Oxygen and Hydrogen Isotopic Preference in Hydration Spheres of Chloride and Sulfate Ions

By Takao Oi* and Hiroaki Morimoto

Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan

This paper is dedicated to Professor Hans-Heinrich Limbach on the occasion of his 70th birthday

Molecular orbital calculations were performed to estimate the $^{18}O/^{16}O$ and D/H isotopic reduced partition function ratios (RPFRs) of water molecules around chloride and sulfate ions. $Cl^-(H_2O)_n$ and $SO_4^{2-}(H_2O)_n$ clusters with n up to 120 were considered as models of aqueous solution containing those anions. The calculations indicated that the decreasing order of the ^{18}O preference over ^{16}O in the primary hydration sphere is: (bulk water) $> SO_4^{2-} > Cl^-$. That is, water molecules in the primary hydration spheres of those anions are expected to be depleted in the heavier isotope of oxygen relative to water molecules in bulk, and the degree of the depletion is larger for the chloride ion than for the sulfate ion. Similar tendency was also observed for the isotope preference of hydrogen. No such isotopic preference was observed either for oxygen or for hydrogen in the secondary and outer hydration spheres.

1. Introduction

Between pure liquid water and its vapor 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 vapor. This is called vapor pressure isotope effects (VPIEs) of water [1,2]. Based on the theory of equilibrium isotope effects [3], preferential fractionation of heavier isotopes into the liquid phase occurs because the sum of forces acting on an oxygen atom or a hydrogen atom of a water molecule is larger in the liquid phase than in the vapor phase due to the formation of O···H hydrogen bonds (HBs) in the former phase. When salt is added to the liquid phase, the degrees of the $^{18}O/^{16}O$ and D/H isotope fractionations change depending on the kind of salt added and its concentration (isotope salt effects), although the direction of the fractionations does not change [4–7]. It also sometimes happens that the addition of a salt does not cause

---

* Corresponding author. E-mail: t-ooi@sophia.ac.jp

a substantial isotope salt effect. For instance, the addition of sodium chloride increases the D/H isotopic ratio in the vapor phase relative to that in the case of pure water, but little affects the VPIE of oxygen [8]. To understand and elucidate these experimental results, knowledge on $^{18}O/^{16}O$ and D/H isotope effects in hydration spheres of solute ions is certainly required. The sum of forces acting on an oxygen atom or a hydrogen 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 $^{18}O/^{16}O$ and D/H reduced partition function ratios (RPFRs) of water [3], which will cause changes in the degree of isotope fractionation.

The $^{18}O/^{16}O$ and D/H RPFRs of waters in aqueous solutions can be estimated by molecular orbital (MO) calculations on appropriate model species. In our previous papers [9–11], we reported the estimation of the $^{18}O/^{16}O$ and D/H RPFRs of water molecules in hydration spheres of group 1 metal ions (Li^+, Na^+ and K^+) and group 2 metal ions (Mg^{2+}, Ca^{2+}) based on the MO calculations as a step towards the satisfactory elucidation of isotope salt effects experimentally observed. The calculations indicated that the decreasing order in the $^{18}O/^{16}O$ RPFR value in the primary hydration sphere was: $Mg^{2+} > Ca^{2+} > Li^+$ (> bulk water (the oxygen atom with two HBs)) $> Na^+ > K^+$. Relative to oxygen atoms with two HBs of bulk water molecules, those in primary hydration spheres of Mg^{2+}, Ca^{2+} and Li^+ ions are to be enriched in the ^{18}O and those in primary hydration spheres of Na^+ and K^+ ions are to be slightly depleted in the same isotope. Contrary to the $^{18}O/^{16}O$ RPFR, the presence of those ions has a minimal effect on the RPFR values of hydrogen atoms with a HB in the primary hydration sphere around them. The presence of the Li^+, Na^+, K^+ and Mg^{2+} ions in liquid water has a negligible effect on the hydrogen isotopic preference around those ions, and the lighter isotope of hydrogen may be enriched very slightly around the Ca^{2+} ion.

Similar calculations are certainly required for anionic species for quantitative discussion on isotope salt effects of aqueous solutions. In this paper, we report the results of MO calculations on the $^{18}O/^{16}O$ and D/H RPFRs of water molecules around chloride (Cl^-) and sulfate (SO_4^{2-}) ions.

2. Theory and computational method

When two chemical species containing a common element or two phases of a substance are in equilibrium with each other, the heavier isotope of the element tends to be enriched in the species or the phase with a larger RPFR. The general expression for the RPFR is, under Born-Oppenheimer and harmonic oscillator approximations, given as,

$$(s/s')f = \prod_{i=1}^{p} \frac{u_i \exp(-u_i/2)/\{1 - \exp(-u_i)\}}{u_i' \exp(-u_i'/2)/\{1 - \exp(-u_i')\}} \tag{1}$$

where $u_i = hc\omega_i/(kT)$ and $u_i' = hc\omega_i'/(T)$; p, the degree of freedom of molecular vibration; h, the Planck's constant; c, the velocity of light; ω_i and ω_i', the wave numbers of the ith molecular vibration of the heavier and the lighter isotopic species, respectively; k, the Boltzmann constant; and T, the absolute temperature [3].

As models of Cl^- ion-bearing aqueous solution, we considered $Cl^-(H_2O)_n$ clusters with n up to 120. We tried to locate the Cl^- ion at the center of the cluster as much as

possible. In the clusters, a water molecule in the primary hydration sphere was defined as the one that directly interacted with the Cl^- ion through its hydrogen atom. A water molecule in the secondary hydration sphere was defined as the one hydrogen-bonded to a water molecule in the primary hydration sphere, and so forth. As models of a water molecule in the primary hydration sphere in Cl^- ion-bearing aqueous solutions, we considered water molecules in $Cl^-(H_2O)_n$ that directly interacted with the Cl^- ion and were surrounded by (in most cases, hydrogen-bonded to) water molecules in the secondary hydration sphere. Similarly, as models of the water molecule in the secondary hydration sphere in Cl^- ion-bearing aqueous solutions, we considered water molecules in $Cl^-(H_2O)_n$ that were hydrogen-bonded to water molecule(s) in the primary hydration sphere and surrounded by other water molecules, and so forth.

The procedure to generate models for the SO_4^{2-} ion is the same as that for the Cl^- ion except that a water molecule in the primary hydration sphere was defined as the one that directly interacted with an oxygen atom of the SO_4^{2-} ion through its hydrogen atom.

All MO calculations were made at the HF/6-31G(d) level of theory for the consistency with our previous calculations on water clusters, $(H_2O)_n$ with n up to 100, modeling bulk water [12] and on $M^+(H_2O)_n$ (M = Li, Na, K) and $M^{2+}(H_2O)_n$ (M = Mg, Ca) clusters with n up to 100, modeling groups 1 and 2 metal ion-bearing aqueous solutions [9–11]. The Gaussian 03 and 09 program packages (Gaussian Inc.) were used for the MO calculations [13], and Gauss View (Gaussian Inc.) and Free Wheel (Butch Software Studio) were used for the graphics. The value of the scale factor for the wave number correction was 0.8985, having been determined by the least-squares method using the observed and calculated wave numbers of monomeric H_2O species in the gas phase [14].

Geometry optimization of the $Cl^-(H_2O)_n$ and $SO_4^{2-}(H_2O)_n$ clusters was carried out in a sequential way. For instance, $Cl^-(H_2O)_{100}$ was optimized starting from the optimized structure of $Cl^-(H_2O)_{90}$ and ten water molecules distributed around it. 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. 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 wave numbers of the isotopic species. Only the mono isotope substitutions were considered for all the possible combinations of isotopic species with the ^{16}O and H basis. That is, for each of the optimized structures, the $^{18}O/^{16}O$ RPFRs of the $Cl^-[H_2^{18}O(H_2^{16}O)_{n-1}]/Cl^-(H_2^{16}O)_n$ or $SO_4^{2-}[H_2^{18}O(H_2^{16}O)_{n-1}]/SO_4^{2-}(H_2^{16}O)_n$ isotopic pairs and the D/H RPFRs of $Cl^-[HD^{16}O(H_2^{16}O)_{n-1}]/Cl^-(H_2^{16}O)_n$ or $SO_4^{2-}[HD^{16}O(H_2^{16}O)_{n-1}]/SO_4^{2-}(H_2^{16}O)_n$ isotopic pairs were estimated.

In addition to the calculations above, $^{18}O/^{16}O$ and D/H RPFRs were estimated for some selected $(H_2O)_n$, $Cl^-(H_2O)_n$ and $SO_4^{2-}(H_2O)_n$ clusters at the HF/6-31+G(d) level of theory to examine the validity of the use of the 6-31G(d) basis set in the present series of calculations. Basis sets without diffuse functions are sometimes not appropriate for systems where electrons are relatively far from the nucleus like anions [15]. If the 6-31G(d) basis set is not appropriate for the estimation of RPFRs of water molecules around Cl^- and SO_4^{2-} ions, then the present study may become largely unreliable and at the worst meaningless. The value of the scale factor for the wave number correction

was 0.9003 for the HF/6-31+G(d), determined by the least-squares method using the observed and calculated wave numbers of monomeric H_2O species.

3. Results and discussion

3.1 Optimized structures

As mentioned above, geometry optimization of the $Cl^-(H_2O)_n$ clusters with n up to 120 was carried out, and for every cluster, we tried to locate the Cl^- ion at its center as much as possible. However, we found it difficult to do so, especially for clusters with a small n, since the Cl^- ion tended to move to the surface of the cluster even if we put it at the center in the Gaussian input. For n up to 56, the Cl^- ion was in fact located at the surface of the cluster at its optimized structure; for n equal to 62 to 80, the Cl^- ion was located at the bottom of a "dent" of the cluster, and for n equal to or larger than 90, it was finally surrounded by water molecules on all sides. The tendency for the Cl^- ion to move to the surface of the cluster rather than to stay on the inside of the cluster is most probably ascribable to the fact that a water molecule is stabilized more substantially by the formation of HBs with neighboring water molecules than by the direct interaction with the Cl^- ion. A molecular dynamics simulation on the $Cl^-(H_2O)_n$ also showed that the Cl^- ion is preferentially solvated near the surface of the cluster [16].

Except for small n values, the hydration number in the primary hydration sphere of the Cl^- ion was six or seven, which was within the range of −1.1 to 13.2 reported in the literature [17–19], and seems reasonable. The hydration number of six seems a consensus estimate of the Cl^- ion by experiments but many molecular dynamics (MD) simulations give the hydration number of seven or larger [16]. The hydration number of six or seven was not an intentionally fixed value in the present calculations; they sometimes replaced one another in the process of geometry optimization with increasing cluster size. This is probable because the Cl^-–H bond between the Cl^- ion and the hydrogen atom of a water molecule is not very strong, and consequently, the addition of several water molecules around the optimized $Cl^-(H_2O)_n$ cluster easily changed the hydration structure around the Cl^- ion. For the evaluation of RPFRs, we only used the clusters with the hydration number of seven in the primary hydration sphere.

With a few exceptions, each oxygen atom in the primary hydration sphere of the Cl^- ion has two HBs with water molecules in the secondary hydration sphere. The calculated average distances of shorter and longer $O \cdots H$ HBs were 1.901 and 1.954 Å, respectively. No HB was found between water molecules in the primary hydration sphere. The calculated average distances of shorter and longer HBs in the secondary hydration sphere were 1.871 and 1.914 Å, respectively, and those in the third hydration sphere were 1.874 and 1.932 Å, respectively. The sum of the shorter and longer HB distances of the secondary and third hydration spheres is 3.785 and 3.806 Å, respectively, nearly equivalent to each other but smaller than that of the primary hydration sphere, 3.855 Å. This is reflected in that the $^{18}O/^{16}O$ RPFR value in the primary hydration sphere of the Cl^- ion is smaller than those of the secondary and third hydration spheres (*vide post*).

There are two kinds of hydrogen atom in the primary hydration sphere of the Cl^- ion, one directly bonded to the Cl^- ion and the other hydrogen-bonded to a water

molecule in the secondary hydration sphere. The calculated average distances of Cl^-–H bond and $H\cdots O$ HB were 2.549 and 1.870 Å, respectively. The calculated average HB distance in the secondary and third hydration spheres was 1.899 and 1.914 Å, respectively.

Contrary to the case of the Cl^- ion, it was possible to place the SO_4^{2-} ion at or near the center of the optimized $SO_4^{2-}(H_2O)_n$ clusters. For larger n values, the hydration number in the primary hydration sphere of the SO_4^{2-} ion was eleven; one of the four oxygen atoms of the anion had two O_s–H bonds with O_s denoting an oxygen atom of the SO_4^{2-} ion and each of the remaining three oxygen atoms had three O_s–H bonds. The hydration number of eleven is within the range of 8 to 14 reported in the literature [17,20,21]. With a few exceptions, each oxygen atom of a water molecule in the primary hydration sphere of the SO_4^{2-} ion has two HBs. Contrary to the case of the Cl^- ion, HBs were formed with water molecules not only in the secondary hydration sphere but also in the primary hydration sphere. The calculated average distances of shorter and longer HBs were 1.914 and 1.977 Å, respectively. Those bond distances are slightly longer than the corresponding distances around the Cl^- ion, which indicates that the hydration sphere around the SO_4^{2-} ion is slightly more spacious and roomier than around the Cl^- ion.

There are two kinds of hydrogen atom in the primary hydration sphere of the SO_4^{2-} ion, one directly bonded to an oxygen atom of the SO_4^{2-} ion and the other hydrogen-bonded to a water molecule. The calculated average distances of O_s–H bond and $H\cdots O$ HB were 1.936 and 1.927 Å, respectively. Hydrogen atoms hydrogen-bonded to a water molecule may be further divided into two groups; one hydrogen-bonded to a water molecule in the secondary hydration sphere and the other hydrogen-bonded to a water molecule in the primary hydration sphere. The calculated average $H\cdots O$ HB distance was 1.914 and 1.970 Å for the former and for the latter, respectively.

We were not able to provide information on HB distances in the secondary hydration sphere of the SO_4^{2-} ion since we could not gather a sufficient number of water molecules that were surrounded by water molecules in the third hydration sphere in the optimized $SO_4^{2-}(H_2O)_n$ clusters.

3.2 Correlation of reduced partition function ratios with bond distances

In Fig. 1, the logarithms of $^{18}O/^{16}O$ RPFRs, $\ln(s/s')f(O)$, in the primary hydration sphere of the Cl^- ion at 25 °C are plotted against the sum of the shorter and longer $O\cdots H$ HB distances ($[O\cdots H]_{short}$ and $[O\cdots H]_{long}$) where O is the oxygen atom for which the RPFR was estimated (●). As is seen in the figure, the $\ln(s/s')f(O)$ in the primary hydration sphere of the Cl^- ion is well inversely correlated with the sum of the two HB distances with the correlation coefficient value of -0.871. We made similar plots of the $\ln(s/s')f(O)$ value against the shorter and longer HB distances, but no better correlations were obtained; the correlation coefficient value was -0.821 and -0.759 for the former and for the latter, respectively. The $\ln(s/s')f(O)$ values of oxygen atoms with two HBs in the primary hydration sphere of the Cl^- ion are thus better correlated with the sum of the shorter and longer $O\cdots H$ HBs than with the individuals of the two kinds of HB.
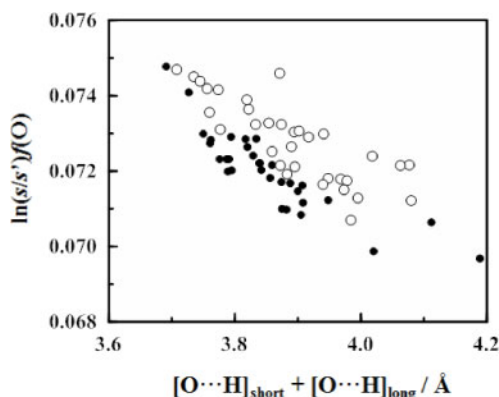
Fig. 1. Plot of the $\ln(s/s')f(O)$ values of oxygen atoms with two HBs in the primary hydration sphere of the Cl^- ion (•) or the SO_4^{2-} ion (○) at 25 °C against the sum of the distances of the shorter and longer $O\cdots H$ HBs ($[O\cdots H]_{short}$ and $[O\cdots H]_{long}$) where O is the oxygen atom for which the RPFR was estimated.
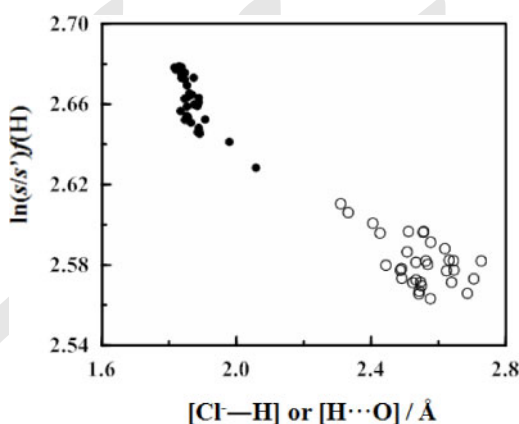

Fig. 2. Plot of the $\ln(s/s')f(H)$ values of hydrogen atoms in the primary hydration sphere of the Cl^- ion at 25 °C against the Cl^-–H bond distance (○) or the $H\cdots O$ HB distance (•) where H is the hydrogen atom for which the RPFR was estimated.

In Fig. 2, the logarithms of D/H rpfrs, $\ln(s/s')f(H)$, in the primary hydration sphere of the Cl^- ion at 25 °C are plotted against the Cl^-–H bond distance (○) or the $H\cdots O$ HB distance (•) where H is the hydrogen atom for which the RPFR was estimated. The correlation coefficient values were -0.556 and -0.768 for the former and the latter correlations, respectively. Thus, the $\ln(s/s')f(H)$ value is moderately inversely correlated with the Cl^-–H bond distance and the HB distance in the primary hydration sphere of the Cl^- ion.

The $\ln(s/s')f(O)$ values in the primary hydration sphere of the SO_4^{2-} ion at 25 °C are plotted against the sum of the shorter and longer $O\cdots H$ HB distances where O is the oxygen atom for which the RPFR was estimated (○) in Fig. 1. As in the case of the Cl^- ion (•), the $\ln(s/s')f(O)$ in the primary hydration sphere of the SO_4^{2-} ion is well in-
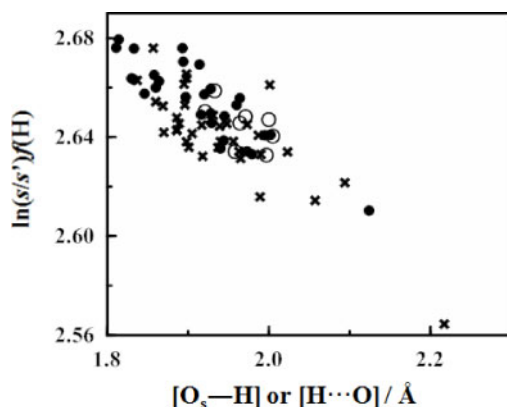
Fig. 3. Plots of $\ln(s/s')f(H)$ values of hydrogen atoms in the primary hydration sphere of the SO_4^{2-} ion at 25 °C against the O_s–H bond distance ($\times$), against the distance of the HB with an oxygen atom in the secondary hydration sphere ($\bullet$) or against the distance of the HB with an oxygen atom in the primary hydration sphere ($\circ$).

versely correlated with the sum of the two HB distances with the correlation coefficient value of -0.814. It is also seen in Fig. 1 that the $\ln(s/s')f(O)$ value is slightly larger with the SO_4^{2-} ion than with the Cl⁻ ion at a given value of $[O \cdots H]_{short} + [O \cdots H]_{long}$.

Three correlations are drawn in Fig. 3. The values of $\ln(s/s')f(H)$ in the primary hydration sphere of the SO_4^{2-} ion at 25 °C are plotted against the O_s–H bond distance ($\times$), against the $H \cdots O$ HB distance where O is an oxygen atom in the secondary hydration sphere ($\bullet$) or against the $H \cdots O$ HB distance where O is an oxygen atom in the primary hydration sphere ($\circ$). There seems no substantial difference among the three correlations with the overall correlation coefficient of -0.816, which indicates that the O_s–H interaction is essentially the same as hydrogen bonding interaction between water molecules ($H \cdots O$). In other words, the O_s–H bond is a HB.

3.3 Reduced partition function ratios

The average values of the $\ln(s/s')f(O)$ of oxygen atoms with two HBs in the primary hydration sphere of the Cl⁻ ion surrounded by water molecules in the secondary hydration sphere at 25 °C are plotted against n in $Cl^-(H_2O)_n$ in Fig. 4 ($\bullet$). Those oxygen atoms started appearing at $n = 28$ in the present calculations. Fluctuation in the $\ln(s/s')f(O)$ value as a function of n is rather large and does not seem to have converged even at $n = 120$. Calculations with $n > 120$ seem necessary to confirm the convergence. The average of the averages at $n = 100$ and 120 is 0.07242. We may tentatively regard this as the $\ln(s/s')f(O)$ value of the oxygen atom with two HBs in the primary hydration sphere of the Cl⁻ ion in aqueous Cl⁻ ion-bearing solutions at 25 °C. This value is smaller by about 1.8% than 0.07376, the solid line in Fig. 4, estimated for bulk water, which indicates that the heavier isotope of oxygen tends to be slightly depleted in the primary hydration sphere of the Cl⁻ ion compared to the bulk.
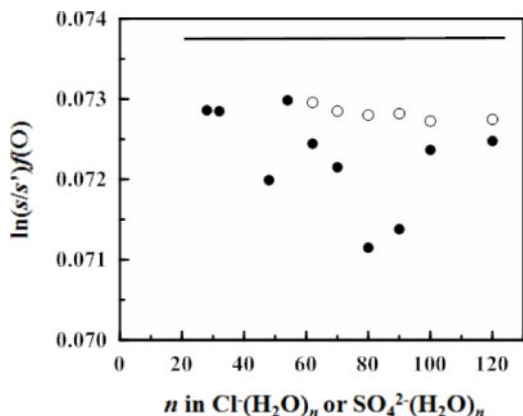
Fig. 4. Plots of the average $\ln(s/s')f(O)$ values of oxygen atoms with two HBs in the primary hydration sphere of the Cl^- ion ($\bullet$) or the SO_4^{2-} ion ($\circ$) at 25 °C against n in $Cl^-(H_2O)_n$ or in $SO_4^{2-}(H_2O)_n$. The solid line represents the $\ln(s/s')f(O)$ value of 0.07376 estimated for an oxygen atom with two hydrogen bonds in bulk water at 25 °C [12].

Fig. 5. Plots of the average $\ln(s/s')f(O)$ values of oxygen atoms with two HBs in the primary ($\bullet$), secondary ($\circ$) and third ($\times$) hydration spheres of the Cl^- ion at 25 °C against n in $Cl^-(H_2O)_n$. The solid line represents the $\ln(s/s')f(O)$ value of 0.07376 estimated for an oxygen atom with two hydrogen bonds in bulk water at 25 °C [12].
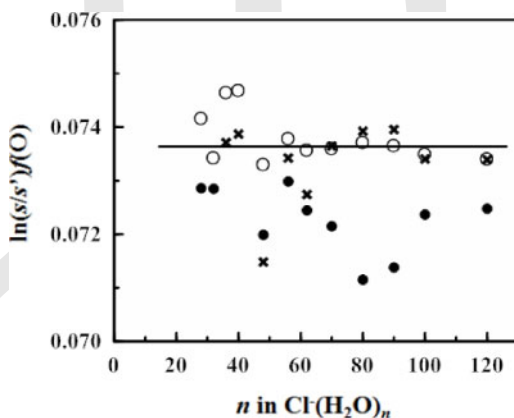
The average values of $\ln(s/s')f(O)$ of oxygen atoms with two HBs in the secondary ($\circ$) and third ($\times$) hydration spheres of the Cl^- ion at 25 °C are plotted against n in Fig. 5, together with those of the primary hydration sphere ($\bullet$). Contrastively to the $\ln(s/s')f(O)$ values in the primary hydration sphere, their average values in the secondary and third hydration spheres around the Cl^- ion are nearly the same as that of the oxygen atom with two HBs in bulk water (the solid line). This indicates that the presence of the Cl^- ion affects only the RPFR of an oxygen atom in the primary hydration sphere in an aqueous Cl^- ion-bearing solution and has little effect on the RPFRs in the secondary and outer hydration spheres.
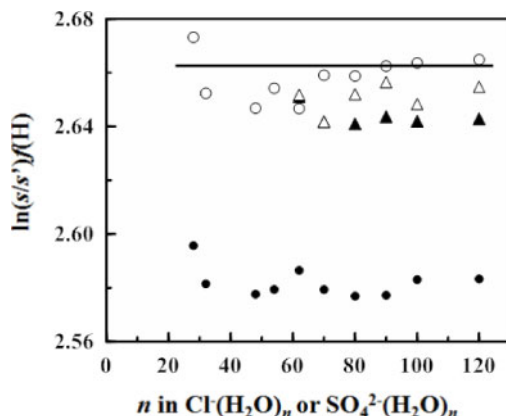
Fig. 6. Plots of the average $\ln(s/s') f(\mathrm{H})$ values of hydrogen atoms in the primary hydration sphere of the Cl$^-$ ion or the SO$_4^{2-}$ ion at 25 °C against n in Cl$^-$(H$_2$O)$_n$ or in SO$_4^{2-}$(H$_2$O)$_n$. The ● and ○ marks denote the average $\ln(s/s') f(\mathrm{H})$ values of hydrogen atoms forming a Cl$^-$–bond and a HB in the primary hydration sphere of the Cl$^-$ ion, respectively. The ▲ and △ marks denote the average $\ln(s/s') f(\mathrm{H})$ values of hydrogen atoms forming a HB with an oxygen atom of the SO$_4^{2-}$ ion and a HB with the oxygen atom of a water molecule in the primary hydration sphere of the SO$_4^{2-}$ ion, respectively. The solid line represents the $\ln(s/s') f(\mathrm{H})$ value of 2.66279 estimated for a hydrogen atom with a HB in bulk water at 25 °C [12].

The average values of the $\ln(s/s') f(\mathrm{H})$ of hydrogen atoms bonded to the Cl$^-$ ion (●) and hydrogen-bonded to a water molecule (○) in the primary hydration sphere of the Cl$^-$ ion at 25 °C are plotted against n in Cl$^-$(H$_2$O)$_n$ in Fig. 6. We can see the substantial difference in the $\ln(s/s') f(\mathrm{H})$ value between hydrogen atoms with a Cl$^-$–H bond and with a H$\cdots$O HB; the former (●) shows a much smaller $\ln(s/s') f(\mathrm{H})$ value than the latter (○), which is nearly equivalent to the value of the bulk water (the solid line). This indicates that, while the hydrogen atom directly bonded to the Cl$^-$ ion tends to be depleted in the heavier isotope of hydrogen, the hydrogen-bonded hydrogen atom has no isotopic preference. Taking the average of the averages at $n = 100$ and 120, the $\ln(s/s') f(\mathrm{H})$ values of the former and the latter hydrogen atoms are 2.58318, about 3.0% smaller than the value of the bulk water, and 2.66424, respectively. We may be able to regard the average of these two values, 2.62371, as the $\ln(s/s') f(\mathrm{H})$ value of the hydrogen atom in the primary hydration sphere of an aqueous Cl$^-$ ion at 25 °C. This value is smaller by about 1.5% than the value of the bulk water.

The average values of the $\ln(s/s') f(\mathrm{H})$ of hydrogen-bonded hydrogen atoms in the primary (●), secondary (○) and third (×) hydration spheres of the Cl$^-$ ion at 25 °C are plotted against n in Cl$^-$ (H$_2$O)$_n$ in Fig. 7. We can see that at larger n values, the three are nearly equivalent to each other and to the value of the bulk water (the solid line). It is thus indicated that the presence of the Cl$^-$ ion little affects the $\ln(s/s') f(\mathrm{H})$ of the hydrogen-bonded hydrogen atom in any hydration sphere of the Cl$^-$ ion.

The average values of the $\ln(s/s') f(\mathrm{O})$ of oxygen atoms with two HBs in the primary hydration sphere of the SO$_4^{2-}$ ion surrounded by water molecules in the secondary hydration sphere at 25 °C are plotted against n in SO$_4^{2-}$(H$_2$O)$_n$ in Fig. 4 (○). Those oxy-
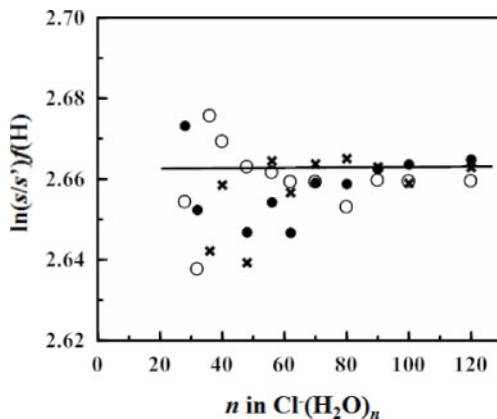
Fig. 7. Plots of the average $\ln(s/s')f(H)$ values in the primary (●), secondary (○) and third (×) hydration spheres of the Cl^- ion at 25 °C against n in $Cl^-(H_2O)_n$. The solid line represents the $\ln(s/s')f(H)$ value of 2.66279 estimated for the hydrogen atom with a HB in bulk water at 25 °C [12].

gen atoms started appearing at $n = 62$ in the present calculations. Fluctuation in the $\ln(s/s')f(O)$ value as a function of n is small and seems to have converged at larger n values. The average of the averages at $n = 90$, 100 and 120 is 0.07277. We may be able to regard this as the $\ln(s/s')f(O)$ value of the oxygen atom with two HBs in the primary hydration sphere of the aqueous SO_4^{2-} ion at 25 °C. This value is smaller by about 1.3% than 0.07376, the solid line, estimated for bulk water, but is slightly large compared to that around the Cl^- ion (●). Thus, as in the case of the Cl^- ion, the heavier isotope of oxygen is expected to be slightly depleted in the primary hydration sphere of the SO_4^{2-} ion compared to the bulk, but the degree of depletion may be slightly less substantial than that around the Cl^- ion.

The average values of the $\ln(s/s')f(H)$ of hydrogen atoms bonded to an oxygen atom of the SO_4^{2-} ion (▲) and hydrogen-bonded to a water molecule (△) in the primary hydration sphere of the SO_4^{2-} ion at 25 °C are plotted against n in Fig. 6. We can see that the $\ln(s/s')f(H)$ value of the former is slightly smaller than that of the latter and both are smaller than the value of the bulk water. This means the two kinds of hydrogen atom are both depleted in the heavier isotope compared to the bulk water. Taking the average of the averages at $n = 90$, 100 and 120, the $\ln(s/s')f(H)$ values of hydrogen atoms with an O_s–H bond and with a H$\cdots$O HB are 2.64284 and 2.65320, respectively. We may be able to regard the average of these two values, 2.64802, as the $\ln(s/s')f(H)$ value of the hydrogen atom in the primary hydration sphere of an aqueous SO_4^{2-} ion at 25 °C. This value is only slightly smaller by about 0.6% than the value of the bulk water.

As for the secondary hydration sphere of the SO_4^{2-} ion, we could not collect enough data points to draw decisive conclusion on the oxygen and hydrogen isotopic preference. Judging from the results on alkali and alkaline metal ions [9–11] and on the Cl^- ion above, however, it is highly probable the presence of the SO_4^{2-} ion little affects $\ln(s/s')f(O)$ and $\ln(s/s')f(H)$ values of water molecules in its secondary and higher hydration spheres.

Table 1. Comparison of $^{18}O/^{16}O$ and D/H RPFRs of water calculated with 6-3lG(d) and 6-31+G(d) basis sets.

Cluster	Basis set	O $\ln(s/s')f(O)$	H bonded to H_2O $\ln(s/s')f(H)$	H bonded to Cl⁻ or SO₄²⁻ $\ln(s/s')f(H)$
$(H_2O)_{100}$	6-3lG(d) **A**	0.07386	2.66307	–
	6-31+G(d) **B**	0.07326	2.67706	–
	A–B	0.00060	−0.01399	–
Cl⁻ $(H_2O)_{120}$	6-3lG(d) **A**	0.07248	2.66555	2.58426
	6-31+G(d) **B**	0.07199	2.68697	2.59443
	A–B	0.00049	−0.02142	−0.01017
$SO_4^{2-}(H_2O)_{90} +$ $SO_4^{2-}(H_2O)_{100}$	6-3lG(d) **A**	0.07283	2.66048	2.63729
	6-31+G(d) **B**	0.07260	2.66316	2.65216
	A–B	0.00023	−0.00268	−0.01487

Our present and previous MO calculations showed that the influence of a solute ion (both cations and anions) on $^{18}O/^{16}O$ and D/H RPFRs of water molecules in aqueous solutions is limited to those in the primary hydration spheres. This is consistent with the results of previous works found in the literature. 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*. [22] stated that the addition of ions had no influence on the rotational dynamics of water molecules outside the first salvation shells of the ions. Molecular dynamics study on HB structure in aqueous electrolytes by Guàrdia *et al*. [23] showed that modifications in the water HB architecture are more noticeable in the first ionic solvation shells and do not persist beyond the second shells. It has been shown in experiments on isotope salt effects on VPIEs of water that isotope salt effects are linearly dependent on molality of solute ions up to, say, 4 mol/kg [5,6]; if the solute ion influences beyond the primary hydration spheres, isotope salt effects cannot be linear functions of solute concentration up to such high concentration because of the lack of water molecules.

The present calculations also showed that, contrary to the cases of cations where the presence of a cation influences mostly the $^{18}O/^{16}O$ RPFR and has minimal effects on the D/H RPFR, the presence of anions affects both $^{18}O/^{16}O$ and D/H RPFR values. This is consistent with the statement by Kakiuchi in his isotope salt effects study [8] that "the hydrogen isotope effect is mainly influenced in anions rather than in cations."

3.4 Comparison of computational results with 6-31G(d) and 6-31+G(d) basis sets

The logarithms of $^{18}O/^{16}O$ and D/H RPFRs were calculated for the $(H_2O)_{100}$, $Cl^-(H_2O)_{120}$, $SO_4^{2-}(H_2O)_{90}$ and $SO_4^{2-}(H_2O)_{100}$ clusters with the 6-31+G(d) basis set and the results are compared with the corresponding results with the 6-31G(d) basis set. The comparison is summarized in Table 1.

In the analyses of the isotope salt effects, what is most important is not the absolute value of a RPFR but the difference in the RPFR value between pure liquid water and aqueous solution. As is seen in Table 1, the 6-31+G(d) basis set yielded a slightly smaller $\ln(s/s')f(O)$ value and a slightly larger $\ln(s/s')f(H)$ value than the 6-31G(d) basis set did for every cluster studied; the differences in the $\ln(s/s')f$ value calculated with and without the diffuse function for the given isotopic pair ($^{18}O/^{16}O$ or D/H) more or less cancel out. Thus, we may be able to conclude that the $\ln(s/s')f(O)$ and $\ln(s/s')f(H)$ calculations with the 6-31G(d) basis set are as reliable as the calculations with the 6-31+G(d) basis set, and the $\ln(s/s')f(O)$ and $\ln(s/s')f(H)$ for the anion systems in the present study can be compared with the cation systems in our previous papers [9–11].

4. Conclusions

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

The presence of chloride and sulfate ions both reduces the $^{18}O/^{16}O$ RPFR value in their primary hydration sphere relative to that of bulk water with the degree of reduction being larger for the chloride ion. Their presence also reduces the D/H RPFR value in their primary hydration spheres. Thus, the primary hydration spheres of the chloride and sulfate ions are expected to be enriched in the lighter isotopes of oxygen and hydrogen relative to the bulk water. The influence of those anions, however, is confined to their primary hydration spheres and no $^{18}O/^{16}O$ and D/H isotopic preference is expected in outer hydration spheres.

References

1. J. Horita and D. J. Wesolowski, Geochim. Cosmochim. Acta **58** (1994) 3425.
2. M. Kakiuchi and S. Matsuo, Geochem. J. **13** (1979) 307.
3. J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15** (1947) 261.
4. J. R. O'Neil and A. H. Truesdell, in: Stable Isotope Geochemistry: a Tribute to Samuel Epstein, H. P. Taylor Jr., J. R. O'Neil, and I. R. Kaplan (Eds.), The Geochem. Soc., Canada (1991), p. 17.
5. M. Kakiuchi, Z. Naturforsch. **52a** (1997) 811.
6. J. Horita, Geochem. J. **39** (2005) 481.
7. M. Kakiuchi, Z. Naturforsch. **62a** (2007) 721.
8. M. Kakiuchi, Bull. Chem. Soc. Jpn **74** (2001) 2011.
9. T. Oi and A. Otsubo, Z. Naturforsch. **66a**, (2011) 242.
10. T. Oi, Z. Naturforsch. **66a** (2011) 569.
11. T. Oi, K. Sato, and K. Umemoto, Z. Naturforsch., in press, published online, 6 February 2013.
12. T. Oi and A. Otsubo, J. Nucl. Sci. Technol. **47** (2010) 323.

13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Revision B.01 Gaussian, Inc., Wallingford, CT (2010).
14. T. Oi, J. Nucl. Sci. Technol. **39**, 419 (2002).
15. J. B. Foresman and Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd edn., Gaussian Inc., Pittsburgh (1996).
16. S. J. Stuart and B. J. Berne, J. Phys. Chem. **100** (1996) 11934.
17. P. Bergström, J. Lindgren, and O. Kristiansson, J. Phys. Chem. **95** (1991) 8575.
18. D. H. Dunsyuryun, G. V. Karpov, and I. I. Morozov, Chem. Phys. Lett. **242** (1995) 390.
19. R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci, and A. K. Soper, J. Phys. Chem. B **111** (2007) 13570.
20. R. Buchner, S. G. Capewell, G. Hefter, and P. M. May, J. Phys. Chem. B **103** (1999) 1185.
21. V. Vchirawongkwin, B. M. Rode, and I. Persson, J. Phys. Chem. B **111** (2007) 4150.
22. A. W. Omta, M. F. Kropman, S. Woutersen, and H. J. Bakker, Science **301** (2003) 347.
23. E. Guàrdia, D. Laria, and J. Marti, J. Phys. Chem. **110** (2006) 6332.