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Isotope Effects of Water Molecules on the Hydration of Alkali Metal and Halide Ions

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Based on the results of hydrogen isotope fractionation in aqueous alkali halide solutions at 25 °C, reported in previous papers, the hydrogen isotope effect between water molecules hydrated to a cation or an anion and bulk water molecules is estimated with the assumption that the equilibrium constant of the hydrogen isotope exchange reaction between the hydration water of sodium ion and bulk water is unity. The orders of the hydrogen isotope effects of alkali metal cations and halide anions are found to be $Cs^+ > K^+ > Na^+ > Li^+$, and $I^- > Br^- > Cl^-$ for a constant hydration number, respectively, and the hydrogen isotope effect is mainly influenced in anions rather than in cations. The oxygen isotope effect for alkali and halide ions is evaluated from the literature. The hydrogen and oxygen isotopic effects for the cations and anions show the same trend, but the magnitude of the hydrogen isotope effect for anions is significantly larger than that of the oxygen isotope effect.

The free energy of transfer of alkali metal and halide ions from H_2O to HDO is calculated from the hydrogen isotope effect for the individual ions. The calculated values are compared with the free energy of transfer from H_2O to D_2O obtained by electromotive force measurements, and are compared with the free energy of transfer from $H_2{}^{16}O$ to $H_2{}^{18}O$ calculated from the oxygen isotope effect.

The studies reported in this paper are based on hydrogen isotope fractionation in aqueous alkali halide solutions obtained by the hydrogen gas-liquid water equilibration method in previous papers.[1–3] The method consists of equilibrating the hydrogen isotopes of hydrogen gas with pure water and with aqueous solutions at constant temperature. We found that the deuterium content (the D/H atomic ratio) of hydrogen gas equilibrated with aqueous alkali halide solution at 25 °C increased upon the addition of salts. The changes in the deuterium content were roughly linear with the molality of the solute, which is taken to indicate a constant hydration number of the solute. The magnitudes of the hydrogen isotope effect of alkali halides are in the order $KI > NaI > KBr > CsCl \geqq NaBr > KCl > NaCl > LiCl$.

From a mechanistic point of view, the hydrogen isotope effect in aqueous solutions appears to be primarily due to a difference in the structure caused by the two isotopic water molecules, H_2O and D_2O. The effect on the difference is equivalent to the origin of the solvent isotope effect. A study of the hydrogen isotope effect in water molecules in the aqueous solutions consisted of monatomic ions, such as alkali halide solutions, may be useful for confirming the structure model of hydration. For this purpose we divide the fractionation factors into contributions of individual monatomic ions to evaluate their effects on the structure of the solvent water. By separating the contributions of individual ions, differences in the hydration properties of individual ions in H_2O and D_2O can be quantitatively estimated.

In addition, the hydration properties of individual ions in H_2O and D_2O thus estimated can be directly correlated to the thermodynamic properties of liquid H_2O and D_2O, such as vapor-pressure isotope effects,[4] and can be strongly correlated with the spectroscopic properties of H_2O and D_2O, such as infrared[5] and Raman[6] frequencies. For the same purpose as the present study, Newton and Friedman[7] proposed a neutron-diffraction method for investigating the solute-solvent D/H exchange equilibrium in aqueous solution, using semitransparent water, which has a hydrogen isotopic composition of 35.7%D (64.3%H).

The purpose of the present study is to elucidate the isotopic site preference of water molecules in an aqueous solution originating from the energy difference between the water molecules bound to ions and bulk water molecules, and an evaluation of the sign and magnitude of the isotope effects. In this paper, from the hydrogen isotope effect between aqueous alkali halide solutions and pure water obtained by previous studies,[1–3] we estimate the equilibrium constants of the hydrogen isotope exchange reaction between the hydration water of alkali metal cations or halide anions and bulk water molecules. On the basis of the equilibrium constants of hydrogen isotopes and the hydration numbers for the individual ions, we evaluate the free energy of transfer from H_2O to HDO, and compare with the data of oxygen isotope fractionation[8–12] and those of electromotive force measurements in H_2O and D_2O.[13,14] The structure and isotopic properties for the alkali metal and halide ions are discussed in terms of hydrogen bonding. For nonelectrolytes, the structure and isotopic properties of urea solution have already been interpreted based on hydrogen bonding.[15]

Isotope Effects between Aqueous Solution and Pure Water

The ratio of the hydrogen isotope fractionation factors between pure water-hydrogen gas (or water vapor) and aqueous solution-hydrogen gas (or water vapor) systems, β_D, is given by the following expression and obtained by measurements of the D/H ratio of the hydrogen gas[1–3] (or water vapor[15–17]) equilibrated with the liquid phase when identical water is used for the pure water and the aqueous solutions:

$$\beta_D = R_g^{pw}/R_g^{sol} \ (= R_V^{pw}/R_V^{sol}), \tag{1}$$

where R_g^{pw} and R_g^{sol} (R_V^{pw} and R_V^{sol}) are the D/H ratios of the hydrogen gas (or water vapor) equilibrated with pure water and the solution, respectively.

In the hydrogen gas–liquid water equilibration technique, in order to facilitate a measurement of the D/H ratios of hydrogen gas with a mass spectrometer designed for natural abundance measurements, the deuterium content of water is adjusted to a D/H ratio of about 5.9×10^{-4}. The D/H ratio of hydrogen gas in equilibrium with aqueous solutions made-up from the deuterium enriched water are generally around ratios of about 1.5×10^{-4}, because the fractionation factor between liquid pure water and hydrogen gas at 25 °C is 3.81.[18]

All of the β_D values for aqueous alkali halide solutions at 25 °C are smaller than unity,[3] which indicates that the D/H ratio of the hydrogen gas (water vapor) equilibrated with aqueous solution is higher than that of the hydrogen gas (water vapor) equilibrated with pure water. The values of $\beta_D - 1$ of aqueous alkali halide solutions in lower concentrations at 25 °C are presented in Table 1, and are obviously linear with the molality of alkali halide. The ratios between the values of $\beta_D - 1$ and the molality, $10^3 (\beta_D - 1)/m$, are averaged and the averaged ratios are presented in Table 1.

In order to compare the hydrogen isotope effect with the oxygen isotope effect,[8–12] the ratio of the oxygen isotope fractionation factors between pure water and the solution, $\beta^{18}O$, is analogously given by the CO_2-solution equilibration technique which Taube[9] first applied to his studies of the hydration of ions as:

$$\begin{aligned}\beta^{18}O &= R(^{18}O)_V^{pw}/R(^{18}O)_V^{sol} \\ &= R(^{18}O)_{CO_2}^{pw}/R(^{18}O)_{CO_2}^{sol},\end{aligned} \tag{2}$$

where $R(^{18}O)$ is the $^{18}O/^{16}O$ ratio of oxygen specified by the indexes V, CO_2, pw and sol, respectively. The average ratios of $(\beta^{18}O - 1)/m$ for aqueous alkali halide solutions in the concentration range up to 5.55 *m* were calculated from the compiled data by Bopp et al.[8] at 25 °C, which was obtained by the carbon dioxide–liquid water equilibration method, and are presented in Table 1. For alkali halide salts, the value of $\beta^{18}O - 1$ was found to be positive for LiCl, nearly zero for NaCl, and negative for KCl, CsCl, KBr, NaI and KI.

Origin of Isotope Effects on the Hydration of Ions

The hydrogen isotopic composition of hydrogen gas (water vapor) and the oxygen isotopic composition of carbon dioxide (water vapor) in equilibrium with liquid water change when a solute is dissolved in the liquid phase. The hydrogen and oxygen isotope effects are consequences of the different fractionation factors between hydrogen gas (water vapor and carbon dioxide) and various aqueous solutions. If the solute alters the water structure, the resultant changes caused by hydration of the solute should change the hydrogen gas- (water vapor- and carbon dioxide-) liquid water fractionation factor with a corresponding change in the isotope composition of the hydrogen gas (water vapor and carbon dioxide).

The above hypothesis is not readily amenable to a quantitative treatment. It is instructive, however, to point out that there is a problem in relating the absolute magnitude of the isotope effect observed to the thermodynamic properties of the solution. There is no doubt that ions in aqueous solutions are solvated and that the bonds between the water molecules and the solute ions are different from the bonds between the water molecules themselves. There are different species of water molecules in aqueous solution, and each species has its unique isotopic properties. In other words, the water molecules of the aqueous solution divide into the hydration water and the bulk water molecules, and bulk water remains the bond of pure water in a lower concentration range of the solution. However, bulk water molecules in a concentrated solution should have isotopic properties that are different from the bond of pure water. In fact, Kakiuchi[1] experimentally observed that the hydrogen isotope fractionation between LiCl solutions and pure water depends linearly on the LiCl concentration up to ca.12 *m*, and at higher concentrations a marked deviation from linearity takes place, as was also observed for the oxygen isotope fractionation measured by Bopp et al.[8]

The observed isotopic effects undoubtedly arise from both a separation of the water into three water species (H_2O, HDO and D_2O), and a change in the structure of the water species upon the addition of a solute. In order to delineate these effects, experiments must be performed accurately and precisely. For a quantitative interpretation, a suitable model of the aqueous solution structure and the criteria of the structure affecting properties of ions are needed. The isotopic exchange reaction of water molecules offers a model for such a direct means of making a distinction between the water in the hydration sphere of ions and the other water. The models proposed by Frank and Evans[19] and Frank and Wen[20] can already be applied to the oxygen isotope effects of salts, through an equation that relates the concentration of ions, their hydration number, and the fractionation factor between the hydration water and bulk water molecules.[9,12]

In addition, the isotope effects of water molecules on hydration must be significantly larger in the primary hydration sphere than in the secondary hydration sphere. We assumed that the effect of ions on the water molecules outside of the primary hydration sphere is negligible. The interaction of water molecules in the secondary hydration sphere may be almost the same as that of the remaining bulk water molecules.

Isotope Fractionation between the Hydration Water of Individual Ions and Bulk Water

We chose to explain the observed hydrogen and oxygen isotope effects in terms of separating the available water into at least three different species in the lower concentration range: water molecules bound in the primary hydration sphere of a cation (H_2O(c)), water molecules bound in the hydration sphere of an anion (H_2O(a)) and remaining bulk water molecules (H_2O(b)).

Table 1. Values of $10^3\ (\beta_\mathrm{D} - 1)$ as Functions of the Molality of Aqueous Alkali Halide Solutions in the Lower Concentration Range at 25 °C for the Hydrogen Isotope Effect Obtained by Kakiuchi,[3] and Averaged Values of the Slope of the Line $10^3\ (\beta - 1)$ Versus Molality, $10^3\ (\beta_\mathrm{D} - 1)/m$ and $10^3\ (\beta^{18}\mathrm{O} - 1)/m$, for Hydrogen Isotope Obtained by Kakiuchi and for Oxygen Isotope Obtained by Bopp et al.[8]

Salt	Molality (m)	$10^3\ (\beta_\mathrm{D} - 1)$	$10^3\ (\beta_\mathrm{D} - 1)/m$[a)] (Av)	$10^3\ (\beta^{18}\mathrm{O} - 1)/m$[b)] ($m < 5.55$) (Av)
LiCl	1.9	−2.5 ± 2.6	−1.2 ± 0.6	0.12 ± 0.01
	3.1	−3.6 ± 3.2		
	5.0	−5.4 ± 0.6		
NaCl	2.0	−4.8 ± 1.4	−2.3 ± 0.4	0.00
	4.0	−8.8 ± 0.7		
KCl	2.0	−5.8 ± 0.6	−2.7 ± 0.2	−0.14 ± 0.01
	3.0	−7.8 ± 0.8		
	4.0	−10.0 ± 1.1		
CsCl	2.0	−6.2 ± 0.7	−3.0 ± 0.2	−0.21 ± 0.02
	2.6	−7.5 ± 0.5		
	4.1	−11.9 ± 0.6		
NaBr	2.0	−5.3 ± 1.5	−2.9 ± 0.4	
	3.0	−9.0 ± 0.4		
KBr	2.0	−6.6 ± 0.6	−3.4 ± 0.2	−0.17 ± 0.01
	3.0	−10.4 ± 0.5		
NaI	2.0	−8.0 ± 0.6	−4.0 ± 0.2	−0.08 ± 0.01
	4.0	−15.7 ± 0.9		
KI	2.0	−8.8 ± 0.8	−4.2 ± 0.2	−0.20 ± 0.01
	4.0	−15.6 ± 0.7		

a) Hydrogen isotope effect between aqueous solutions and pure water obtained by the hydrogen gas–liquid water equilibration method[3]

b) Oxygen isotope effect between aqueous solutions and pure water obtained by the carbon dioxide–liquid water equilibration method[8]

Between these three species there are hydrogen and oxygen isotopic exchange reactions, such as:

$$\begin{aligned}&\mathrm{H_2O(c) + HDO(b) = HDO(c) + H_2O(b)},\\&\mathrm{H_2{}^{16}O(c) + H_2{}^{18}O(b) = H_2{}^{18}O(c) + H_2{}^{16}O(b)},\end{aligned}\tag{3}$$

$$\begin{aligned}&\mathrm{H_2O(a) + HDO(b) = HDO(a) + H_2O(b)},\\&\mathrm{H_2{}^{16}O(a) + H_2{}^{18}O(b) = H_2{}^{18}O(a) + H_2{}^{16}O(b)}.\end{aligned}\tag{4}$$

The equilibrium constants for these isotopic exchange reactions, ε_c and ε_a, can be expressed as

$$\varepsilon_\mathrm{c} = R_\mathrm{c}/R_\mathrm{b},\tag{5}$$

$$\varepsilon_\mathrm{a} = R_\mathrm{a}/R_\mathrm{b},\tag{6}$$

where R_c and R_a are the D/H and $^{18}\mathrm{O}/^{16}\mathrm{O}$ ratios of water molecules bound in the hydration sphere of the cation and anion, respectively, and R_b is the D/H and $^{18}\mathrm{O}/^{16}\mathrm{O}$ ratios of bulk water molecules.

From mass-balance considerations, we obtain the following relationship for the alkali halide solutions:

$$n_\mathrm{c} m R_\mathrm{c} + n_\mathrm{a} m R_\mathrm{a} + \{55.5 - (n_\mathrm{c} + n_\mathrm{a})\, m\}\, R_\mathrm{b} = 55.5 R_\mathrm{L}{}^\mathrm{sol},\tag{7}$$

where n_c and n_a are the hydration numbers of a cation and an anion, respectively, m is the molality of alkali halide, and $R_\mathrm{L}{}^\mathrm{sol}$ is the D/H and $^{18}\mathrm{O}/^{16}\mathrm{O}$ ratios of the solvent.

Assuming that the energy state of bulk water is equal to that of pure water, the isotope fractionation factor between water vapor and bulk water in the lower concentration range of alkali halide solutions is equal to that between water vapor (carbon dioxide) and pure water, i.e.,

$$R_\mathrm{L}{}^\mathrm{pw}/R_\mathrm{V}{}^\mathrm{pw} = R_\mathrm{b}/R_\mathrm{V}{}^\mathrm{sol},\ (R_\mathrm{L}{}^\mathrm{pw}/R_{\mathrm{CO_2}}{}^\mathrm{pw} = R_\mathrm{b}/R_{\mathrm{CO_2}}{}^\mathrm{sol})\tag{8}$$

and $R_\mathrm{L}{}^\mathrm{sol}/R_\mathrm{b}$ is equal to $(R_\mathrm{L}{}^\mathrm{sol}/R_\mathrm{V}{}^\mathrm{sol})\ (R_\mathrm{V}{}^\mathrm{sol}/R_\mathrm{b})$, and $(R_\mathrm{L}{}^\mathrm{sol}/R_{\mathrm{CO_2}}{}^\mathrm{sol})\ (R_{\mathrm{CO_2}}{}^\mathrm{sol}/R_\mathrm{b})$ which are the same as β_D and $\beta^{18}\mathrm{O}$, according to Eqs. 1 and 2, and $R_\mathrm{L}{}^\mathrm{sol} = R_\mathrm{L}{}^\mathrm{pw}$. Therefore, Eq. 7 can be rewritten as follows, using β (β_D or β^{18}O):

$$n_c m\varepsilon_c + n_a m\varepsilon_a + \{55.5 - (n_c + n_a)\, m\} = 55.5\beta. \tag{9}$$

Re-arranging Eq. 9,

$$\beta - 1 = \{n_c\,(\varepsilon_c - 1) + n_a\,(\varepsilon_a - 1)\}\, m/55.5. \tag{10}$$

Eq. 10 requires a linear variation of $\beta - 1$ with molality of alkali halide, if the hydration numbers (n_c and n_a) are constant, and the equilibrium constants (ε_c and ε_a) depend only on temperature and not on the molality.

Though it is obvious that the hydration number depends on the concentration, both values of $\beta - 1$ for hydrogen and oxygen isotopes in the lower concentration range for aqueous alkali halide solutions have a linear variation with molality. Assuming a constant hydration number for all of the alkali cations and halide anions (n_c and n_a) in Eq. 10, $\beta - 1$ has a linear variation with molality. We attempt to evaluate the products of the hydration number by the difference in the equilibrium constant from unity with respect to the ionic species, n_c ($\varepsilon_c - 1$) and n_a ($\varepsilon_a - 1$), in Eq. 10. We also used the assumption that the equilibrium constants of the hydrogen and oxygen isotope exchange reactions between the hydration water of sodium ion and bulk water, ε_c (Na$^+$), is unity, in order to compare with the thermodynamic properties for the free energy of transfer from H_2O to D_2O for the individual ions. This assumption, although no longer fashionable, is quite useful for employing the hydration concept. In other words, we assumed that the D/H and ^{18}O/^{16}O ratios of the hydration water molecules bound to Na$^+$ ion are equal to those of bulk water molecules. Splitting the values of 10^3 ($\beta - 1$)/m in the lower concentration range into the ionic components, the hydrogen and oxygen isotope effects of various single ions of alkali halides, n_c ($\varepsilon_c - 1$) and n_a ($\varepsilon_a - 1$), can be obtained, and are presented in Table 2.

Both ε_c (Li$^+$) values are higher than unity, which indicates that the D/H and ^{18}O/^{16}O ratios of the water molecules bound to Li$^+$ ion are higher than those of the hydration water bound to the Na$^+$ ion or those of bulk water molecules. The ε_c and ε_a values, except for the Li$^+$ ion, are smaller than unity, which means that HDO and $H_2{}^{18}O$ are depleted in the water molecules hydrated to a cation or an anion.

As shown in Table 2, for the hydrogen isotope effect, the n_a ($\varepsilon_a - 1$) values of the halide anions significantly deviate from zero more than the n_c ($\varepsilon_c - 1$) values of the alkali metal cations. This means that in aqueous alkali halide solutions the contribution of the hydrogen isotope fractionation between the water molecules hydrated to the halide anions and bulk water molecules is more dominant than that of the fractionation between the water molecules hydrated to the alkali metal cations

Table 2. The Products of the Hydration Number by the Difference of the D/H and ^{18}O/^{16}O Equilibrium Constants between Hydration Water and Bulk Water Molecules from Unity for Alkali Metal and Halide Ions at 25 °C, n ($\varepsilon - 1$), and the Values of the Free Energy Transfer, ΔG_t^0, from H_2O to D_2O, from H_2O to HDO and from $H_2{}^{16}O$ to $H_2{}^{18}O$

Ion	n_c (ε_aD $-$ 1)	$\Delta G_t^0 H_2O$–D_2O b)	$\Delta G_t^0 H_2O$–HDO c)	n_c ($\varepsilon_c{}^{18}$O $-$ 1)	$\Delta G_t^0 H_2{}^{16}O$–$H_2{}^{18}O$ e)
	n_a (ε_aD $-$ 1) a)	J mol^{-1}	J mol^{-1}	n_a ($\varepsilon_a{}^{18}$O $-$ 1) d)	J mol^{-1}
Li$^+$	0.062 ±0.037	−339 ± 389	−154 ± 92	0.0070 ±0.0007	−17 ± 2
Na$^+$	0	0	0	0	0
K$^+$	−0.020 ±0.012	54 ± 42	50 ± 30	−0.0073 ±0.0005	18 ± 1
Cs$^+$	−0.038 ±0.016		94 ± 40	−0.0114 ±0.0011	28 ± 3
Cl$^-$	−0.129 ±0.016	472 ± 42	320 ± 40	−0.0003 ±0.0003	1 ± 1
Br$^-$	−0.165 ±0.014	706 ± 42	409 ± 35	−0.0021 ±0.0008	5 ± 2
I$^-$	−0.217 ±0.010	957 ± 42	538 ± 25	−0.0041 ±0.0005	10 ± 1

a) Calculated values from the data of Table 1, using Eq. 10.

b) Values of the free energy of transfer from H_2O to D_2O calculated from the data of the electromotive force measurements by Greyson.[14]

c) Values of the free energy of transfer from H_2O to HDO calculated from the values of n (εD $-$ 1)

d) Calculated values from the data compiled by Bopp et al.[8] shown in Table 1, using Eq. 10.

e) Values of the free energy of transfer from $H_2{}^{16}O$ to $H_2{}^{18}O$ calculated from the values of n (ε^{18}O $-$ 1) and bulk water molecules. Concerning the hydrogen isotope effect, it becomes clear that the hydration caused by an anion is more influenced than by a cation. On the other hand, for the oxygen isotope effect the n_c ($\varepsilon_c - 1$) values of the alkali metal cations significantly deviate from zero more than the n_a ($\varepsilon_a - 1$) values of the halide anions. These facts indicate that the isotope effects on hydration are strongly influenced by the water molecules in the primary hydration sphere of the ions.

Comparing the hydrogen and oxygen isotope effects for alkali metal cations and halide anions, the correlation between the values of n ($\varepsilon_D - 1$) for the hydrogen isotopes and those of n ($\varepsilon^{18}O - 1$) for the oxygen isotopes is shown in Fig. 1 with the assumption that both ε values of the Na^+ ion for the hydrogen and oxygen isotopes are unity. The hydrogen and oxygen isotope effects for the cations and anions show the same trend, but the magnitude of the hydrogen isotope effect for the anions is clearly larger than that of the oxygen isotope effect. The D/H and $^{18}O/^{16}O$ ratios of the hydration water molecules bound to alkali metal and halide ions except Li^+ ion are lower than those of the hydration water bound to Na^+ ions (or lower than those of bulk water). Both the hydrogen and oxygen isotope effects in aqueous alkali halide solutions are obviously dependent on not only the cations, but also the anions, as shown in Fig. 1. The hydrogen isotope effect on hydration is caused by anions rather than by cations; on the other hand, the oxygen isotope effect is mainly caused by cations rather than anions. It is concluded that water molecules in the primary hydration sphere of ions mainly contribute to the isotope effects on hydration. The hydrogen isotope effect caused by alkali metal and halide ions must mainly be attributed to the energy change in the hydrogen bonding between the water molecules hydrated to these ions and the remaining bulk water molecules. On the other hand, the oxygen isotope effect must be mainly attributed to the energy changes between the cation and the coordinated water molecules.

Free Energy of Transfer from H_2O to HDO or D_2O and from $H_2{}^{16}O$ to $H_2{}^{18}O$

Greyson[13,14] measured the electromotive force (emf) of electrochemical cells of several alkali halides containing D_2O and H_2O solutions. The change in the free energy ($\Delta G_t{}^0{}_{H_2O-D_2O}$) measured by electrochemical cells with dilute solutions suggests that most salts have a higher standard free energy in D_2O than in H_2O. Friedman and Krishnan[20] tried to divide the various data of the free energy of transfer from H_2O to D_2O into the ionic ones with the conventional assumption that the free energy of transfer from H_2O to D_2O for sodium ion is zero. Based on the same assumption, the free energy of transfer from H_2O to D_2O ($\Delta G_t{}^0{}_{H_2O-D_2O}$) for alkali halide ions from the data obtained by Greyson[14] can be calculated. The values are shown in the third column of Table 2. The correlation between the hydrogen isotope effect for alkali halide ions, n ($\varepsilon_D - 1$), and the free energy of transfer from H_2O to D_2O, $\Delta G_t{}^0{}_{H_2O-D_2O}$, are shown in Fig. 2. Judging from the n ($\varepsilon_D - 1$) values and the $\Delta G_t{}^0{}_{H_2O-D_2O}$ values, the orders of the effects of alkali metal cations and halide anions on the structure of water are clearly found to be $Li^+ > Na^+ \geqq K^+$, and $I^- > Br^- > Cl^-$, respectively. The orders indicate the structure-making effects of alkali metal cations and the structure-breaking effects of halide

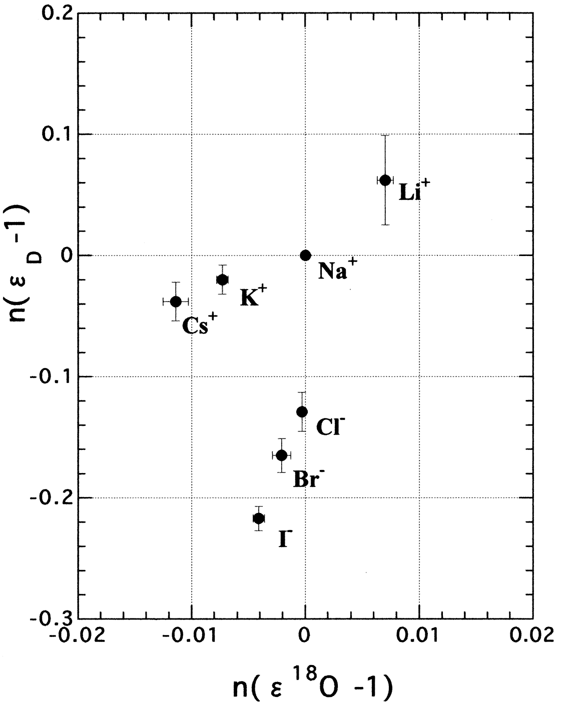

Fig. 1. Correlation of the hydrogen and oxygen isotope fractionations between hydration water and bulk water molecules, n ($\varepsilon_D - 1$) and n ($\varepsilon^{18}O - 1$), for alkali metal and halide ions at 25 °C.

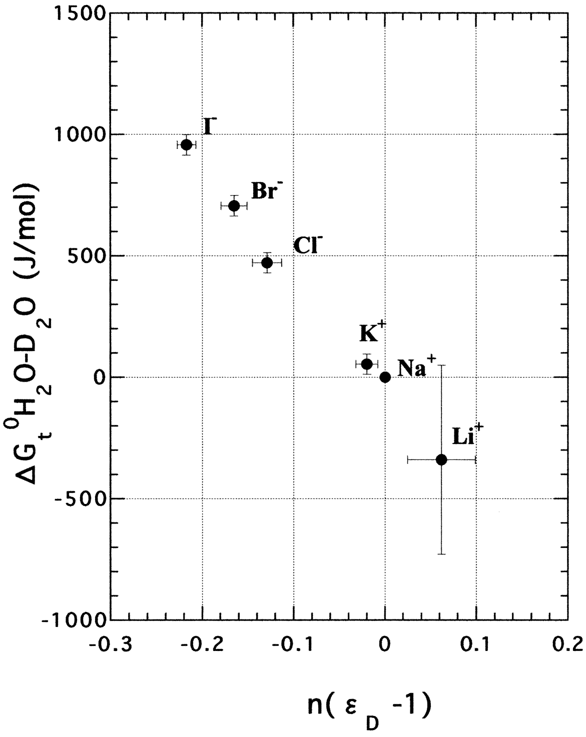

Fig. 2. Variation of the hydrogen isotope effect, n ($\varepsilon_D - 1$), obtained by this work and the free energy of transfer from H_2O to D_2O, $\Delta G_t{}^0{}_{H_2O-D_2O}$, calculated from the data obtained by the electromotive force measurements of alkali halides containing H_2O and D_2O,[14] for alkali metal and halide ions at 25 °C.

anions. As shown in Fig. 2, the correlation of the hydrogen isotope effect and the free energy of transfer from H_2O to D_2O for alkali halide ions at 25 °C are significantly good. Although the results of the free energy of transfer are obtained by a dilute salt solution and the results of the hydrogen isotope effect are obtained by dilute HDO in H_2O solution, the quantitative properties of these two values are obviously correlated.

We thus attempt to estimate the values of the thermodynamic free energy difference between H_2O and HDO ($\Delta G_t^0 H_2O\text{–}HDO$), from the hydrogen isotope effect between water molecules hydrated to a cation or an anion and bulk water molecules, n_c ($\varepsilon_c - 1$) and n_a ($\varepsilon_a - 1$), using by Eq. 10. Based on the criteria, $\varepsilon_c D$ (Na^+) = 1 and ΔG_t^0 (Na^+) $H_2O\text{–}HDO = 0$, the values of the single-ion contribution of the free energy of transfer from H_2O to HDO can be obtained as follows. With the assumption that the hydration number of ions in H_2O and HDO solutions is the same, the equilibrium reactions between water molecules bound to a cation or an anion and bulk water molecules in an aqueous alkali halide (MX) solution are written as:

$$(1/n_c)\ M\ (H_2O)_{n_c}{}^{+} + HDO = (1/n_c)\ M\ (HDO)_{n_c}{}^{+} + H_2O, \tag{11}$$

$$(1/n_a)\ X\ (H_2O)_{n_a}{}^{-} + HDO = (1/n_a)\ X\ (HDO)_{n_a}{}^{-} + H_2O. \tag{12}$$

The equilibrium constants of these reactions (K_c and K_a) are written as:

$$\begin{aligned} K_c &= [M\ (HDO)_{n_c}{}^{+}]^{1/n_c}\ [H_2O]/[M\ (H_2O)_{n_c}{}^{+}]^{1/n_c}\ [HDO] \\ &= (D/H)_{h_c}/(D/H)_b = \varepsilon_c D, \end{aligned} \tag{13}$$

$$\begin{aligned} K_a &= [X\ (HDO)_{n_a}{}^{-}]^{1/n_a}\ [H_2O]/[X\ (H_2O)_{n_a}{}^{-}]^{1/n_a}\ [HDO] \\ &= (D/H)_{h_a}/(D/H)_b = \varepsilon_a D. \end{aligned} \tag{14}$$

Using the relationship between the free energy of transfer and the equilibrium constant, $\Delta G = -RT \ln K$, the values of $\Delta G_t^0 H_2O\text{–}HDO$ at 25 °C can be calculated from the values of n ($\varepsilon D - 1$), and are shown in the fourth column of Table 2.

The obtained $\Delta G_t^0 H_2O\text{–}HDO$ values are evidently smaller than the $\Delta G_t^0 H_2O\text{–}D_2O$ values calculated from the emf data.[14] While the $\Delta G_t^0 H_2O\text{–}D_2O$ values are the processes of the reactions for M $(H_2O)_{n_c}{}^{+}\{H_2O\} \rightarrow$ M $(D_2O)_{n_c}{}^{+}\{D_2O\}$ and X $(H_2O)_{n_a}{}^{-}\{H_2O\} \rightarrow$ X $(D_2O)_{n_a}{}^{-}\{D_2O\}$, the $\Delta G_t^0 H_2O\text{–}HDO$ values are the processes of reactions for M $(H_2O)_{n_c}{}^{+}\{H_2O\} \rightarrow$ M $(HDO)_{n_c}{}^{+}\{HDO\}$ and X $(H_2O)_{n_a}{}^{-}\{H_2O\} \rightarrow$ X $(HDO)_{n_a}{}^{-}\{HDO\}$, respectively, where { } denotes the bulk solution. Thus, both ΔG_t^0 values are completely correlated and the $\Delta G_t^0 H_2O\text{–}HDO$ values are about half of the $\Delta G_t^0 H_2O\text{–}D_2O$ values, as shown in Table 2. This fact indicates that the change in the isotopic composition of water vapor in equilibrium with liquid water when a salt is added reflects the phenomenon of the hydration of ions correctly. It seems that the law of the geometric mean of the $\Delta G_t^0 H_2O\text{–}HDO$ and $\Delta G_t^0 H_2O\text{–}D_2O$ values is not established in Table 2. Though the law of the geometric mean on hydrogen isotope effect of water molecules is not strictly accurate, as mentioned in a previous paper,[22] in respect of the level of precision of both analyses, especially the emf measurements,[13,14] we can not discuss this point in detail.

Analogously, we attempted to estimate the values of thermodynamic free energy difference between $H_2{}^{16}O$ and $H_2{}^{18}O$, $\Delta G_t^0 H_2{}^{16}O\text{–}H_2{}^{18}O$, from the oxygen isotope effect between the hydration water of the cation or anion and bulk water, n_c ($\varepsilon_c{}^{18}O - 1$) and n_a ($\varepsilon_a{}^{18}O - 1$), using Eq. 10. Based on the criteria $\varepsilon_c{}^{18}O$ (Na^+) = 1 and ΔG_t^0 (Na^+) $H_2{}^{16}O\text{–}H_2{}^{18}O = 0$, the values of the single ion contributions of the free energy of transfer from $H_2{}^{16}O$ to $H_2{}^{18}O$ at 25 °C can be similarly calculated from the n ($\varepsilon^{18}O - 1$) values and are shown in the sixth column of Table 2.

The oxygen isotope effect between the hydration water and bulk water molecules, n ($\varepsilon^{18}O - 1$), caused by alkali halides, are significantly small in comparison with the hydrogen isotope effect, n ($\varepsilon D - 1$). Thus, the values of the free energy of transfer from $H_2{}^{16}O$ to $H_2{}^{18}O$ ($\Delta G_t^0 H_2{}^{16}O\text{–}H_2{}^{18}O$) are apparently very much smaller than those of the free energy of transfer from H_2O to HDO ($\Delta G_t^0 H_2O\text{–}HDO$).

Conclusions

1. The hydrogen isotopic compositions of hydrogen gas (water vapor) and the oxygen isotopic compositions of carbon dioxide in equilibrium with aqueous solutions correctly reflect phenomena on the hydration of solutes.
2. The water molecules in the primary hydration sphere of ions mainly contribute to the hydrogen and oxygen isotope effects on hydration.
3. The hydrogen and oxygen isotope effects (i.e., the products of the hydration number by the difference of the equilibration constant of the isotope exchange reactions between hydration water and bulk water from unity) for alkali metal and halide ions, n ($\varepsilon - 1$), show the same trend. The magnitude of the hydrogen isotope effect for anions is significantly larger than that of the oxygen isotope effect.
4. The hydrogen isotope effect caused by alkali metal and halide ions must be mainly attributed to an energy change in the hydrogen bonding between the water molecules hydrated to these ions and the remaining bulk water molecules. On the other hand, the oxygen isotope effect must be mainly attributed to energy changes between the cation and the coordinated water molecules.
5. The hydrogen isotope effect for alkali metal and halide ions, n ($\varepsilon D - 1$), obtained by this work are evidently correlated to the free energy of transfer from H_2O to D_2O obtained by the electromotive force measurements.

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