Oxygen and Hydrogen Isotopic Preference in Hydration Spheres of Magnesium and Calcium Ions

Takao Oi, Kunihiko Sato, and Kazuki Umemoto

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

Reprint requests to T. O.; E-mail: t-ooi@sophia.ac.jp

Z. Naturforsch. **68a,** 362 – 370 (2013) / DOI: 10.5560/ZNA.2012-0122
Received September 6, 2012 / revised November 26, 2012 / published online February 6, 2013

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 magnesium and calcium ions. As model for water molecules in the *i*th hydration sphere of the cation in aqueous solutions containing that cation, 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, $M^{2+}(H_2O)_n$ (M = Mg or Ca; *n* up to 100). The calculations indicated that the decreasing order of the ^{18}O preference over ^{16}O in the primary hydration sphere is $Mg^{2+} > Ca^{2+} >$ bulk water. That is, water molecules in the primary hydration spheres of the Mg^{2+} and Ca^{2+} ions are expected to be enriched in the heavier isotope of oxygen relative to water molecules in bulk, and the degree of the enrichment is larger for the Mg^{2+} ion than for the Ca^{2+} ion. No such preference was observed for hydrogen isotopes in any hydration sphere or for oxygen isotopes in the secondary and outer hydration spheres.

Key words: Reduced Partition Function Ratio; Isotope Salt Effects; Hydrogen and Oxygen Isotopes; Vapour Pressure Isotope Effects; Hydration Spheres.

1. Introduction

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. For instance, variations of $^{18}O/^{16}O$ and D/H in water and ice cores are important indicators of present and past hydrologic processes and climate [1]. 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 (vapour pressure isotope effects of water) [2, 3]. Even if salt is added to the liquid phase, the direction of the $^{18}O/^{16}O$ and D/H isotope fractionations does not change, but the degrees of the fractionation change depending on the kind of salt added and its concentration (isotope salt effects) [4 – 7]. For instance, the addition of potassium chloride reduces the $^{18}O/^{16}O$ isotopic ratio difference between the two phases relative to that in the case of pure water. To understand and elucidate these experimental results, knowledge on $^{18}O/^{16}O$ and D/H isotope effects in hydration spheres around 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 [8], which will cause changes in the degree of isotope fractionation.

Estimation of rpfrs 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, since the equilibrium constant of the isotope exchange reaction between two chemical species or between two phases of the same substance is given as the ratio of the rpfrs of the two. In our previous papers [9, 10], we reported the estimation of the $^{18}O/^{16}O$ and D/H rpfrs of water molecules in hydration spheres around Group 1 metal ions (Li^+, Na^+, and K^+) based on the MO calculations as a step towards the satisfactory elucidation of isotope salt effects experimentally observed. Similar calculations were extended to Group 2 metal ions, magnesium and calcium ions. In this paper, we report the results of such calculations and compare the $^{18}O/^{16}O$ and D/H rpfrs of water molecules around Group 1 and 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,

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

where $u_i = hc\omega_i/(kT)$ and $u'_i = hc\omega'_i/(kT)$; p is the degree of freedom of molecular vibration, h the Planck's 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 [8].

As models of a magnesium ion- or calcium ion-bearing aqueous solution, we considered $M^{2+}(H_2O)_n$ (M = Mg, Ca) clusters with n up to 100. We tried to locate the metal 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 metal ion through its oxygen 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 magnesium ion- or calcium ion-bearing aqueous solutions, we considered water molecules in $M^{2+}(H_2O)_n$ (M = Mg, Ca) that directly interacted with the metal 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 magnesium ion- or calcium ion-bearing aqueous solutions, we considered water molecules in $M^{2+}(H_2O)_n$ (M = Mg, Ca) that were hydrogen-bonded to water molecule(s) in the primary hydration sphere and surrounded by other water molecules, 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 [11] and on rpfrs of $M^+(H_2O)_n$ (M = Li, Na, K) clusters with n up to 100, modelling Group 1 metal ion-bearing aqueous solutions [9, 10]. The Gaussian 98 and 03 program packages (Gaussian Inc.) were used for the MO calculations [12], 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 [13].

Structure optimization of the $M^{2+}(H_2O)_n$ clusters (M = Mg, Ca; n up to 100) was carried out in a sequential way. For instance, $Mg^{2+}(H_2O)_{100}$ was optimized starting from the optimized structure of $Mg^{2+}(H_2O)_{90}$ 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 rpfrs of the $M^{2+}[H_2{}^{18}O(H_2{}^{16}O)_{n-1}]/M^{2+}(H_2{}^{16}O)_n$ and $M^{2+}[HD^{16}O(H_2{}^{16}O)_{n-1}]/M^{2+}(H_2{}^{16}O)_n$ (M = Mg, Ca) isotopic pairs were estimated.

3. Results and Discussion

3.1. Hydration Numbers in the Primary Hydration Spheres

We first determined the hydration number in the primary hydration sphere of the magnesium ion using small clusters, $Mg^{2+}(H_2O)_n$ ($n = 6, 8, 10$). For a given n, we obtained optimized structures with the hydration number 5 or 6, depending on the initial arrangements of water molecules around the magnesium ion. Comparison of electronic energy between $[Mg^{2+}(H_2O)_6](H_2O)_{n-6}$, in which six water molecules were directly bonded to the magnesium ion and the remaining $n-6$ molecule(s) was(were) in the secondary hydration sphere and $[Mg^{2+}(H_2O)_5](H_2O)_{n-5}$ in which five water molecules were directly bonded to the magnesium ion and the remaining $n-5$ molecule(s) was(were) in the secondary hydration sphere, revealed that the former was slightly more stable than the latter. $[Mg^{2+}(H_2O)_6]$ was more stable by 23 kJ mol^{-1} than $[Mg^{2+}(H_2O)_5](H_2O)$, and the energy difference became smaller with increasing n. We thus decided to fix the hydration number of six in the primary hydration sphere of the magnesium ion in the $Mg^{2+}(H_2O)_n$ clusters ($n > 11$). The hydration number six of the magnesium ion agrees with that of previous studies [14, 15].

To determine the hydration number in the primary hydration sphere around the calcium ion, we first optimized small $Ca^{2+}(H_2O)_n$ clusters with n six to ten. The obtained hydration number in the optimized structures was 6, 7 or 8. For $n = 7$, $[Ca^{2+}(H_2O)_6](H_2O)$ was more stable by 5.8 kJ mol^{-1} than $[Ca^{2+}(H_2O)_7]$. Similarly, for $n = 8$, $[Ca^{2+}(H_2O)_6](H_2O)_2$ was more stable by 4.7 kJ mol^{-1} than $[Ca^{2+}(H_2O)_7](H_2O)$. However, for $n = 9$ and 10, the structure with the hydration number of seven in the primary hydration sphere was more stable by 3.2 and 2.5 kJ mol^{-1}, respectively, than the corresponding structure with the hydration number of six. Those electronic energy differences were, however, within computational uncertainties, indicating that the hydration numbers six and seven were evenly possible. Contrary to this, $[Ca^{2+}(H_2O)_6](H_2O)_{n-6}$ was more stable by 14, 16, and 17 kJ mol^{-1} than $[Ca^{2+}(H_2O)_8](H_2O)_{n-8}$ for $n =$ 8, 9, and 10, respectively, which meant the structure with the hydration number of six in the primary hydration sphere was more stable than the structure with the hydration number of eight. Given those results, we decided to fix the hydration number of six in the primary hydration sphere of the calcium ion in the $Ca^{2+}(H_2O)_n$ clusters ($n > 11$). The hydration number six of the calcium ion is within the range of five to thirteen reported previously [13, 15 – 17].

3.2. Optimized Structures

As an example of the optimized structures of the $M^{2+}(H_2O)_n$ (M = Mg, Ca) clusters considered, that of the $Mg^{2+}(H_2O)_{100}$ cluster is shown in Figure 1. No imaginary wave number was obtained in the vibrational analyses of those clusters that were used for the rpfr estimation. Every optimized structure was thus at the global or local minimum of the potential energy surface.

As is seen in the $Mg^{2+}(H_2O)_{100}$ cluster given as an example in Figure 2, water molecules in the primary hydration sphere of the magnesium ion were divided into two groups, G1 and G2. The oxygen atom of the G1 water molecule was directly bonded to the magnesium ion with the calculated average Mg^{2+}–O bond distance of 2.142 Å and hydrogen-bonded to a water molecule in the secondary hydration sphere with the calculated average hydrogen bond distance of 1.966 Å. Contrary to oxygen atoms belonging to G1 water molecules, the oxygen atom of the G2 water molecule was directly bonded to the magnesium ion with the calculated average Mg^{2+}–O bond distance of 2.079 Å, slightly shorter than that of the G1 oxygen atoms, but has no hydrogen bond. Two water molecules at positions trans to each other belonged to G1 and the remaining four to G2. Each hydrogen atom of every water molecule, G1 and G2, in the primary hydration sphere around the magnesium ion was hydrogen-bonded to a water molecule in the secondary hydration sphere with the average hydrogen bond distance of 1.867 Å. No hydrogen bond was found between water molecules in the primary hydration sphere. The number of water molecules in the secondary hydration

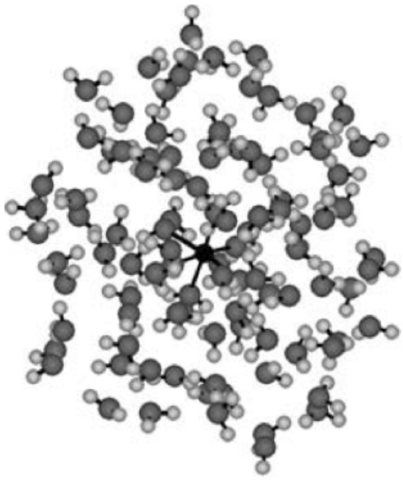

Fig. 1. Optimized structure of the $Mg^{2+}(H_2O)_{100}$ cluster. The black sphere at the center denotes the magnesium ion, and the darker and lighter gray spheres denote oxygen and hydrogen atoms, respectively. No meaning is attached to the relative sizes of the spheres. Mg–O bonds and O–H covalent bonds are shown with a solid line. Hydrogen bonds are not drawn.

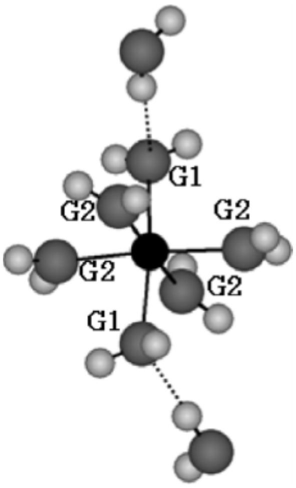

Fig. 2. Water molecules with an oxygen atom forming a hydrogen bond (G1) and forming no hydrogen bond (G2) in the primary hydration sphere of the magnesium ion in the optimized $Mg^{2+}(H_2O)_{100}$ cluster. The black sphere denotes the magnesium ion, and the darker and lighter gray spheres denote oxygen and hydrogen atoms, respectively. No meaning is attached to the relative sizes of the spheres. Mg–O bonds and O–H covalent bonds are shown with a solid line. O···H hydrogen bonds are drawn with a broken line. Unnecessary water molecules of the outer spheres are all omitted.

sphere was 14 obtained for the $Mg^{2+}(H_2O)_n$ clusters with a large n value.

As in the case of the magnesium ion, water molecules in the primary hydration sphere of the calcium ion were also divided into two groups, G1 and G2. The calculated average Ca^{2+}–O and hydrogen bond distances of the oxygen atom of the G1 water molecule were 2.456 Å and 1.965 Å, respectively, and the calculated average distance of Ca^{2+}–O bond of the oxygen atom of the G2 water molecule was 2.393 Å, slightly shorter than that of the G1 oxygen atoms. Two water molecules at positions trans to each other belonged to G1 as in the case of the magnesium ion. Each hydrogen atom of every water molecule in the primary hydration sphere around the calcium ion was hydrogen-bonded to a water molecule in the secondary hydration sphere with the average hydrogen bond distance of 1.866 Å. No hydrogen bond was found between water molecules in the primary hydration sphere. The number of water molecules in the secondary hydration sphere was 14 or 15 obtained for the $Ca^{2+}(H_2O)_n$ clusters with a large n value.

Hydration numbers and calculated distances of metal ion–O bonds and O···H hydrogen bonds in the primary hydration spheres of Group 1 and 2 metal ions are summarized in Table 1 [9, 10].

3.3. Correlation of Reduced Partition Function Ratios with Bond Distances

In Figure 3 are plotted the logarithms of $^{18}O/^{16}O$ rpfrs, $\ln(s/s')f(O)$, in the primary hydration spheres at 25 °C against the sum of the distances of the M^{2+}–O bond (M = Mg, Ca) and the O···H hydrogen bond where O is the oxygen atom for which the rpfr was estimated (● for Mg and ▲ for Ca). The $\ln(s/s')f(O)$ value of the G1 oxygen is well inversely correlated with the sum of the M^{2+}–O and O···H distances with the correlation coefficient value of -0.945 and -0.866 for the magnesium and calcium ions, respectively. We made similar plots of the $\ln(s/s')f(O)$ value in the primary hydration sphere against the M^{2+}–O bond distance and against the O···H hydrogen bond distance, but no better correlations were obtained; the correlation coefficient values for the former were -0.822 and -0.446 for magnesium and calcium, respectively, and those for the latter were -0.845 and -0.727 for magnesium and calcium, respectively. The $\ln(s/s')f(O)$ values in

Table 1. Hydration numbers and bond distances in the primary hydration spheres of Group 1 and 2 metal ions.

Element	Hydration number		O with hydrogen bond			O w/o hydrogen bond		H
	primary hydration sphere	secondary hydration sphere	Number of water molecules	$M^{(2)+}$–O (Å)	O···H (Å)	Number of water molecules	$M^{(2)+}$–O (Å)	H···O (Å)
Li	4	11	3	1.995	1.975	1	1.946	1.898
Na	6	18	6	2.472	1.947	0	–	1.962
K	6	17 or 18	6	2.829	1.894	0	–	1.940
	7	20 or 21	7	2.942	1.896	0	–	
Mg	6	14	2	2.142	1.966	4	2.079	1.867
Ca	6	14 or 15	2	2.456	1.965	4	2.393	1.866

the primary hydration sphere of the M^{2+} (M = Mg, Ca) ion with a hydrogen bond are thus better correlated with the sum of the distances of the M^{2+}–O bond and the O$\cdots$H hydrogen bond than with the individuals of the M^{2+}–O bond distance and the O$\cdots$H hydrogen bond distance.

In Figure 3, we further notice that the inverse correlation of $\ln(s/s')f(\mathrm{O})$ with the sum of the M^{2+}–O and O$\cdots$H distances holds well for magnesium and calcium not only individually but also combinedly. The combined correlation coefficient is -0.982.

In Figure 3, the $\ln(s/s')f(\mathrm{O})$ value is also plotted against twice the M^{2+}–O bond distance for the G2 oxygen atoms around the magnesium (○) or calcium ion (△). The factor of 2 with no physical meaning attached was chosen so that the plots for the G2 oxygen atoms (○ and △) fell in a similar *x*-axis range as that for the G1 oxygen atoms (● and ▲). For the G2 oxygen, the $\ln(s/s')f(\mathrm{O})$ value is well inversely correlated with the M^{2+}–O bond distance with the correlation coefficient of -0.960 and -0.944 for magnesium and calcium, respectively.

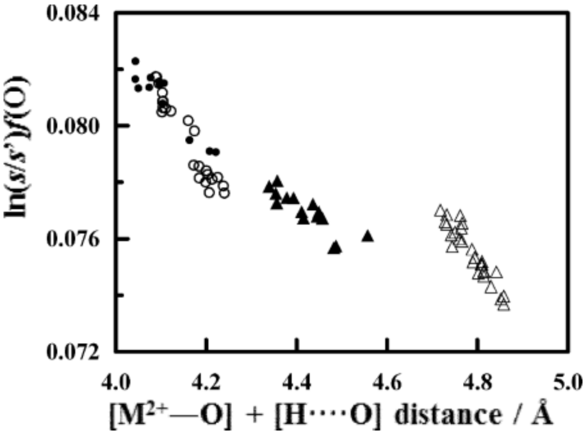

Fig. 3. Plots of the $\ln(s/s')f(\mathrm{O})$ values in the primary hydration spheres at 25 °C against the sum of the distances of the M^{2+}–O bond (M = Mg, Ca) and the O$\cdots$H hydrogen bond where O is the oxygen atom for which the rpfr was estimated. The ● and ▲ marks denote the $\ln(s/s')f(\mathrm{O})$ values of oxygen atoms with a hydrogen bond around the magnesium and calcium ion, respectively. The $\ln(s/s')f(\mathrm{O})$ values of oxygen atoms without a hydrogen bond around the magnesium ion (○) and calcium ion (△) are plotted against twice the M^{2+}–O bond distance (M = Mg, Ca) instead of the sum of the distances of the M^{2+}–O bond and O$\cdots$H hydrogen bond.

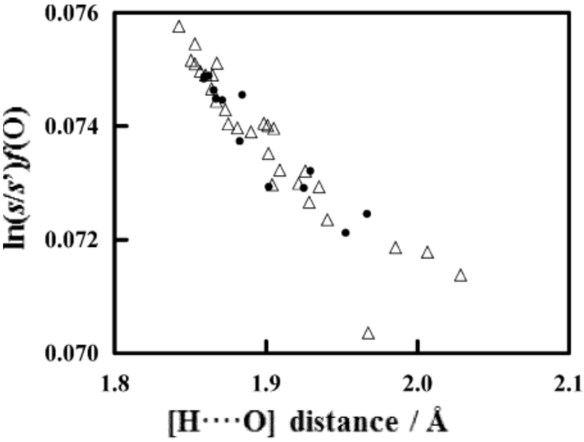

Fig. 4. Plots of the $\ln(s/s')f(\mathrm{O})$ values in the secondary hydration spheres at 25 °C against the O$\cdots$H hydrogen bond distance where O is the oxygen atom for which the rpfr was estimated (● for magnesium and △ for calcium).

In Figure 4 are plotted $\ln(s/s')f(\mathrm{O})$ in the secondary hydration spheres at 25 °C against the O$\cdots$H hydrogen bond distance where O is the oxygen atom for which the rpfr was estimated (● for Mg and △ for Ca). Again, the $\ln(s/s')f(\mathrm{O})$ value is well inversely correlated with the hydrogen bond distance. Moreover, the correlations for magnesium and calcium fell on a single line with the correlation coefficient of -0.932. This suggested that the presence of a magnesium or calcium ion little

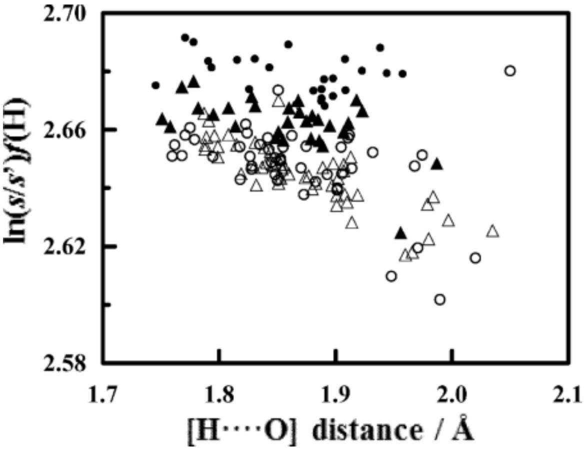

Fig. 5. Plots of the $\ln(s/s')f(\mathrm{H})$ values in the primary hydration spheres at 25 °C against the O$\cdots$H hydrogen bond distance where H is the hydrogen atom for which the rpfr was estimated. The ● and ○ marks denote the $\ln(s/s')f(\mathrm{H})$ values of hydrogen atoms of water molecules around the magnesium ion whose oxygen atom has a hydrogen bond and does not have a hydrogen bond, respectively. The ▲ and △ marks denote the $\ln(s/s')f(\mathrm{H})$ values of hydrogen atoms around the calcium ion whose oxygen atom has a hydrogen bond and does not have a hydrogen bond, respectively.

affects the rpfr of an oxygen atom of a water molecule beyond its primary hydration sphere.

In Figure 5, the logarithms of D/H rpfrs, $\ln(s/s')f(\mathrm{H})$, in the primary hydration spheres at 25 °C are plotted against the O···H hydrogen bond distance where H is the hydrogen atom for which the rpfr was estimated. The $\ln(s/s')f(\mathrm{H})$ value is shallowly inversely correlated with the hydrogen bond distance with the correlation coefficient of −0.403, and seems nearly independent of the kind of 2nd group element (Mg, Ca). There seems, however, a difference between hydrogen atoms of G1 water molecules (● and ▲) and those of G2 water molecules (○ and △). Interestingly enough, the former hydrogen atoms have slightly larger $\ln(s/s')f(\mathrm{H})$ values than the latter at a given hydrogen bond distance.

3.4. Reduced Partition Function Ratios

The average values of the logarithms of $^{18}O/^{16}O$ rpfrs, $\ln(s/s')f(\mathrm{O})$, of oxygen atoms in the primary hydration spheres of magnesium and calcium ions at 25 °C are plotted against n in $M^{2+}(H_2O)_n$ in Figure 6.

As for the $Mg^{2+}(H_2O)_n$ clusters, water molecules in the primary hydration sphere surrounded by water molecules in the secondary hydration sphere started appearing at $n = 42$ in the present calculations. The $\ln(s/s')f(\mathrm{O})$ values of the oxygen atoms around the magnesium ion, both with and without a hydrogen bond (● and ○), are larger than the value for the oxygen atom with two hydrogen bonds in bulk water (0.07376; the solid line in Figure 6), which means that the heavier isotope of oxygen tends to be enriched in the primary hydration sphere of the magnesium ion rather than in the bulk. The oxygen atoms with a hydrogen bond (●; G1 oxygen) have larger $^{18}O/^{16}O$ rpfr values than those without a hydrogen bond (○; G2 oxygen), which indicates that the formation of the hydrogen bond enhances the $^{18}O/^{16}O$ rpfr value. Taking the average of the averages at $n = 80$, 90, and 100, the $\ln(s/s')f(\mathrm{O})$ value of the oxygen atoms with and without a hydrogen bond in the primary hydration sphere are estimated to be 0.08033 and 0.07942, respectively. We may be able to regard the average of these two values weighted by the number of oxygen atoms belonging to the respective groups, 0.07982, as the $\ln(s/s')f(\mathrm{O})$ value of the oxygen atom in the primary hydration sphere of an aqueous magnesium ion at 25 °C, which is by about 8.2% larger than the value of bulk water.

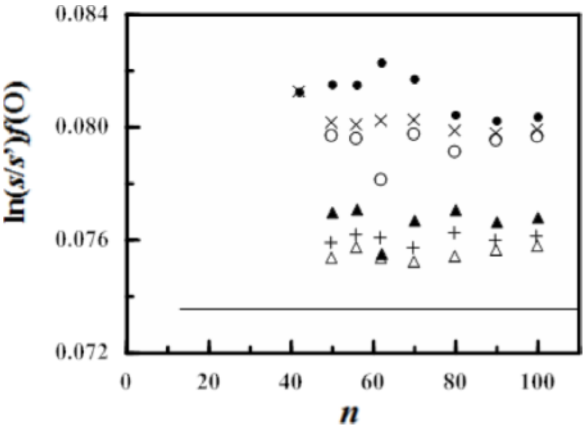

Fig. 6. Plots of the average $\ln(s/s')f(\mathrm{O})$ values in the primary hydration spheres at 25 °C against n in $M^{2+}(H_2O)_n$ (M = Mg, Ca). The ● and ○ marks respectively denote the average $\ln(s/s')f(\mathrm{O})$ values of oxygen atoms with and without a hydrogen bond around the magnesium ion, and the × marks are the weighted averages of the two averages at a given n. The ▲ and △ marks respectively denote the average $\ln(s/s')f(\mathrm{O})$ values of oxygen atoms with and without a hydrogen bond around the calcium ion and the + marks are the weighted averages of the two averages at a given n. The solid line represents the $\ln(s/s')f(\mathrm{O})$ value of 0.07376 estimated for an oxygen atom with two hydrogen bonds in bulk water at 25 °C [11].

As for the $Ca^{2+}(H_2O)_n$ clusters, water molecules in the primary hydration sphere surrounded by water molecules in the secondary hydration sphere started appearing at $n = 50$ as is seen in Figure 6. The $\ln(s/s')f(\mathrm{O})$ values of the oxygen atoms around the calcium ion, both with and without a hydrogen bond (▲ and △), are larger than the value of 0.07376 for bulk water as in the case of the magnesium ion. The heavier isotope of oxygen thus tends to be enriched in the primary hydration sphere of the calcium ion rather than in the bulk, although the degree of enrichment is less substantial than in the case of the magnesium ion. The G1 oxygen atoms (▲) have larger $^{18}O/^{16}O$ rpfr values than the G2 oxygen atoms (△) possibly due to the formation of the hydrogen bond. Taking the average of the averages at $n = 80$, 90, and 100, the $\ln(s/s')f(\mathrm{O})$ value of the oxygen atoms with and without a hydrogen bond in the primary hydration sphere around the calcium ion are estimated to be 0.07678 and 0.07559, respectively. The weighted average of the two, 0.07609, can be regarded as the $\ln(s/s')f(\mathrm{O})$ value of the oxygen atom in the primary hydration sphere of an aqueous calcium ion at 25 °C, which is by about 3.2% larger than the value of bulk water.

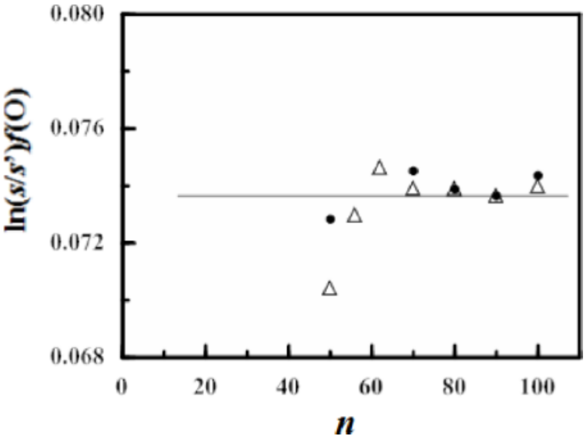

Fig. 7. Plots of the average $\ln(s/s')f(\mathrm{O})$ values in the secondary hydration spheres of magnesium ion (●) and calcium ion (△) at 25 °C against n in $M^{2+}(H_2O)_n$ (M = Mg, Ca).

The $\ln(s/s')f(\mathrm{O})$ value of the oxygen atom in the primary hydration sphere of aqueous magnesium and calcium ions at 25 °C estimated in this study should be compared with the similar estimation for aqueous Group 1 metal ions in our previous papers [9, 10]; it was 0.07585, 0.07276, and 0.07177 for lithium, sodium, and potassium ions, respectively. Thus the decreasing order in the $\ln(s/s')f(\mathrm{O})$ value is $Mg^{2+} > Ca^{2+} > Li^{+} >$ bulk water (the oxygen atom with two hydrogen bonds) $> Na^{+} > K^{+}$. Relative to oxygen atoms with two hydrogen bonds of bulk water molecules, those in primary hydration spheres of magnesium, calcium, and lithium ions are to be enriched in the ^{18}O and those in primary hydration spheres of sodium and potassium ions are to be depleted in the same isotope.

The average values of $\ln(s/s')f(\mathrm{O})$ of oxygen atoms in the secondary hydration spheres of magnesium and calcium ions at 25 °C are plotted against n in Figure 7. Contrary to the $\ln(s/s')f(\mathrm{O})$ values in the primary hydration spheres, their average values in the secondary hydration spheres around magnesium and calcium ions both seem to fluctuate around the value of the oxygen atom with two hydrogen bonds in bulk water with increasing n value. This indicates that the presence of magnesium or calcium ion affects only the rpfr of an oxygen atom of a water molecule in the primary hydration sphere in an aqueous Mg^{2+} or Ca^{2+} ion-bearing solution and has little effect on the rpfr of an oxygen atom in the secondary and outer hydration spheres as in the case of lithium, sodium, and potassium ions [9, 10].

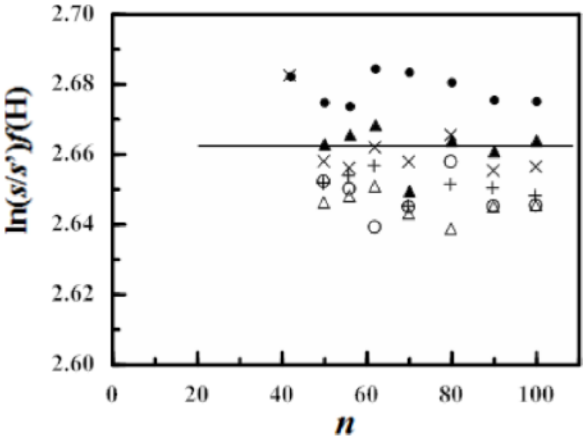

Fig. 8. Plots of the average $\ln(s/s')f(\mathrm{H})$ values in the primary hydration spheres at 25 °C against n in $M^{2+}(H_2O)_n$ (M = Mg, Ca). The ● and ○ marks respectively denote the average $\ln(s/s')f(\mathrm{H})$ values of hydrogen atoms of a water molecule whose oxygen atom forms and does not form a hydrogen bond around the magnesium ion, and the × marks are the weighted averages of the two averages at a given n. The ▲ and △ marks respectively denote the average $\ln(s/s')f(\mathrm{H})$ values of hydrogen atoms of a water molecule whose oxygen atom forms and does not form a hydrogen bond around the calcium ion and the + marks are the weighted averages of the two averages at a given n. The solid line represents the $\ln(s/s')f(\mathrm{H})$ value of 2.66279 estimated for the hydrogen atom with a hydrogen bond in bulk water at 25 °C [11].

The average values of the logarithms of D/H rpfrs, $\ln(s/s')f(\mathrm{H})$, of hydrogen atoms in the primary hydration spheres around magnesium and calcium ions at 25 °C are plotted against n in $M^{2+}(H_2O)_n$ in Figure 8. As for the $Mg^{2+}(H_2O)_n$ clusters, we can find a small difference in the $\ln(s/s')f(\mathrm{H})$ value between the hydrogen atoms of the G1 water molecules (●) and the hydrogen atoms of the G2 water molecules (○). The former has a larger $\ln(s/s')f(\mathrm{H})$ value than the latter at a given n, and furthermore, while the $\ln(s/s')f(\mathrm{H})$ value of the former is slightly larger than that for bulk water (2.66279; the solid line in Fig. 8), the $\ln(s/s')f(\mathrm{H})$ value of the latter is slightly smaller. Taking the average of the averages at $n = 80$, 90, and 100, the $\ln(s/s')f(\mathrm{H})$ values of the hydrogen atom covalently bonded to the oxygen atom with a hydrogen bond and the hydrogen atom covalently bonded to the oxygen atom without a hydrogen bond in the primary hydration sphere around the magnesium ion are estimated to be 2.67703 and 2.64922, respectively. We may be able to regard the average of these two values weighted by the number of hydrogen atoms belonging to the respective categories, 2.65887, as the $\ln(s/s')f(\mathrm{H})$ value of the hydrogen atom in the primary hydration sphere of an aqueous magnesium ion at 25 °C. This value is very close to the value of 2.66279 estimated for the hydrogen with a hydrogen bond in bulk water, only by 0.1% smaller than the value for bulk water; the difference is well within the computational uncertainty.

As for the $Ca^{2+}(H_2O)_n$ clusters, we can also find a small difference in the $\ln(s/s')f(\mathrm{H})$ value between the hydrogen atoms of the G1 water molecules (▲) and the hydrogen atoms of the G2 water molecules (△) as in the case of the $Mg^{2+}(H_2O)_n$ clusters. Both have slightly smaller $\ln(s/s')f(\mathrm{H})$ values than that of bulk water with the former having a larger $\ln(s/s')f(\mathrm{H})$ value than the latter at a given n. Taking the average of the averages at $n = 80$, 90, and 100, the $\ln(s/s')f(\mathrm{H})$ values of the hydrogen atom covalently bonded to the G1 oxygen atom and the hydrogen atom covalently bonded to the G2 oxygen atom in the primary hydration sphere around the calcium ion are estimated to be 2.66293 and 2.64281, respectively. The weighted average of the two, 2.64976, can be regarded as the $\ln(s/s')f(\mathrm{H})$ value of the hydrogen atom in the primary hydration sphere of an aqueous calcium ion at 25 °C. This value is close to the value of 2.66279 estimated for the hydrogen atom with a hydrogen bond in bulk water, by only 0.5% smaller than the value for bulk water.

As a summary of the $\ln(s/s')f(\mathrm{H})$ estimation around magnesium and calcium ions, we can conclude that the presence of those ions has a minimal effect on the rpfr values of hydrogen atoms with a hydrogen bond in any hydration sphere around them. The presence of the magnesium ion in liquid water has a negligible effect on the hydrogen isotope preference around the magnesium ion, and the lighter isotope of hydrogen may be enriched very slightly around the calcium ion.

The present calculations showed that the influence of a solute metal ion (Mg^{2+}, Ca^{2+}) on $^{18}O/^{16}O$ and D/H rpfrs of water molecules in aqueous solutions is limited to water molecules in the primary hydration spheres. 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) [5, 6]. The present calculations also showed that the influences of 2nd group metal ions (Mg^{2+}, Ca^{2+}) on $^{18}O/^{16}O$ rpfrs in the primary hydration spheres are more substantial than those of 1st group metal ions (Li^+, Na^+, K^+) [9, 10]. This agrees, in a qualitative fashion, with experimental results that $^{18}O/^{16}O$ isotope salt effects are larger for a magnesium or calcium ion-bearing solution than for a lithium, sodium or potassium ion-bearing solution [6] and seems consistent with the statement by Kakiuchi [5] that the oxygen isotope effect is mainly caused by the cation species. Our present and previous calculations [9, 10] revealed that Group 1 and 2 metal ions have only minimal effects on D/H rpfrs in their hydration spheres; similar MO calculations on anionic species are certainly required for the elucidation of the reported D/H isotope salt effects.

4. Conclusions

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

The $^{18}O/^{16}O$ rpfr of a water molecule in the primary hydration sphere of magnesium and calcium ions are different from each other and from those of Group 1 metal ions and of bulk water. The presence of magnesium and calcium ions both enhances the $^{18}O/^{16}O$ rpfr value relative to that of bulk water with the degree of enhancement being higher for the magnesium ion. The influence of the magnesium and calcium ions, however, is confined to their primary hydration spheres; the $^{18}O/^{16}O$ rpfr of water molecules in the secondary hydration spheres is practically the same as that of the oxygen atom with two hydrogen bonds in bulk water. Contrary to the $^{18}O/^{16}O$ rpfr, the effect of the presence of magnesium and calcium ions on the D/H rpfr is minimal in any hydration sphere around them.

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