D/H and ^{18}O/^{16}O Isotopic Reduced Partition Function Ratios of Water Molecules around a Sodium Ion

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With the final goal set at theoretical elucidation of experimentally observed isotope salt effects, molecular orbital calculations were performed to estimate the D/H and ^{18}O/^{16}O isotopic reduced partition function ratios (RPFRs) of water molecules around a sodium ion. As model water molecules in the *i*th hydration sphere of the sodium ion in sodium ion-bearing aqueous solution, we considered water molecules in the *i*th hydration sphere that were surrounded by water molecules in the (*i*+1)th hydration sphere in clusters, $\mathrm{Na^+(H_2O)}_n$ (n up to 100). The calculations indicated that the ^{18}O/^{16}O RPFR in the primary hydration sphere is slightly smaller than that of bulk water while the D/H RPFR is practically the same as that of bulk water, and that the influence of the existence of the sodium ion is limited to the primary hydration sphere.

Key words: Reduced Partition Function Ratio; Isotope Salt Effects; Sodium Ion; Hydrogen and Oxygen Isotopes.

1. Introduction

Estimation of isotopic reduced partition function ratios (RPFRs) [1] based on molecular orbital (MO) calculations is a useful tool for the elucidation of equilibrium isotope effects that solely depend on the molecular vibration of isotopic species. We demonstrated the effectiveness of the MO approach to understanding boron isotope effects in aqueous media [2 – 4] and lithium isotope effects in aqueous ion exchange systems and in redox systems [5 – 8]. Vapour pressure isotope effects in methyl fluoride were able to be reproduced reasonably well by density functional theory calculations [9]. It was shown that the hydroxide hydrogen atom and hydrogen atoms of water hydrogen-bonded to the hydroxide oxygen atom both tended to be depleted in deuterium relative to hydrogen atoms of bulk (or ‘free’) water [10].

Distribution of isotopic water molecules in vapour and liquid phases has been and still is of great concern in such areas as geochemical studies on the natural isotope fractionation processes of water and isotope separation by distillation techniques. Between pure liquid water and its vapour in equilibrium, the heavier isotopes of oxygen (^{18}O) and hydrogen (D) are both preferentially fractionated into the liquid phase and the lighter ones (^{16}O and H) into the vapour [11, 12]. Even if salt is added to the liquid phase, the direction of the D/H and ^{18}O/^{16}O isotope fractionations does not change, but the degrees of the fractionation change depends on the kind of salt added and its concentration (isotope salt effects) [13 – 16]. To understand and elucidate these experimental results, knowledge on D/H and ^{18}O/^{16}O isotope effects in hydration spheres around solute ions is certainly required.

The sum of forces acting on a hydrogen atom or an oxygen atom of a water molecule forming hydration spheres around a solute ion in aqueous solution may be different from that in bulk water. In relation with isotope effects, this difference will be reflected in the values of the D/H and ^{18}O/^{16}O RPFRs of water, which will cause changes in the degree of isotope fractionation. In the present study, we estimated the D/H and ^{18}O/^{16}O RPFRs of water molecules in hydration spheres around a sodium ion based on the MO calculations as a step towards the satisfactory elucidation of isotope salt effects.

2. Theory and Calculational Method

Based on the theory on the equilibrium isotope effects that solely depend on the difference in the molecular vibrational states between isotopic species, the heavier isotope prefers the species or the position whose RPFR $(s/s')f$ is larger [1]; when two chemical species or two phases are in equilibrium with each other, the heavier isotope tends to be enriched in the species or the phase with a larger RPFR. The general expression of the RPFR is, under Born-Oppenheimer and harmonic oscillator approximations, given as

$$(s/s')f = \prod_{i=1}^{f} \frac{u_i \exp(-u_i/2)/\{1-\exp(-u_i)\}}{u'_i \exp(-u'_i/2)/\{1-\exp(-u'_i)\}}, \quad (1)$$

where $u_i = hc\omega_i/(kT)$ and $u'_i = hc\omega'_i/(kT)$; f is the degree of freedom of molecular vibration, h the Planck constant, c the velocity of light, ω_i and ω'_i are the wave numbers of the ith molecular vibration of the heavier and the lighter isotopic species, respectively, k is the Boltzmann constant, and T the absolute temperature [1].

We considered $Na^+(H_2O)_n$ clusters with n up to 100 as models of sodium ion-bearing aqueous solution. We tried to locate the sodium ion at the center of the cluster as much as possible. In the clusters, a water molecule in the primary hydration sphere (PHS) was defined as the one that directly interacted with the sodium ion through its oxygen atom. A water molecule in the secondary hydration sphere (SHS) was the one hydrogen-bonded to a water molecule in the PHS, and so forth. As model of a water molecule in the PHS in sodium ion-bearing aqueous solution, we considered water molecules in $Na^+(H_2O)_n$ that directly interacted with the sodium ion and were surrounded by (hydrogen-bonded to) water molecules in the SHS. Similarly, as model of the water molecule in the SHS in sodium ion-bearing aqueous solution, we considered water molecules in $Na^+(H_2O)_n$ that were hydrogen-bonded to water molecule(s) in the PHS and surrounded by water molecules in the third hydration sphere (THS), and so forth.

All MO calculations were made at the HF/6-31G(d) level of theory for the consistency with our previous calculations on RPFRs of water clusters, $(H_2O)_n$ with n up to 100, modelling bulk water [17]. The Gaussian 98 and 03 program packages (Gaussian Inc.) were used for the calculations [18], and Gauss View (Gaussian Inc.) and Free Wheel (Butch Software Studio) were used for the graphics. The value of the scale factor for the frequency correction was 0.8985, having been determined by the least-squares method using the observed and calculated frequencies of monomeric H_2O species in the gas phase [19]. We first optimized the structures of the $Na^+(H_2O)_n$ clusters (n = 1 – 10, 12, 16, 20, 24, 28, 32, 36, 40, 44, 50, 56, 62, 70, 80, 90, and 100). No symmetry consideration was made in the geometry optimization calculations: For each of the structures considered, bond lengths, bond angles, and dihedral angles were varied independently to achieve the geometry optimization. Structure optimization was performed sequentially. For example $Na^+(H_2O)_{100}$ was optimized starting from the optimized structure of $Na^+(H_2O)_{90}$ and then ten water molecules setting up around it. At the optimized structure, the vibrational analysis was carried out. The RPFR of a specific hydrogen or oxygen atom was then calculated by using scaled frequencies of the isotopic species. Only the mono isotope substitutions were considered for all the possible combinations of isotopic species with the H and ^{16}O basis. That is, for each of the optimized structures, the RPFRs of the $Na^+[HD^{16}O(H_2{}^{16}O)_{n-1}]/Na^+(H_2{}^{16}O)_n$ and $Na^+[H_2{}^{18}O(H_2{}^{16}O)_{n-1}]/Na^+(H_2{}^{16}O)_n$ isotopic pairs were estimated.

3. Results and Discussion

As an example of the optimized structures of the $Na^+(H_2O)_n$ clusters considered, that of $Na^+(H_2O)_{100}$ is shown in Figure 1. No imaginary frequency was observed in the vibrational analyses of those clusters that were used for the RPFR estimation. Every optimized

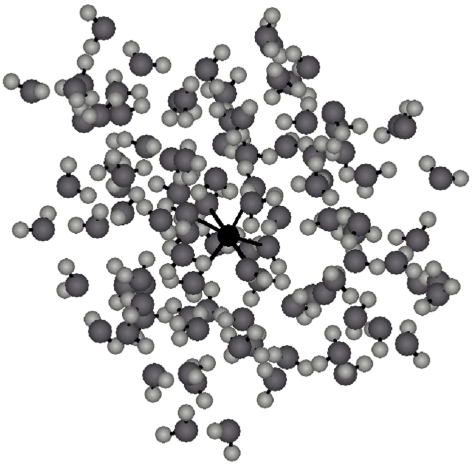

Fig. 1. Optimized structure of $Na^+(H_2O)_{100}$. The black sphere denotes the sodium ion, and the darker and lighter gray spheres denote oxygen and hydrogen atoms, respectively. No meaning is attached to the relative sizes of the spheres. Na-O bonds and O-H covalent bonds are shown with a solid line. Hydrogen bonds are not shown.

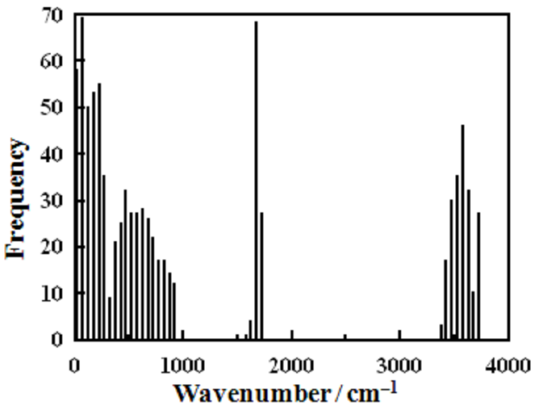

Fig. 2. Frequency distribution of $Na^+(H_2O)_{100}$. The distribution is expressed as a histogram of wavenumber in the step of 50 cm^{-1}.

structure was thus at the global or local minimum of the potential energy surface.

In Figure 2, the frequency distribution of Na^+-$(H_2O)_{100}$ is depicted as a histogram of wavenumber in the step of 50 cm^{-1}. The populations around 3600 and 1700 cm^{-1} are the O-H stretching and H-O-H bending modes of water molecules, respectively, and wavenumbers smaller than 950 cm^{-1} correspond to other vibrational modes including Na-O stretching modes; the Na-O stretching mode of $Na^+(H_2O)$ is calculated at 292 cm^{-1}.

Except for small n values, the hydration number in the PHS around the sodium ion was six, the generally accepted value for the aqueous sodium ion. The oxygen atom of every water molecule in the PHS was directly bonded to the sodium ion with the calculated average Na^+-O bond length of 2.472 Å and hydrogen-bonded to a water molecule in the SHS, and every hydrogen atom in the PHS was also hydrogen-bonded to a water molecule in the SHS. No hydrogen bond was found between water molecules in the PHS. The number of water molecules in the SHS was 18 obtained for the $Na^+(H_2{}^{16}O)_n$ clusters with n equal to or larger than 56.

The logarithms of ^{18}O/^{16}O RPFRs, $\ln(s/s')f(\mathrm{O})$, of oxygen atoms in the PHS and in the SHS at 25 °C are plotted against n in Figure 3. In the figure, the • and ◦ marks denote the average ln(RPFR(O)) values of oxygen atoms in the PHS and in the SHS, respectively, at a given n and the solid line is the $\ln(s/s')f(\mathrm{O})$ value of 0.07376 estimated for bulk water at 25 °C [17]. Water molecules in the PHS surrounded by water molecules in the SHS started appearing at $n = 36$, and likewise water molecules in the SHS surrounded by water molecules in the THS at $n = 62$. As is seen in the figure, the $\ln(s/s')f(\mathrm{O})$ values in the PHS are slightly smaller than the value for the bulk at n equal to 40 or larger, which means that the lighter isotope of oxygen tends to be slightly enriched in the PHS of the sodium ion rather than in the bulk. Taking the average of the averages at $n = 90$ and 100, we estimate the $\ln(s/s')f(\mathrm{O})$ of the oxygen atom in the PHS around an aqueous sodium ion to be 0.07276, by about 1.3 % smaller than the value of bulk water at 25 °C. Contrary to this, Figure 3 shows that the $\ln(s/s')f(\mathrm{O})$

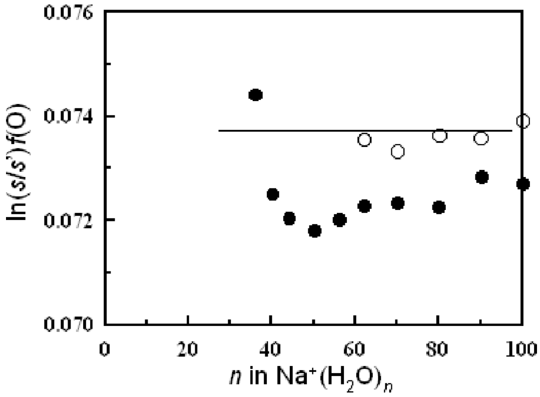

Fig. 3. Plots of average ln(RPFR(O)) at 25 °C against n in $Na^+(H_2O)_n$. The • and ◦ marks denote the average ln(RPFR(O)) values of oxygen atoms in the PHS and in the SHS, respectively. The solid horizontal line denotes the ln(RPFR(O)) value (= 0.07376) estimated for bulk water at 25 °C [17].

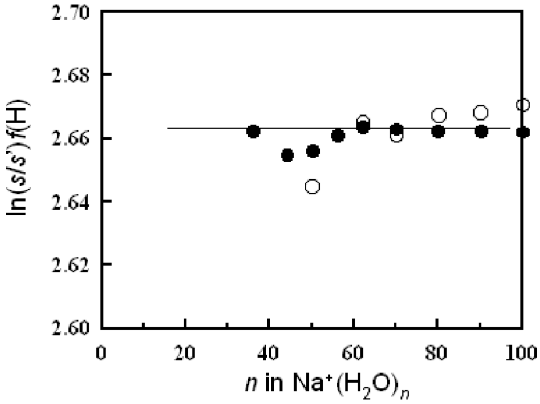

Fig. 4. Plots of average ln(RPFR(H)) at 25 °C against n in $Na^+(H_2O)_n$. The • and ◦ marks denote the average ln(RPFR(O)) values of oxygen atoms in the PHS and in the SHS, respectively. The solid horizontal line denotes the ln(RPFR(O)) value (= 2.66279) estimated for bulk water at 25 °C [17].

value of a water molecule in the SHS (0.07371, calculated using the data at $n = 80$, 90, and 100) is nearly the same as that of bulk water. This indicates that a sodium ion affects only the RPFR of an oxygen atom of a water molecule in the PHS in sodium ion-bearing solution and has little effect on the RPFR of an oxygen atom in the SHS and in the outer spheres.

The logarithms of D/H RPFRs, $\ln(s/s')f(\mathrm{H})$, of hydrogen atoms in the PHS and in the SHS around a sodium ion at 25 °C are plotted against n in Figure 4. In the figure, the • and ○ marks denote the average $\ln(\mathrm{RPFR(H)})$ values of hydrogen atoms in the PHS and in the SHS at a given n, respectively, and the solid line is the $\ln(s/s')f(\mathrm{H})$ value of 2.66279 estimated for bulk water at 25 °C [19]. As is seen in the figure, both the $\ln(s/s')f(\mathrm{H})$ values in the PHS and in the SHS (2.66243 and 2.66630, respectively, both estimated using the data at $n = 62$ through 100) are nearly equal to that of bulk water, which means that the existence of a sodium ion has little effect on the $\ln(s/s')f(\mathrm{H})$ value of water in sodium ion-bearing aqueous solution.

In their femtosecond pump-probe spectroscopic study on the orientational correlation time of water molecules in $Mg(ClO_4)_2$, $NaClO_4$, and Na_2SO_4 solutions, Omta et al. [20] stated that the addition of ions had no influence on the rotational dynamics of water molecules outside the first salvation shells of the ions. Tanaka and Aida [21] reported that the effect of Na^+ orbitals reaches as far as 7 Å in aqueous solution of Na^+ as studied by the MO method with the aid of the quantum mechanical/molecular dynamics method. Although their calculation indicated that the central Na^+ ion exerts its influence on water molecules not only in the PHS but also in the SHS and THS, they also stated that the actual effect of the Na^+ ion on outer spheres is small. Thus, our present results agree with the findings of those studies in terms of the ranges of the influences of cationic species to their hydration spheres.

Although it is beyond the scope of this study to apply the present results to any actual experimental system, they seem to be able to explain experimental results on isotope salt effects in some aspects. First of all, the present calculation showed that the influence of a sodium ion on RPFRs of water molecules in sodium ion-bearing aqueous solutions is limited to water molecules in the PHS. This is consistent with experimental results that isotope salt effects are linearly dependent on molal concentrations of solute ions up to, say, 4 m (mol/kg H_2O) [14, 15]; if the solute ion influences beyond the PHS, isotope salt effects cannot be linear functions of solute concentration up to such a high concentration because of the lack of water molecules. Secondly, the present calculation indicates that the sodium ion influences the RPFR of oxygen atom, while it has little effect on hydrogen RPFR, which is consistent with the statement by Kakiuchi [14] that in aqueous alkali halide solutions, the oxygen isotope effect is mainly caused by the cation species.

4. Conclusions

To summarize the present study, we make the following statements:

A sodium ion slightly reduces the $^{18}O/^{16}O$ RPFR of water molecules directly bonded to it relative to the value of 'bulk' water, whereas it little influences the D/H RPFR of water molecules around it. The influence of the sodium ion is confined only to the primary hydration sphere; the $^{18}O/^{16}O$ RPFR of water molecules in the secondary hydration sphere is practically the same as that of bulk water.

Similar calculations on other cationic species like lithium and potassium ions and anionic species like chloride ion are certainly needed to apply them to the elucidation of the reported isotope salt effects.

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