_{12}$ refers to the difference in the ion interaction between TS and equilibrium water. TS is involved only in the latter, and it is thus not assured *a priori* that $G_{21} - G_{11}$ correlates to $G_{t2} - G_{12}$ and that one is zero when the other vanishes. What is noteworthy here is that the ion-water hydrogen bonding, the driving force identified by EJM,[21,22] has now been correlated through KB-TST with the preferential ion-water interaction in the language of statistical thermodynamics (Eq. (15)). We have thus shown that the preferential ion-water interaction is the major factor influencing the dynamics of water.

4. Self-diffusion coefficients of water

4.1 The diffusion B coefficient and the transition state theory

Here the importance of preferential ion-water interaction is underscored further by the ion-induced changes in the self-diffusion coefficients of water, D. The aim is to interpret on a microscopic scale the following ion concentration n_2 dependence of D

$$\frac{D}{D_0} = 1 + B_D n_2 \tag{16}$$

where B_D is referred to as the diffusion B coefficient and D_0 is D at $n_2 = 0$ (pure water).[6–8,11]

Here we establish a relationship between B_D and Eq. (1). To do so, let us employ the following TST-expression which links the self-diffusion coefficient of pure water D_0 to the activation free energy $\Delta\mu^{\ddagger 0}$:

$$D_0 = \lambda_0^2 \frac{kT}{hN_A}\ e^{-\frac{\Delta\mu^{\ddagger 0}}{RT}} \tag{17}$$

where λ_0 is the distance between two equilibrium positions of water and N_A is the Avogadro constant.[23] In the presence of dilute ions, this expression can be modified into the following form[23]

$$D = \lambda^2 \frac{kT}{hN_A}\ e^{-\frac{\Delta\mu^{\ddagger}}{RT}} \tag{18}$$

where λ and $\Delta\mu^{\ddagger}$ are the values in the presence of salts.

To obtain B_D, the following simple relationship between λ and λ_0, which has been derived by Eyring and coworkers (through a consideration of the volume change upon introducing a solute), will be crucial:[23]

$$\left(\frac{\lambda}{\lambda_0}\right)^2 = \left(\frac{V_0+N_2V_2}{V_0}\right)^{\frac{2}{3}} = (1+n_2V_2^0)^{\frac{2}{3}} \approx 1+\frac{2}{3}n_2V_2^0 \tag{19}$$

where V_2^0 is the partial molar volume of salt at infinite dilution and N_2 is the number of solute molecules. Using Eqs. (16)-(19), we obtain the following classical relationship between the solute-induced change of transition free energy and of the diffusion coefficient:

$$\Delta\mu^{\ddagger} - \Delta\mu^{\ddagger 0} \approx -RT\ln\frac{D}{D_0} + \frac{2}{3}RTn_2V_2^0 \tag{20}$$

Eq. (19) can be rewritten in the following form analogous to Eq. (10):

$$\left(\frac{\partial\Delta\mu^{\ddagger}}{\partial n_2}\right)_{T,P;n_2\to 0} = -RT\left(B_D - \frac{2}{3}V_2^0\right) \tag{21}$$

4.2 Self-diffusion coefficient and the KB theory

Here we obtain the KB integrals for the formation of the transition states, ΔG_{t1} and ΔG_{t2}, based upon the transition state theory of diffusion developed in the previous subsection.

As was the case in Section 3, as well as in our previous work,[25–30] Eq. (21) can be closed with the pressure dependence of D. Let us express the hydrostatic pressure dependence of D in the following simple manner:

$$\frac{D(P)}{D(P_0)} = 1 + \delta_{\mathrm{P}}(P-P_0) \tag{22}$$

Under pressure, λ also changes with pressure, which, in the framework of TST, can be expressed in the following way:

$$\left(\frac{\lambda(P)}{\lambda(P_0)}\right)^2 = \left[\frac{V(P_0)+\left(\frac{\partial V}{\partial P}\right)_T(P-P_0)}{V(P_0)}\right]^{\frac{2}{3}} = [1-\kappa_T(P-P_0)]^{\frac{2}{3}} \tag{23}$$

where $\kappa_T \equiv \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is the isothermal compressibility of water. Combining Eqs. (17), (18), (22) and (23), we obtain

$$\left(\frac{\partial \Delta\mu^{\ddagger}}{\partial P}\right)_{T,N_2\to 0} = \frac{\partial}{\partial P}\left[-RT\frac{\partial \ln[1+\delta_{\mathrm{P}}(P-P_0)]}{\partial P} + \frac{2}{3}RT\frac{\partial \ln[1-\kappa_T(P-P_0)]}{\partial P}\right] \simeq -RT\delta_{\mathrm{P}} - \frac{2}{3}RT\kappa_T \qquad (24)$$

Using experimental data, $\frac{2}{3}RT\kappa_T$ = 0.75 cm^3 mol^{-1}. $RT\delta_P$ term requires a little more justification. According to Krynicki et al.,[49] D =2.30×10^{-9} m^{2}s^{-1} at P =1×10^6 Pa to D =2.31×10^{-9} m^{2}s^{-1} at P =10^8 Pa. Hence δ_P =4.3×10^{-11} Pa^{-1}, therefore $RT\delta_P$=0.11 cm^3 mol^{-1}. Hence ΔG_1 is negligibly small compared to ΔG_2, as is evident upon inspecting Table 2.

From Eqs. (1), (4), (21), and (24), we obtain

$$\Delta G_1 = RT\delta_{\mathrm{P}} + \frac{2}{3}RT\kappa_T \approx 0 \qquad (25)$$

$$\Delta \mathrm{G}_2 \approx B_D - \frac{2}{3}V_2^0 \qquad (26)$$

Here, as shown in Table 2, the second term of Eq. (26) can be evaluated from partial molar volumes of constituent ions.[45,47,48] B_D has been calculated from NMR-based self-diffusion data by Müller and Hertz.[40] The resultant $\Delta \mathrm{G}_2$ based upon such experimental data are summarized in Table 2.

4.3 Self-diffusion coefficients of water are affected via ion-water interaction

KB-TST analysis presented in Figure 2 and Table 2 lead to the following clarification of how the self-diffusion of water is affected by ions.

"Positive hydration" takes place when kosmotropic ions slow down the dynamics of water.[4,6–11,39–43] This is characterized by large negative diffusion B coefficients, when $B_D - \frac{2}{3}V_2 < 0$ is satisfied. According to Eq. (26), this leads to $\Delta G_2 < 0$; from its definition (Eq. (2)), this means that the ions are more excluded from the transition state of water than from the equilibrium position. As shown in Figure 2, the more negative ΔG_2, the more positive $G_{12} - G_{11}$. According to Eqs. (14) and (15), a positive $G_{12} - G_{11}$ signifies a strong ion-water interaction. Thus we arrive at a molecular basis of positive hydration; a strong ion-water interaction makes the transition state more excluded from ions than from equilibrium water. Thus the exclusion of TS from ions is the key for positive hydration.

"Negative hydration" is when the dynamics of water is accelerated by chaotropic ions, which is characterized by the large positive diffusion B coefficient;[4,6–11,39–43] $B_D - \frac{2}{3}V_2 > 0$, which, according to Eq. (26), means that $\Delta G_2 > 0$. This means that the ions interact more preferentially with the transition state than with water at equilibrium. As seen again in Figure 2, the more positive ΔG_2, the more negative $G_{12} - G_{11}$. According to Eqs. (14) and (15), the negative $G_{12} - G_{11}$ signifies a weak ion-water interaction. Thus the molecular basis of negative hydration is a stronger interaction between the transition state and ion, as compared to ion-water interaction. The formation of transition state is favoured through a preferential interaction with ions.

5. Conclusion

How ion affects the dynamics of water has long been attributed to the change of water structure.[1–17,39–45] Yet due to the lack of a theoretical foundation, the definition of the "water structure" in this context has remained unclear. Here we have shown that statistical thermodynamics can provide a link between water structure and dynamics. In doing so, the crucial step was the incorporation of the extended jump model (EJM) of water reorientation and Eyring's classical treatment,[18–22] which identified the structural elements of the transition state (TS) of water dynamics, which is affected by ion-water binding. The TS here refers to the unstable state of a water molecule specified by its mode of interaction, rather than a distinct chemical species.[18–24] Formulated statistical thermodynamically, a clear correlation was observed between ion-water preferential interaction and the ion effect on the activation free energy.[18–22]

With the help of TST, we have now established a statistical thermodynamic theory based upon the Kirkwood-Buff (KB) theory of solutions,[25–38] which attributes the sign and the magnitude of the ion effect on the activation free energy to ion-TS water interaction. We have thus provided a clear molecular meaning of the B coefficients: preferential TS-ion binding compared to water-ion binding. Therefore the microscopic interpretation of structure making and breaking[4,6–11,39–43] has been established in terms of the preferential interaction between ions and TS water. The difference between chaotropes and kosmotropes,[4,6–11,39–43]as well as positive and negative hydration,[4,6–11,39–43] have now been clarified; chaotrope ions tend to bind preferentially to the TS, whereas kosmotropes are excluded from the TS.

Here a comment on the validity of our approach is in place. The applicability of the preferential binding concept is guaranteed automatically when TST is valid for the extended jump dynamics, namely the quasi-equilibrium treatment of the transition state.[23,50] The KB theory, being a rigorous and exact theory, needs no further assumptions for the calculation of preferential binding – all it requires are the pressure- and ion concentration-dependence of the chemical potential,[25] both of which comes from TST. The applicability of TST to EJ dynamics, in turn, comes from extensive molecular dynamics simulations by Laage, Hynes and coworkers, who have successfully demonstrated that the geometrical restriction due to the presence of ions on the jump motion can be decoupled from EJ dynamics.[18–22] These previous achievements have afforded us to focus on linking dynamics to water structure.

Application of our theory to viscosity B coefficient requires further clarifications on the nature of viscosity transition state, as well as the physical meaning of the viscosity B coefficient.[4,6–11,39–43] This problem will be addressed in a forthcoming publication.

ACKNOWLEDGMENTS

We thank Steven Abbott and Ryosuke Ishizuka for stimulating discussions. This work was supported by the Gen Foundation (S.S.), Grants-in-Aid for Scientific Research (Nos. JP15K13550 and JP26240045) from the Japan Society for the Promotion of Science (N.M.) and by the Elements Strategy Initiative for Catalysts and Batteries and the Post-K Supercomputing Project from the Ministry of Education, Culture, Sports, Science, and Technology (N.M.)

Appendix A

Here we provide necessary geometric information for the derivation of Eq. (9).

Consider an extended jump transition of a water molecule from position A in Figure 3. As we discussed in Section 3, we attribute the solute effect on water dynamics exclusively to the water molecules coordinating the solute. Due to the presence of the solute molecule, and its steric exclusion, there is a limit imposed upon the possible direction of the jump. Let us quantify the prohibited jump by the use of the solid angle. In Figure 3, θ defined therein is the maximum angle of geometrically prohibited jump, which can be expressed as

$$\cos\theta = \frac{R_{11}^2}{2R_{21}R_{11}} = \frac{R_{11}}{2R_{21}} \tag{A1}$$

Hence the solid angle Ω for the available jumps are

$$\Omega = 4\pi - 2\pi(1 - \cos\theta) = 2\pi\left(1 + \frac{R_{11}}{2R_{21}}\right) \tag{A2}$$

Because of steric exclusion, Ω is smaller than 4π. The fraction of possible jumps in the presence of a solute can therefore be given as

$$\frac{2\pi\left(1+\frac{R_{11}}{2R_{21}}\right)}{4\pi} = \frac{1}{2}\left(1 + \frac{R_{11}}{2R_{21}}\right) \tag{A3}$$

Eq. (A3) has been used in defining $f(n_2)$ for Eq. (9).

Note that the condition implicit in Eq. (A2), namely, $\cos\theta = \frac{R_{11}}{2R_{21}} \leq 1$ does not pose any restrictions on the applicability of Eq. (A3). To see this clearly, let r_2 and r_1 be the radius of ion and water, respectively. Since $R_{11} = 2r_1$ and $R_{21} = r_1 + r_2$, $\frac{R_{11}}{2R_{21}} \leq 1$ is equivalent to $r_2 \geq 0$. Hence there is no size restrictions on the validity of Eq. (A3).

Appendix B

Here we derive Eq. (15) using the KB theory. Our goal is to obtain the n_2-coefficient of hydration free energy (pseudochemical potential, μ_1^*),[34] parallel to that for the activation free energy. To do so, let us start from a relationship between μ_1 and μ_1^*,[34]

$$d\mu_1 = d\mu_1^* + kTd\ln n_1, \tag{B1}$$

as well as a result of KB theory,[25–38]

$$\left(\frac{\partial\mu_1}{\partial n_2}\right)_{T,P} = -\frac{RT}{n_1}\frac{1}{1+n_2(G_{22}-G_{21})} \tag{B2}$$

At $n_2 \to 0$, Eq. (B2) becomes:

$$\left(\frac{\partial\mu_1}{\partial n_2}\right)_{T,P;n_2\to 0} \approx -RTV_1^0 \tag{B3}$$

where V_1^0 is the partial molar volume of pure water. Combining (B1) and (B3),

Eq. (B1) can be rewritten as:

$$\left(\frac{\partial\mu_1^*}{\partial n_2}\right)_{T,P;n_2\to 0} = \left(\frac{\partial\mu_1}{\partial n_2}\right)_{T,P;n_2\to 0} - RTV_1^0\left(\frac{\partial n_1}{\partial n_2}\right)_{T,P;n_2\to 0} = -RTV_1^0 - RTV_1^0\left(\frac{\partial n_1}{\partial n_2}\right)_{T,P} \tag{B4}$$

Deriving Eq. (15) from Eq. (B4) requires the use of the following equation:

$$\left(\frac{\partial n_1}{\partial n_2}\right)_{T,P} = -\frac{V_2}{V_1} \tag{B5}$$

Eq. (B5) can be derived straightforwardly from the following relationship under constant T and P:

$$V_1 dn_1 + V_2 dn_2 = 0 \tag{B6}$$

To prove Eq. (B6), let N_i and V be the number of species i molecules and the volume of the system, respectively, such that $n_i = N_i/V$. Using N_i and V explicitly, we can easily show that the l.h.s. of Eq. (B6) can be transformed into the following form:

$$V_1 d\left(\frac{N_1}{V}\right) + V_2 d\left(\frac{N_2}{V}\right) = \frac{V_1 dN_1 + V_2 dN_2}{V} - \frac{(N_1V_1 + N_2V_2)dV}{V^2} \tag{B7}$$

Eq. (B7) can then be shown to be zero using the Gibbs-Duhem equation ($V = N_1V_1 + N_2V_2$), as well as the definition of partial molar volumes ($dV = V_1 dN_1 + V_2 dN_2$). An alternative derivation of Eq. (B5) based on the KB theory has also been reported in the literature.[34]

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Figure 1

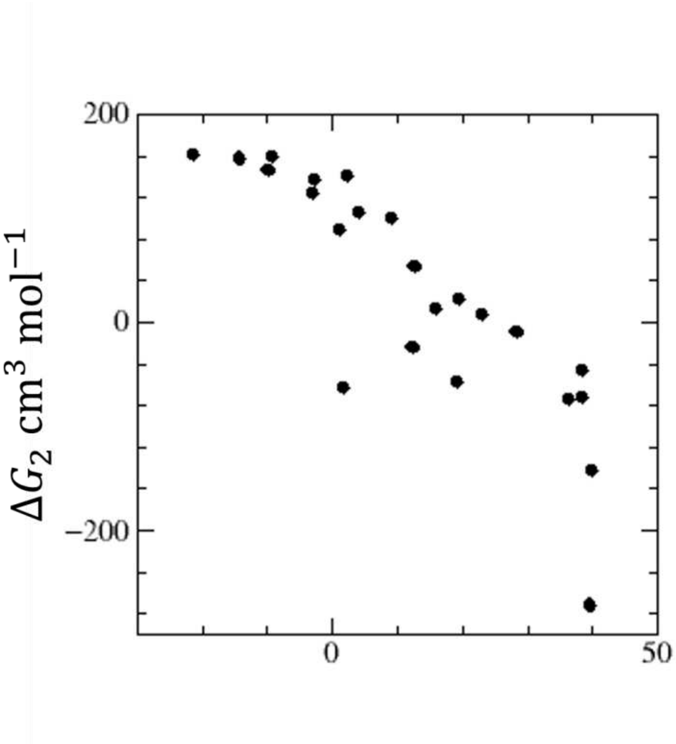

Figure 1. KB integral changes for NMR B coefficient ($\Delta G_2 = G_{t2} - G_{12}$) against preferential ion-water interaction ($G_{21} - G_{11}$). The stronger the ion-water interaction, the more excluded the ion becomes from the transition state, thereby slowing down relaxation. Calculated from experimental data; for procedure, see Tables 1 and 2.

Figure 2

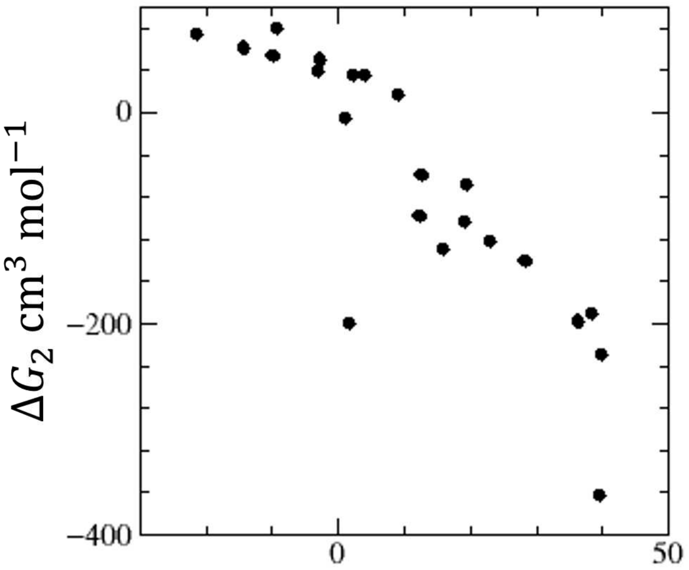

Figure 2. KB integral changes for the self-diffusion coefficient of water ($\Delta G_2 = G_{t2} - G_{12}$) against preferential ion-water interaction ($G_{21} - G_{11}$). The stronger the ion-water interaction, the more excluded the ion becomes from the transition state, thereby slowing down the diffusion process. Calculated from experimental data; for procedure, see Table 3.

Figure 3

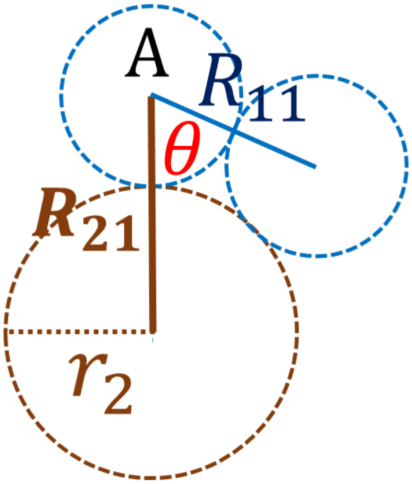

Figure 3. Schematic figure for the estimation of geometrical restriction on extended jump transition of water. (A: original position of water; Blue dotted circles: water molecules; brown dotted circle: ion; θ: maximum angle of geometrically prohibited jump). See Appendix A for discussion.

Tables

Table 1. Literature data on hydration number N_h and ionic radii r_2, derived from diffraction and scattering experiments, for the evaluation of Eq. (13). The radius of the water molecules was set to 0.138 nm.[44]

	N_h	r_2 nm	$\frac{N_h V_1^0}{4}\left(2-\frac{R_{11}}{R_{21}}\right)$ cm^3 mol^{-1}
Li$^+$	6[a]	0.071[a]	18.3
Na$^+$	6[a]	0.097[a]	22.3
K$^+$	6[a]	0.141[a]	27.3
Cs$^+$	7[a]	0.173[a]	35.0
Rb$^+$	8[b]	0.15[b]	37.5
Be^{2+}	4[a]	0.031[a]	6.60
Mg^{2+}	6[a]	0.07[a]	18.2
Ca^{2+}	6[a]	0.103[a]	23.1
Cd^{2+}	6[a]	0.091[a]	21.5
Al^{3+}	6[a]	0.05[a]	14.4
Th^{4+}	9[a]	0.014[a]	7.46
F$^-$	6[a]	0.124[a]	25.6
Cl$^-$	6[a]	0.18[a]	30.6
Br$^-$	6[a]	0.198[a]	31.8
I$^-$	6[a]	0.225[a]	33.5

[a] From Marcus;[44,45] [b] From Mähler and Persson.[46]

Table 2. Calculation of KB integrals for the relaxation dynamics of water in the presence of salts. Unit: $cm^3\ mol^{-1}$

			NMR B coefficient			Self-diffusion	
salts	$V_2^{0\,a}$	G_{21}-G_{11}	$B_{NMR}{}^{b}$	$\frac{N_h V_1^0}{4}\left(\frac{R_{11}}{R_{21}}-2\right)^{c}$	ΔG_2	$B_D{}^{b}$	ΔG_2
KCl	26.8	9.2	-41.8	-57.9	99.7	35.0	17.1
KBr	33.7	2.3	-81.6	-59.1	140.7	57.2	34.7
KI	45.2	-9.2	-98.3	-60.8	159.1	108.9	78.7
RbCl	31.9	4.1	-46.4	-58.7	105.1	56.5	35.2
RbBr	38.8	-2.8	-76.9	-59.9	136.8	76.6	50.8
RbI	50.3	-14.3	-96.6	-61.6	158.2	95.5	62.0
CsCl	39.1	-3.1	-58.8	-65.6	124.4	64.4	38.4
CsBr	46	-10	-79.6	-66.9	146.5	84.6	54.0
CsI	57.5	-21.5	-92.2	-68.5	160.7	112.5	74.2
NaCl	16.6	19.4	30.5	-52.9	22.4	-57.4	-68.4
NaBr	23.5	12.5	0.0	-54.1	54.1	-44.0	-59.6
NaI	35	1.0	-33.6	-55.8	89.4	18.0	-5.4
NaF	-2.4	38.4	94.9	-47.8	-47.0		
LiCl	16.9	19.1	107.0	-48.9	-58.0	-92.7	-103.9
LiBr	23.8	12.2	75.0	-50.2	-24.8	-83.1	-98.9
KF	7.8	28.2	62.4	-52.8	-9.6	-135.6	-140.8
RbF	12.9	23.1	46.9	-53.7	6.8	-113.8	-122.4
CsF	20.1	15.9	48.3	-60.6	12.3	-116.5	-129.9
$CaCl_2$	17.7	36.3	157.7	-84.2	-73.5	-185.5	-197.3
$MgCl_2$	14.4	39.6	350.3	-79.3	-271.0	-352.6	-362.2
$CdCl_2$	15.6	38.4	155.1	-82.6	-72.5	-180.7	-191.1
CdI_2	52.4	1.6	151.9	-88.4	-63.5	-164.4	-199.4
$ZnCl_2$	14	40	222.1	-79.3	-142.8	-220.3	-229.6

[a]Calculated from the individual ionic data compiled by Marcus;[44] [b]Calculated from the experimental data reported by Muller and Hertz;[43] [c]Calculated from the individual ionic values presented in Table 1.

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