$^{18}O/^{16}O$ and D/H Isotopic Preference in Hydration Spheres of Alkali Metal Ions

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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 $^{18}O/^{16}O$ and D/H isotopic reduced partition function ratios (RPFRs) of water molecules around lithium, sodium, and potassium ions. As model 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, $M^+(H_2O)_n$ ($M =$ Li, Na or K; 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: $Li^+ >$ (bulk water) $\geq Na^+ > K^+$. That is, water molecules in the primary hydration spheres of the Li^+, Na^+, and K^+ ions are, respectively, enriched, slightly depleted, and depleted in the heavier isotope of oxygen relative to water molecules in bulk. 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; Alkali Metal Ions; Hydration Spheres.

1. Introduction

The 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 (vapour pressure isotope effects of water) [1, 2]. 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) [3 – 6]. 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 [7], which will cause changes in the degree of isotope fractionation.

Estimation of isotopic reduced partition function ratios (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 paper [8], we reported the estimation of the $^{18}O/^{16}O$ and D/H RPFRs of water molecules in hydration spheres around a sodium ion based on the molecular orbital (MO) calculations as a step towards the satisfactory elucidation of isotope salt effects experimentally observed. Similar calculations were extended to lithium and potassium 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 lithium, sodium, and potassium ions.

2. Theory and Calculational Method

When two chemical species or two phases of a substance 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 for the RPFR is, under Born–Oppenheimer and harmonic oscillator approximations, given as,

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

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'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 [7].

As models of lithium ion- or potassium ion-bearing aqueous solutions, we considered $M^+(H_2O)_n$ (M = Li, K) 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 lithium ion- or potassium ion-bearing aqueous solutions, we considered water molecules in $M^+(H_2O)_n$ (M = Li, K) that directly interacted with the metal ion and were surrounded by (hydrogen-bonded to) water molecules in the secondary hydration sphere. Similarly, as models of the water molecule in the secondary hydration sphere in lithium ion- or potassium ion-bearing aqueous solutions, we considered water molecules in $M^+(H_2O)_n$ (M = Li, K) that were hydrogen-bonded to water molecule(s) in the primary hydration sphere and surrounded by water molecules in the third hydration sphere, 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 [9] and on RPFRs of $Na^+(H_2O)_n$ clusters with n up to 100, modelling sodium ion-bearing aqueous solutions [8]. The Gaussian 98 and 03 program packages (Gaussian Inc.) were used for the MO calculations [10], 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 [11].

We first optimized the structures of the $M^+(H_2O)_n$ clusters (n = 1 – 10, 12, 16, 20, 24, 28, 32, 36, 40, 44, 50, 56, 62, 70, 80, 90, and 100; M = Li and K) in a sequential way. For example, $Li^+(H_2O)_{100}$ was optimized starting from the optimized structure of $Li^+(H_2O)_{90}$ and ten water molecules set up around it. For larger n values, two series of $M^+(H_2O)_n$ clusters were considered; two series of $Li^+(H_2O)_n$ (n = 12 or larger) clusters starting from the optimized $Li^+(H_2O)_8$ and two series of $K^+(H_2O)_n$ (n = 62 or larger) starting from the optimized $K^+(H_2O)_{56}$ were optimized. 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 H and ^{16}O basis. That is, for each of the optimized structures, the RPFRs of the $M^+[HD^{16}O(H_2^{16}O)_{n-1}]/M^+(H_2^{16}O)_n$ and $M^+[H_2^{18}O(H_2^{16}O)_{n-1}]/M^+(H_2^{16}O)_n$ (M = Li, K) isotopic pairs were estimated.

3. Results and Discussion

3.1. Optimized Structures

As an example of the optimized structures of the $M^+(H_2O)_n$ (M = Li, K) clusters considered, that of the $Li^+(H_2O)_{100}$ 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.

Except for small n values, the hydration number in the primary hydration sphere of the lithium ion was four, which was within the range of four to six generally accepted for the aqueous lithium ion [12, 13]. As

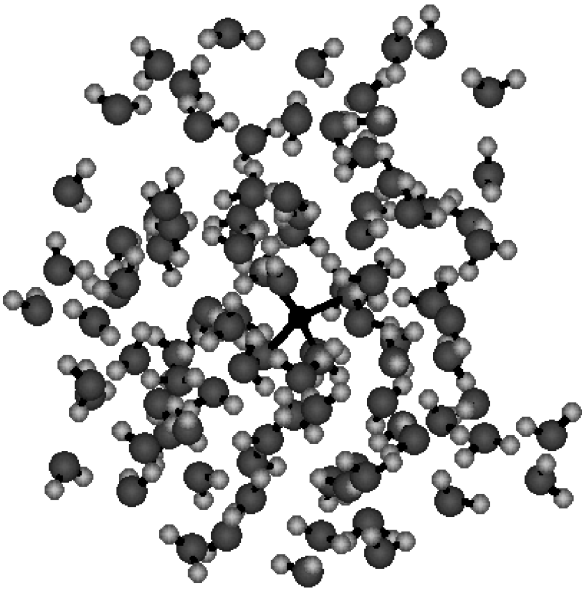

Fig. 1. Optimized structure of the $Li^+(H_2O)_{100}$ cluster. The black sphere denotes the lithium ion and the darker and lighter gray spheres denote oxygen and hydrogen atoms, respectively. No meaning is attached to the relative sizes of the spheres. Li – O bonds and O – H covalent bonds are shown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

is seen in the $Li^+(H_2O)_{100}$ cluster given as an example in Figure 2, water molecules in the primary hydration sphere of the lithium ion were divided into two groups, G1 and G2. The oxygen atom of the G1 water molecule was directly bonded to the lithium ion with the calculated average Li^+– O bond distance of 1.995 Å and hydrogen-bonded to a water molecule in the secondary hydration sphere with the calculated average hydrogen bond distance of 1.975 Å. Contrary to oxygen atoms of G1 water molecules, the oxygen atom of the G2 water molecule was directly bonded to the lithium ion with the calculated average Li^+– O bond distance of 1.946 Å, slightly shorter than that of the G1 oxygen atoms but has no hydrogen bond. Three water molecules belonged to G1 and the remaining one to G2. Each hydrogen atom of every water molecule, G1 and G2, in the primary hydration sphere around the lithium ion was hydrogen-bonded to a water molecule in the secondary hydration sphere with the average hydrogen bond distance of 1.898 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 eleven obtained for the $Li^+(H_2O)_n$ clusters with n equal to or larger than 70.

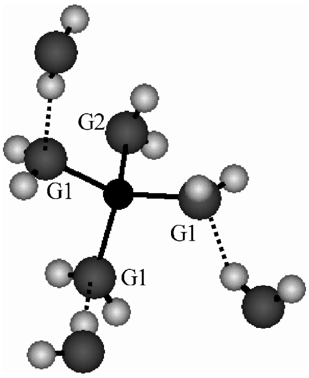

Fig. 2. Water molecules with an oxygen atom with a hydrogen bond (G1) and without a hydrogen bond (G2) in the primary hydration sphere of the lithium ion in the optimized $Li^+(H_2O)_{100}$ cluster. The black sphere denotes the lithium ion and the darker and lighter gray spheres denote oxygen and hydrogen atoms, respectively. No meaning is attached to the relative sizes of the spheres. Li – O bonds and O – H covalent bonds are shown with a solid line. Hydrogen bonds are drawn with a broken line. Unnecessary water molecules of the outer spheres are all omitted.

Except for small n values, the hydration number in the primary hydration sphere of the potassium ion was six or seven, which was within the range of five to ten reported in the literature [14]. 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 K^+– O bond between the potassium ion and the oxygen atom of a water molecule is not very strong, and consequently, the addition of several water molecules around the optimized $K^+(H_2O)_n$ cluster easily changed the hydration structure around the potassium ion. Contrary to oxygen atoms in the primary hydration sphere of the lithium ion, each of oxygen atoms in the primary hydration sphere of the potassium ion directly interacted with the potassium ion and was hydrogen-bonded to a hydrogen atom of a water molecule in the secondary hydration sphere as in the cases of $Na^+(H_2O)_n$ clusters [8]. The average K^+– O bond distance and the average hydrogen bond distance of the oxygen atoms in the octahedral (six-coordination) structure are 2.829 and 1.894 Å, respectively, and the corresponding values for the oxygen atoms in the decahedral (seven-coordination) structure are 2.942 and 1.896 Å, respectively. That is, the average K^+– O bond distance is shorter in the six-coordination than in the seven-coordination in the primary hydration sphere and the average hydrogen bond distance is equivalent regardless of the coordination (hydration) number. Each hydrogen atom of every water molecule in the primary hydration sphere was hydrogen-bonded to a water molecule in the secondary hydration sphere with the average hydrogen bond distance of 1.940 Å. No hydrogen bond was found between water molecules in the primary hydration sphere. The number of water molecules in the secondary hydration sphere could not be fixed; it was seventeen or eighteen for the six-coordination and twenty or twenty-one for the seven-coordination.

3.2. *Correlation of Reduced Partition Function Ratios with Bond Distances*

In Figure 3 are plotted the $\ln(\mathrm{RPFR(O)})$ values in the primary hydration spheres at 25 °C against the sum of the distances of the $\mathrm{M^+{-}O}$ bond ($\mathrm{M = Li,\ Na,\ K}$) and the $\mathrm{O\cdots H}$ hydrogen bond where O is the oxygen atom for which the RPFR was estimated, except for those of oxygen atoms without a hydrogen bond around the lithium ion (G2 oxygen) for which the $\ln(\mathrm{RPFR(O)})$ value is plotted against 2.2 times the $\mathrm{Li^+{-}O}$ bond distance. The factor of 2.2 with no physical meaning attached was chosen so that the plots for the G2 oxygen atoms (○) falled on a similar correlation line with those for the G1 oxygen atoms (●). As is seen in Figure 3, the $\ln(\mathrm{RPFR(O)})$ value in the primary hydration spheres is well inversely correlated with the sum of the $\mathrm{M^+{-}O}$ and $\mathrm{O\cdots H}$ distances with the correlation coefficient value of -0.784, -0.945, and -0.905 for oxygen atoms with a hydrogen bond around the lithium, sodium, and potassium ions, respectively. We made similar plots of the $\ln(\mathrm{RPFR(O)})$ value in the primary hydration sphere against the $\mathrm{M^+{-}O}$ bond distance and against the $\mathrm{O\cdots H}$ hydrogen bond distance, but no better correlations were obtained. The $\ln(\mathrm{RPFR(O)})$ values in the primary hydration sphere of the $\mathrm{M^+}$ ion ($\mathrm{M = Li,\ Na,\ K}$) are thus better correlated with the sum of the distances of the $\mathrm{M^+{-}O}$ bond and the $\mathrm{O\cdots H}$ hydrogen bond than with the $\mathrm{M^+{-}O}$ bond distance and with the $\mathrm{O\cdots H}$ hydrogen bond distance.

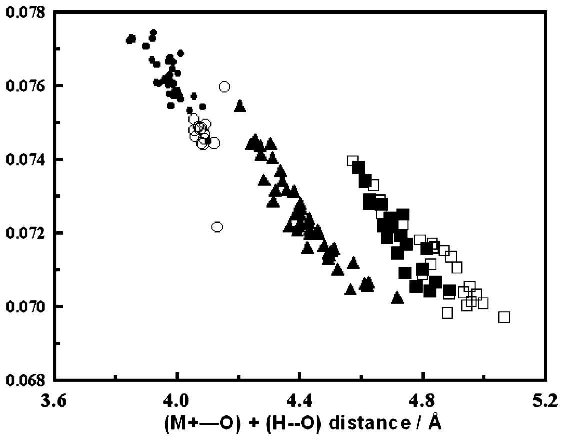

Fig. 3. Plots of the $\ln(\mathrm{RPFR(O)})$ values in the primary hydration spheres at 25 °C against the sum of the distances of the $\mathrm{M^+{-}O}$ bond ($\mathrm{M = Li,\ Na,\ K}$) and the $\mathrm{O\cdots H}$ hydrogen bond where O is the oxygen atom for which the RPFR was estimated. The ● and ○ marks respectively denote the $\ln(\mathrm{RPFR(O)})$ values of oxygen atoms with and without a hydrogen bond around the lithium ion, the ▲ marks denote those around the sodium ion [8], and the ■ and □ marks denote those in the six-coordination structure and in seven-coordination structure, respectively, around the potassium ion. The $\ln(\mathrm{RPFR(O)})$ values of oxygen atoms without a hydrogen bond around the lithium ion (○) are plotted against 2.2 times the $\mathrm{Li^+{-}O}$ bond distance instead of the sum of the distances of the $\mathrm{Li^+{-}O}$ and hydrogen bonds.

In Figure 4, the $\ln(\mathrm{RPFR(H)})$ values in the primary hydration spheres at 25 °C are plotted against the

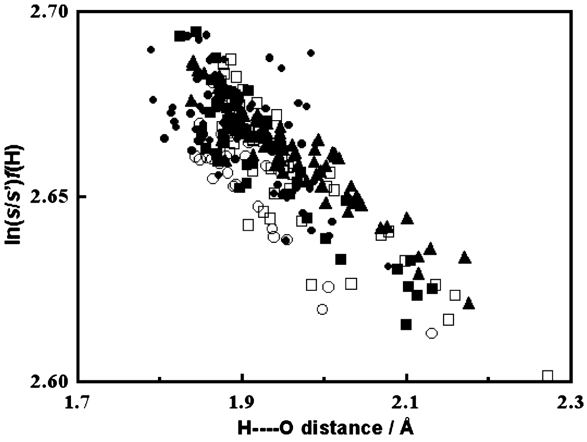

Fig. 4. Plots of the $\ln(\mathrm{RPFR(H)})$ values in the primary hydration spheres at 25 °C against the $\mathrm{O\cdots H}$ hydrogen bond distance where H is the hydrogen atom for which the RPFR was estimated. The ● and ○ marks denote the $\ln(\mathrm{RPFR(H)})$ values of hydrogen atoms of water molecules whose oxygen atoms have a hydrogen bond and do not have a hydrogen bond, respectively. The ▲ marks denote the $\ln(\mathrm{RPFR(H)})$ values of hydrogen atoms around the sodium ion [8], and the ■ and □ marks denote those in the six-coordination structure and in seven-coordination structure, respectively, around the potassium ion.

O$\cdots$H hydrogen bond distance where H is the hydrogen atom for which the RPFR was estimated. As a whole, the ln(RPFR(H)) value is inversely correlated with the hydrogen bond distance with the correlation coefficient of −0.805, and seems nearly independent of the kind of alkali metal ion (Li^+, Na^+, K^+).

3.3. Reduced Partition Function Ratios

The average values of the logarithms of $^{18}O/^{16}O$ RPFRs, $\ln(s/s')f(O)$, of oxygen atoms in the primary hydration spheres of lithium and potassium ions at 25 °C are plotted against n in $M^+(H_2O)_n$ in Figure 5, together with the corresponding data for $Na^+(H_2O)_n$ cited from the previous paper [8].

As for the $Li^+(H_2O)_n$ clusters, water molecules in the primary hydration sphere surrounded by water molecules in the secondary hydration sphere started appearing at $n = 32$ in the present calculations. As is seen in Figure 5, the $\ln(s/s')f(O)$ values of the oxygen atoms around the lithium ion, both with and without a hydrogen bond (● and ○), are larger than the value for bulk water at larger n values, which means that the heavier isotope of oxygen tends to be enriched in the primary hydration sphere of the lithium ion rather than in the bulk. The oxygen atoms with a hydrogen bond (●; G1 oxygen) have larger RPFR(O) values than those without a hydrogen bond (○; G2 oxygen), which shows that the formation of the hydrogen bond enhances the RPFR(O) value. Taking the average of the averages at $n = 90$ and 100, the $\ln(s/s')f(O)$ value of the oxygen atoms with and without a hydrogen bond in the primary hydration sphere around the lithium ion are estimated to be 0.07620 and 0.07480, respectively. We may be able to regard the weighted average of these two values, 0.07585, as the $\ln(s/s')f(O)$ value of the oxygen atom in the primary hydration sphere of an aqueous lithium ion at 25 °C, which is by about 2.8% larger than the value of bulk water.

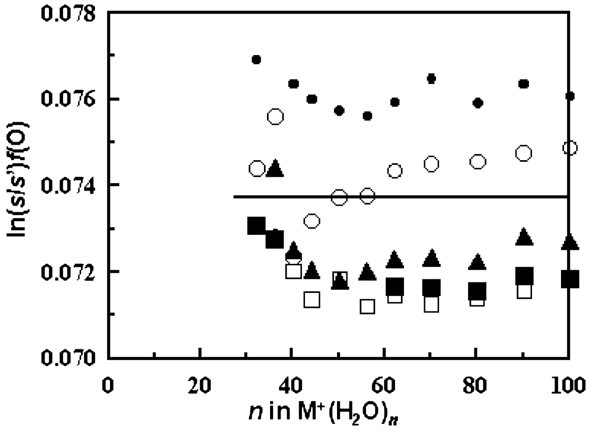

Fig. 5. Plots of the average ln(RPFR(O)) values in the primary hydration spheres at 25 °C against n in $M^+(H_2O)_n$ (M = Li, Na, K). The ● and ○ marks respectively denote the average ln(RPFR(O)) values of oxygen atoms with and without a hydrogen bond around the lithium ion at a given n. The ▲ marks denote the average ln(RPFR(O)) value of oxygen atoms around the sodium ion [8] at a given n. The ■ and □ marks denote the average ln(RPFR(O)) values of oxygen atoms in the six-coordination structure and in seven-coordination structure, respectively, around the potassium ion at a given n. The solid line represents the $\ln(s/s')f(O)$ value of 0.07376 estimated for bulk water at 25 °C [9].

As for the $K^+(H_2O)_n$ clusters, water molecules in the primary hydration sphere surrounded by water molecules in the secondary hydration sphere started appearing at $n = 32$. As is seen in Figure 5, the $\ln(s/s')f(O)$ values of the oxygen atoms in the six-coordination and seven-coordination structures around the potassium ion (■ and □), are both smaller than the value for bulk water, which means that the heavier isotope of oxygen tends to be depleted in the primary hydration sphere of the potassium ion relative to the bulk. They are also smaller than those around the sodium ions (▲), which means that the degree of depletion in the heavier isotope of oxygen around the solute cation is more substantial for the potassium ion than for the sodium ion. Although the $\ln(s/s')f(O)$ values of the oxygen atoms in the six-coordination structure (■) are very slightly larger than those in the seven-coordination structure (□), the difference is minimal and we can conclude that the $\ln(s/s')f(O)$ value of the oxygen atom in the primary hydration sphere of the potassium ion is nearly independent of the hydration number, six or seven. Taking the average of the averages at $n = 90$ and 100, we estimate the $\ln(s/s')f(O)$ of the oxygen atom in the primary hydration sphere around an aqueous potassium ion to be 0.07177, by about 2.7% smaller than the value of bulk water, at 25 °C.

Contrary to the $\ln(s/s')f(O)$ values in the primary hydration spheres, their average values in the secondary hydration spheres around lithium, sodium, and potassium ions all seem to converge to the value of bulk water with increasing n, although the data points for each of the alkali metal ions fluctuate as functions of n. If we use the values at $n = 90$ and 100, the logarithms of $^{18}O/^{16}O$ RPFRs in the secondary hydration spheres around lithium, sodium, and potassium ions at 25 °C are estimated at 0.07383, 0.07379, and 0.07377, respectively. This indicates that the presence of an alkali metal ion (Li^+, Na^+ or K^+) affects only the RPFR of an oxygen atom of a water molecule in the primary hydration spheres in alkali metal ion-bearing solutions and has little effect on the RPFR of an oxygen atom in the secondary and outer hydration spheres.

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 lithium and potassium ions at 25 °C are plotted against n in $M^+(H_2O)_n$ in Figure 6 together with the corresponding data for $Na^+(H_2O)_n$ from the previous paper [8]. The $\ln(s/s')f(\mathrm{H})$ values in the primary hydration spheres around lithium, sodium, and potassium ions estimated using the data at $n = 62$ through 100 are 2.66708, 2.66243, and 2.66216, respectively, all very close to the value of 2.66279 for bulk water. Although the value for the $Li^+(H_2O)_n$ clusters is seemingly slightly larger than for bulk water on the graph, the difference is only 0.16%. The calculated results graphically shown in Figure 6 thus indicate that the presence of an alkali metal ion (Li^+, Na^+, K^+) has little effect on the RPFR of a hydrogen atom in the primary hydration sphere around it. Similarly to the $\ln(s/s')f(\mathrm{H})$ values in the primary hydration spheres, their average values in the secondary hydration spheres around lithium, sodium, and potassium ions all seem nearly equal to that of bulk water. As a summary, we can conclude that the presence of alkali metal ions has little effect on the RPFR values of hydrogen atoms of water molecules in any hydration sphere around them.

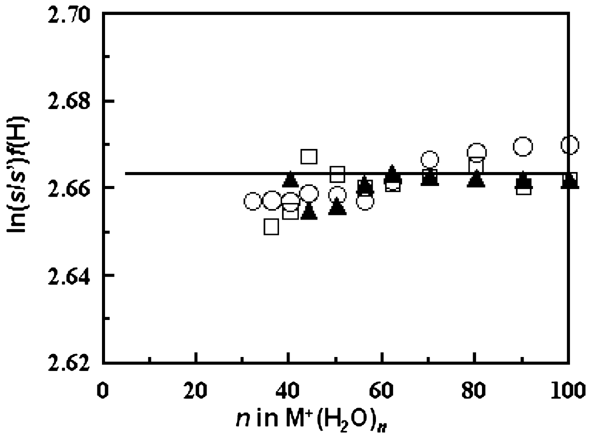

Fig. 6. Plots of the average ln(RPFR(H)) values in the primary hydration spheres at 25 °C against n in $M^+(H_2O)_n$ (M = Li, Na, K). The ○, ▲, and □ marks denote the average ln(RPFR(H)) values of hydrogen atoms for M = Li, Na, K, respectively. The solid line represents the $\ln(s/s')f(\mathrm{H})$ value of 2.66279 estimated for bulk water at 25 °C [9].

As has also been mentioned in the previous paper [8], the present results seem to be able to explain experimental results on isotope salt effects in some aspects, although it is beyond the scope of this study to apply them to any actual experimental system in a quantitative fashion. The present calculations showed that the influence of a solute alkali metal ion (Li^+, Na^+, K^+) on RPFRs of water molecules in metal ion-bearing 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) [4, 5]. The present calculations also indicated that, while they have little effects on D/H RPFRs, the alkali metal ions influence the RPFR values of oxygen atoms, which is consistent with the statement by Kakiuchi [4] 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:

The $^{18}O/^{16}O$ RPFR of a water molecule in the primary hydration sphere of lithium, sodium, and potassium ions are different from each other and from that of bulk water. The presence of lithium, sodium, and potassium ions, respectively, enhances, slightly reduces and reduces the $^{18}O/^{16}O$ RPFR value relative to that of bulk water. The influence of the alkali metal 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 bulk water. Contrary to the $^{18}O/^{16}O$ RPFR, the D/H RPFR is little affected by the presence of the alkali metal ions in any hydration sphere of these ions.

Similar calculations on anionic species like chloride ion are certainly needed to apply them to the elucidation of the reported isotope salt effects.

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