Hydrogen Isotope Fractionation in Aqueous Alkali Halide Solutions

Masahisa Kakiuchi

Department of Chemistry, Faculty of Science, Gakushuin University,
1-5-1 Mejiro, Toshima-ku, Tokyo 171, Japan

Z. Naturforsch. **52a**, 811–820 (1997); received April 15 1997

The D/H ratios of hydrogen gas in equilibrium with aqueous alkali halide solutions were determined at 25 °C, using a hydrophobic platinum catalyst. The hydrogen isotope effect between the solution and pure water changes linearly with the molality of the solution at low concentrations, but deviates from this linearity at higher concentration for all alkali halide solutions. The magnitude of the hydrogen isotope effect is in the order; $KI > NaI > KBr > CsCl \geqq NaBr > KCl > NaCl > LiCl$, at concentrations up to a molality of 4 m. The sign and trend of the hydrogen isotope effect is different from that of oxygen. In aqueous alkali halide solutions, the hydrogen isotope effect is influenced by both the cation and the anion species, while the oxygen isotope effect is mainly caused by the cation species. This suggests that the mechanism of hydrogen isotope fractionation between the water molecules in the hydration spheres and the free water molecules differs from the mechanism of the oxygen isotope fractionation. The hydrogen and oxygen isotope effects for alkali halides, except LiCl and NaCl, may be influenced by changes in energy of the hydrogen bonding in free water molecules.

Key words: Hydrogen Isotope, Alkali halide, D/H fractionation, Thermodynamics, Isotope effect.

Introduction

It is well known that the hydrogen and oxygen isotopic composition of water vapor in equilibrium with liquid water changes when a solute is added [1–8]. In order to explain this isotopic fractionation, the following model has been accepted [1–14]: In aqueous solutions the presence of two species of water molecules is assumed: water forming the hydration spheres and 'free' water (or 'bulk' water). This results in the fractionation of the D/H and $^{18}O/^{16}O$ ratios in water vapor that is assumed to be in equilibrium with free water and hydration water.

The fractionation of hydrogen isotopes is usually measured by the vapor-liquid equilibration technique [1–6]. The ratio $[(D/H)_{solution}/(D/H)_{vapor}]/[(D/H)_{pure\ water}/(D/H)_{vapor}]$ was found to be smaller than unity for most salt solutions, except for Na_2SO_4 and K_2SO_4 solutions, by Stewart and Friedman [1] and Sofer and Gat [2]. In both studies it was concluded that, except for the Na_2SO_4 and K_2SO_4 solutions, the D/H ratio of water molecules bound to ions is lower than that of free water molecules. For non-electrolytes, Kakiuchi and Matsuo [3] measured the effect of urea solutions at 15 and 25 °C and concluded that HDO is isotopically enriched in the urea-water cluster with hydrogen bonding.

Recently, Horita et al. [4–6] measured the effects of hydrogen and oxygen isotopes in single salt solutions from 50 to 100 °C [4], mixed salt solutions [5], and NaCl solution up to 350 °C [6]. However, the vapor-liquid technique is not suitable at low temperatures and high concentrations because it is difficult to sample enough water vapor for mass spectrometric analysis. Kakiuchi [7, 8] developed a new method to determine the D/H ratio of water vapor over an aqueous solution using a hydrophobic platinum catalyst. With this method the D/H ratio of hydrogen gas equilibrated with water vapor over aqueous lithium chloride and pure water solutions at 25 °C [7], and hydrogen gas equilibrated with water vapor over aqueous sodium chloride and pure water solutions from 10 to 95 °C [8] was measured.

Solvation of a solute causes changes in the energy state of water molecules and thereby changes in the distribution of isotopes between water molecules. On the other hand, the vapor pressure for pure H_2O and D_2O solutions changes when dissolving a solute in the respective liquid phase. In the aqueous alkali halide systems, the vapor pressure difference between solutions in H_2O and D_2O has been measured by Pupezin et al. [15] and Jakli et al. [16] at the same aquamolality. Another important thermodynamic property related to this study is the change in free energy associated with the transfer from H_2O to D_2O. Greyson [17, 18] investigated the influence of a solvent on the electro-

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Reprint requests to Dr. M. Kakiuchi; Fax: +81-3-59 92-10 29.

motive force of an ion exchange membrane cell and estimated the free energy of transfer of alkali halide salts.

In this study we present results of the hydrogen isotope fractionation between pure water and hydrogen gas, and aqueous alkali halide solutions and hydrogen gas, and attempt a more quantitative understanding of the hydrogen isotope effect. The experimental data of the hydrogen isotope effect are compared with those of oxygen, and the isotope fractionation between hydration water and free water in aqueous alkali halide solutions, and related thermodynamic effects are discussed.

Experimental

Experimental Procedure

The experimental method used in this study is essentially similar to that used and described in previous papers [7, 8]. Reagent grade alkali halide salts were thoroughly dried in vacuum at 100 °C for a few hours prior to dissolution. In order to facilitate the measurement of the D/H ratios of hydrogen gas with a mass spectrometer designed for natural abundance measurements, the deuterium content of water was adjusted to a D/H ratio of about 5.9×10^{-4}. The D/H ratios 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 [19]. In order to minimize the effect of contamination from ambient water vapor to the solvent, the deuterium-enriched water was prepared gravimetrically from heavy and normal water for each experiments with different solutes and concentrations.

The hydrogen gas-liquid water equilibration apparatus is identical to the one used in [7, 8]. The solutions are gravimetrically prepared by dissolving dried alkali halide salts in the deuterium-enriched water. The equilibration apparatus in which the hydrogen gas and liquid water sample is stored is immersed in a water bath at 25.0 ± 0.1 °C, which is regulated by a thermostat. Aqueous solution samples of sodium- and potassium iodide are covered with a light-intercepting film in order to prevent the production of I_3^- ions by daylight. The time required for equilibration was established by repeated analyses of the isotopic composition of the hydrogen gas in contact with the aqueous alkali halide solutions collected sequentially. Pure water required several hours to obtain a constant isotopic composition, but for concentrated solutions of alkali halides more than a few days were required.

After equilibration the hydrogen gas was separated from the liquid phase and the catalyst, and then the water vapor was removed by cooling it down to liquid nitrogen temperature. The hydrogen gas was collected using a Toepler pump, and then analyzed for its D/H ratio.

Isotopic Analysis

The isotopic analysis of aqueous solutions using the H_2 equilibration method is described in [7, 8]. In this method, one uses pure water (pw) and an aqueous solution (sol) which have the same isotope ratio (R_L) in the liquid state (L). The ratio (β_D) of the D/H ratios of R_V^{pw} and R_V^{sol} of the water vapors (V) in equilibrium with these liquids is determined by measuring the D/H ratios of R_g^{pw} and R_g^{sol} of hydrogen gas (g) in equilibrium with these water vapors. This is possible because at equilibrium R_g^{pw}/R_V^{pw} is equal to R_g^{sol}/R_V^{sol}, so that β_D is defined as,

$$\beta_D = R_V^{pw}/R_V^{sol} \tag{1}$$

and consequently

$$\beta_D = R_g^{pw}/R_g^{sol}. \tag{2}$$

In this study, liquid water with a D/H ratio of 5.9×10^{-4} and a tank hydrogen gas with a ratio of 3×10^{-5} were used. Although the molar ratio of hydrogen gas to liquid water was low during the experiments, the D/H ratio of liquid water changed slightly after equilibration with the hydrogen gas, because the D/H ratio of the two substances differs considerably. In order to obtain the β_D value relevant to the initial liquid water, the following material balance correction is necessary:

$$R_c = [1 + (n_g/n_L)/\alpha_{L-g}]\, R_g - [(n_g/n_L)/\alpha_{L-g}]\, R_g^i, \tag{3}$$

where, n_L and n_g are the respective molar amounts of liquid water and hydrogen gas, α_{L-g} is the D/H fractionation factor between liquid water and hydrogen gas, and R_g^i is the D/H ratio of hydrogen gas in equilibrium with the initial liquid water (R_L^i). The value of R_g is measured and R_g^i, n_g/n_L and α_{L-g} are known. Thus R_c can be determined by means of (3). R_g^{pw} and R_g^{sol} in (2) are the R_c values determined for pure water and the aqueous solution, respectively.

Measured D/H ratios (R) are usually expressed in terms of δD values (the delta notation) relative to a standard value R_s, defined as

$$\delta D = [(R/R_s) - 1] \times 10^3 . \tag{4}$$

Equation (3) can be rewritten using the delta notation, by replacing the R's by $(1 + 10^{-3}\,\delta D)\,R_s$,

$$\delta D_c = [1 + (n_g/n_L)/\alpha_{L-g}]\,\delta D_g - [(n_g/n_L)/\alpha_{L-g}]\,\delta D_g^i . \tag{5}$$

where, δD_c is the calculated value of hydrogen gas in equilibrium with the initial liquid (corresponding to R_c), δD_g is the measured value of the equilibrated hydrogen gas (R_g), and δD_g^i is the value of tank hydrogen gas used for the equilibration (R_g^i). Typical experimental values are $n_L = 0.3$ mol (corresponding to ca. 5 ml of pure water), $n_g = 0.4$ mmol, $\alpha_{L-g} = 3.81$ at 25 °C [19], and $\delta D_g^i = -800$‰. Equation (2) can be rewritten as follows using the delta notation:

$$\beta_D = R_c^{pw}/R_c^{sol} = (1 + 10^{-3}\,\delta D_c^{pw})/(1 + 10^{-3}\,\delta D_c^{sol}), \tag{6}$$

where, δD_c^{pw} and δD_c^{sol} are the δD_c values calculated in (5) for pure water and the aqueous solution, respectively.

Results

Results of the β_D determinations of the alkali halides, with concentrations up to 8 m at 25 °C, are presented in Table 1. Each data point represents the average value of several measurements. The overall error is estimated to be smaller than ±2 in terms of $10^3(\beta_D - 1)$. As shown in Table 1, the values obtained for δD_c^{sol} are higher than those of δD_c^{pw}, and all the β_D values are smaller than unity. This indicates that the D/H ratio of the hydrogen gas (the water vapor) equilibrated with an aqueous solution is higher than that of the hydrogen gas (the water vapor) equilibrated with pure water.

In Figs. 1 and 2, the $10^3(\beta_D - 1)$ values are plotted versus the molality of alkali chloride, and sodium and potassium halide solutions, respectively. For comparison, $10^3(\beta_D - 1)$ values are calculated from the results of Stewart and Friedman [1] and Sofer and Gat [2] at 20 °C, and are also plotted. The difference in $10^3(\beta_D - 1)$ values, because of the 5 °C temperature difference, is estimated to be within experimental error. While the data of Stewart and Friedman [1] show good agreement with the data derived from this study, the data for NaCl by Sofer and Gat [2] do not. In general, the larger the radius of the alkali and/or halide ions, the more negative the values of $10^3(\beta_D - 1)$. The magnitudes of the hydrogen isotope effect between the solution and pure water are in the order CsCl > KCl > NaCl > LiCl, KBr > NaBr, NaI > NaBr > NaCl, and KI > KBr > KCl. NaI and KI have very similar effects. These results indicate that both the alkali metal cations and halide anions influence the hydrogen isotope effect in aqueous alkali halide solutions.

As shown in Figs. 1 and 2 for the alkali halide solutions, the values of $\beta_D - 1$ seem to depend linearly on the molality. The salts with the highest solubilities (e.g., LiCl and NaBr) have a linear relation between $\beta_D - 1$ and the molality up to concentrations of 8 m. However at higher concentrations, for some salts (e.g., CsCl and KI) the values of $\beta_D - 1$ deviate clearly from this linearity. The ratios between the values of $\beta_D - 1$ and molality, $10^3(\beta_D - 1)/\mathrm{m}$, in aqueous alkali halide solutions are listed in Table 2. The linear curves are calculated from the data at concentrations up to 4 m.

Discussion

Hydrogen Isotope Fractionation between Hydrated Water and Free Water Molecules

Water molecules co-ordinated to a solute ion or molecule have different energies to free water molecules that are not involved in the hydration sphere of the solute. The difference in energy between the two water species results in unequal partitioning of hydrogen and oxygen isotopes between the two species.

Let us assume that an aqueous alkali halide solution is composed of two species of water molecules: free water ($H_2O(f)$) not interacting with cations or anions, and water bound in the first hydration sphere of cations and anions ($H_2O(h)$). Between these two species there is an isotopic exchange reaction

$$H_2O(h) + HDO(f) = HDO(h) + H_2O(f). \tag{7}$$

The equilibrium constants for the isotopic exchange reaction (ε_D) can be expressed as

$$\varepsilon_D = R_h/R_f , \tag{8}$$

where R_h and R_f are the D/H ratio of water bound in the hydration sphere of a solute and that of free water, respectively.

Table 1. Values of δD_c^{sol} and δD_c^{pw} (±1 standard deviation) as functions of the molality of aqueous alkali halide solution up to 8 m, and values of β_D calculated by (6), at 25 °C. Values in parenthesis are the number of measurements.

Salt	Molality	δD_c^{sol}	δD_c^{pw}	β_D	$10^3(\beta_D-1)$
LiCl[1]	1.9 m	67.2±1.5 (7)	64.5±2.1 (5)	0.9975	−2.5±2.6
	3.1 m	72.5±2.6 (9)	68.6±1.9 (4)	0.9964	−3.6±3.2
	5.0 m	4.3±0.3 (5)	−1.1±0.5 (4)	0.9946	−5.4±0.6
	6.0 m	76.0±1.8 (3)	70.2±1.6 (3)	0.9946	−5.4±2.4
	7.9 m	75.7±1.1 (5)	67.6±1.2 (6)	0.9925	−7.5±1.6
NaCl[2]	2.0 m	−32.9±1.2 (4)	−37.5±0.7 (5)	0.9952	−4.8±1.4
	4.0 m	−23.0±0.5 (6)	−31.6±0.5 (7)	0.9912	−8.8±0.7
	6.0 m	−21.7±0.3 (5)	−34.0±0.6 (5)	0.9874	−12.6±0.7
KCl	2.0 m	−45.4±0.5 (2)	−50.9±0.4 (3)	0.9942	−5.8±0.6
	3.0 m	17.6±0.3 (4)	9.7±0.7 (5)	0.9922	−7.8±0.8
	4.0 m	−41.2±0.8 (4)	−50.8±0.8 (4)	0.9900	−10.0±1.1
	4.8 m[3]	30.9±0.2 (5)	19.5±0.3 (9)	0.9889	−11.1±0.4
CsCl	2.0 m	−44.4±0.4 (7)	−50.3±0.6 (8)	0.9938	−6.2±0.7
	2.6 m	−42.2±0.3 (6)	−49.4±0.4 (4)	0.9925	−7.5±0.5
	4.1 m	−38.4±0.5 (4)	−49.8±0.3 (5)	0.9881	−11.9±0.6
	4.9 m	−37.7±0.5 (10)	−49.9±0.2 (11)	0.9873	−12.7±0.5
	7.4 m	−31.9±0.4 (10)	−48.6±0.3 (8)	0.9827	−17.3±0.5
	8.0 m	18.5±0.2 (7)	−1.5±0.7 (6)	0.9804	−19.6±0.7
NaBr	2.0 m	−45.8±0.7 (4)	−50.9±1.3 (3)	0.9947	−5.3±1.5
	3.0 m	−26.9±0.3 (7)	−35.7±0.2 (4)	0.9910	−9.0±0.4
	5.0 m	−20.9±0.8 (5)	−33.5±0.6 (10)	0.9871	−12.9±1.0
	6.0 m	52.7±0.3 (5)	36.4±0.4 (7)	0.9845	−15.5±0.5
	7.5 m	−15.4±0.3 (7)	−35.4±0.3 (5)	0.9797	−20.3±0.4
KBr	2.0 m	34.1±0.4 (8)	27.3±0.4 (9)	0.9934	−6.6±0.6
	3.0 m	−26.1±0.5 (7)	−36.2±0.2 (6)	0.9896	−10.4±0.5
	5.0 m	−20.9±1.3 (7)	−36.9±1.2 (7)	0.9837	−16.3±1.8
NaI	2.0 m	−25.5±0.4 (6)	−33.3±0.5 (6)	0.9920	−8.0±0.6
	4.0 m	−15.2±0.6 (7)	−30.7±0.7 (7)	0.9843	−15.7±0.9
	6.0 m	−14.1±0.3 (7)	−36.1±0.4 (5)	0.9777	−22.3±0.5
	8.0 m	65.3±0.7 (8)	36.5±0.5 (10)	0.9730	−27.0±0.9
KI	2.0 m	−22.9±0.5 (5)	−31.5±0.6 (7)	0.9912	−8.8±0.8
	4.0 m	−20.7±0.6 (7)	−36.0±0.4 (7)	0.9844	−15.6±0.7
	6.0 m	43.1±0.3 (8)	20.5±0.1 (5)	0.9783	−21.7±0.3
	8.0 m	43.8±0.4 (9)	16.7±0.4 (6)	0.9740	−26.0±0.6

The D/H ratios of hydrogen gas, δD_c^{sol} and δD_c^{pw}, are expressed as δD_c values relative to the laboratory standard. The values of δD_c^{pw} are scattered because the pure water used as a solvent for the alkali halide solutions was prepared by diluting the heavy water independently for each concentration.

[1] Recalculated values by using (5) and (6) from previous work [7].

[2] Values from previous work [8].

[3] Saturated solution.

Table 2. Calculated values of the slope of the line $10^3(\beta_D-1)$ versus molality, $10^3(\beta_D-1)/m$, for various alkali halide solutions at 25 °C from our works in Table 1. 'Av.' is the average slope which is calculated from the values up to 4 m.

Salt	m	β_D	$10^3(\beta_D-1)/m$	Av.
LiCl	1.9	0.9975	−1.3	−1.2
	3.1	0.9964	−1.2	
	5.0	0.9946	−1.1	
	6.0	0.9946	−0.9	
	7.9	0.9925	−0.9	
NaCl	2.0	0.9952	−2.4	−2.3
	4.0	0.9912	−2.2	
	6.0	0.9874	−2.1	
KCl	2.0	0.9942	−2.9	−2.7
	3.0	0.9922	−2.6	
	4.0	0.9900	−2.5	
	4.8*	0.9889	−2.3	
CsCl	2.0	0.9938	−3.1	−3.0
	2.6	0.9925	−2.9	
	4.1	0.9881	−2.9	
	4.9	0.9873	−2.6	
	7.4	0.9827	−2.3	
	8.0	0.9804	−2.5	
NaBr	2.0	0.9947	−2.7	−2.9
	3.0	0.9910	−3.0	
	5.0	0.9871	−2.6	
	6.0	0.9845	−2.6	
	7.5	0.9797	−2.7	
KBr	2.0	0.9934	−3.3	−3.4
	3.0	0.9896	−3.5	
	5.0	0.9837	−3.3	
NaI	2.0	0.9920	−4.0	−4.0
	4.0	0.9843	−3.9	
	6.0	0.9777	−3.7	
	8.0	0.9730	−3.4	
KI	2.0	0.9912	−4.4	−4.2
	4.0	0.9844	−3.9	
	6.0	0.9783	−3.6	
	8.0	0.9740	−3.3	

* Saturation

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

$$n_h\, m\, R_h + (55.5 - n_h\, m)\, R_f = 55.5\, R_L^{sol}\,, \tag{9}$$

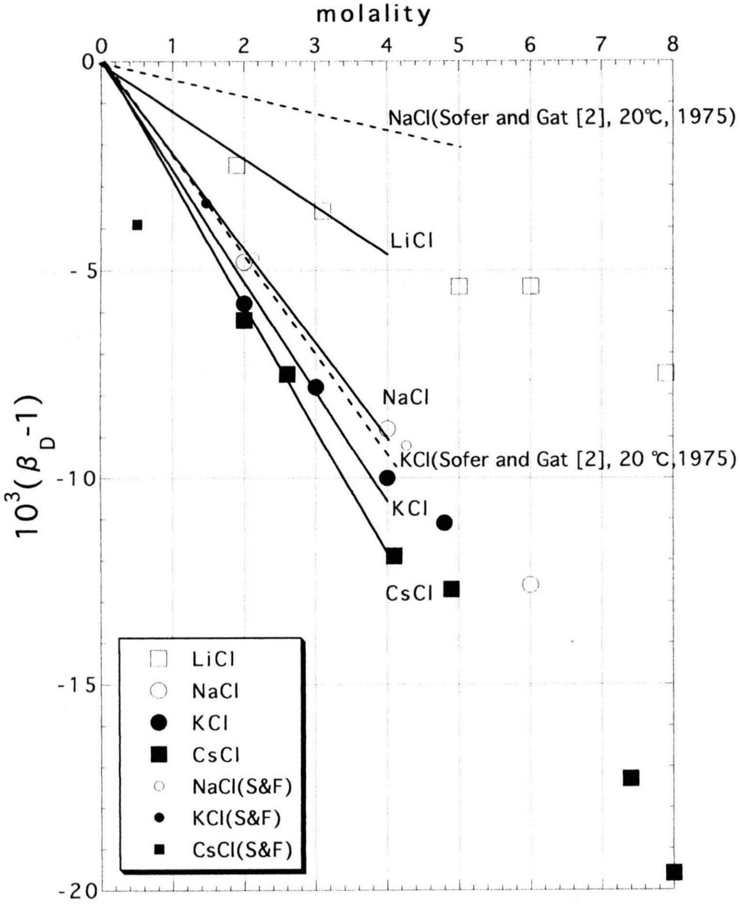
where n_h is the hydration number of the solute, m is the molality of the solution, and R_L^{sol} is the D/H ratio of the solvent.

Assuming that free water is identical with pure water, the isotopic fractionation factor between water vapor and free water in the lower concentration range of alkali halide solutions should be equal to that between water vapor and pure water, i.e.

$$R_L^{pw}/R_V^{pw} = R_f/R_V^{sol}\,, \tag{10}$$

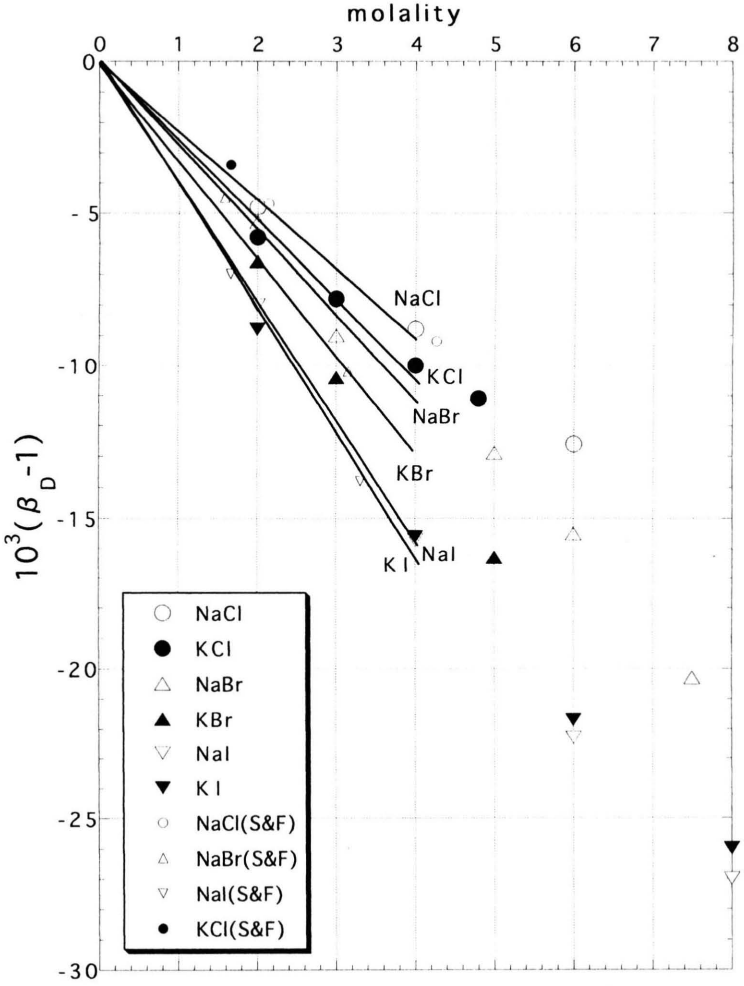
and R_L^{sol}/R_f is equal to $(R_L^{sol}/R_V^{sol})(R_V^{sol}/R_f)$, which is the same as β_D according to (1) and $R_L^{sol} = R_L^{pw}$. Therefore, (9) can be rewritten as follows, using β_D:

$$n_h\, m\, \varepsilon_D + (55.5 - n_h\, m) = 55.5\, \beta_D\,. \tag{11}$$



S&F : Stewart and Friedman [1], 20℃ (1975)

Fig. 1. The $10^3(\beta_D-1)$ values are plotted versus alkali chloride solutions at 25 °C up to a concentration of 8 m. The linear curves are calculated from the data at concentrations up to 4 m. The data of S&F (smaller symbols) were calculated from the measured values by Stewart and Friedman [1] at 20 °C. The hatched lines (20 °C) were taken from Sofer and Gat [2].



S&F : Stewart and Friedman [1], 20℃ (1975)

Fig. 2. $10^3(\beta_D-1)$ values for sodium and potassium halide solutions at 25 °C up to a concentration of 8 m. The data of S&F (smaller symbols) were calculated from the measured values by Stewart and Friedman [1] at 20 °C. The linear curves were fitted from the data for concentrations up to 4 m.

Rearranging (11):

$$\beta_D - 1 = n_h(\varepsilon_D - 1)\, m/55.5 . \tag{12}$$

Equation (12) requires a linear variation of $\beta_D - 1$ with molality, if the hydration number (n_h) is constant at lower concentrations, and the fractionation factor (ε_D) depends only on temperature and not on molality.

Figures 1 and 2 show that the value of $10^3(\beta_D - 1)$ varies linearly with molality at low concentrations. In the case of a salt deviating from this linearity at higher concentrations (e.g., CsCl and K1), it is possible that the hydration number is not constant up to saturation and/or that the fractionation factor is dependent on the molality. Even though it is obvious that the hydration numbers depend on concentration at higher concentrations, the values of $10^3(\beta_D - 1)/m$ in the lower concentration range of aqueous alkali halide solutions up to 4 m were averaged in Table 2. Assuming a constant hydration number (n_h) and a constant fractionation factor (ε_D), in (12), $\beta_D - 1$ varies linearly with the molality. In order to evaluate the fractionation factor (ε_D) for aqueous alkali halide solutions with constant hydration number (n_h), we assumed the sum of the hydration numbers for alkali halides. Bernal and Fowler [20] theoretically concluded that singly charged ions are 4-coordinated in aqueous solution. On the other hand, by X-ray diffraction the hydration number for all alkali cations and halide anions was experimentally determined to be 4 or 6 [21]. Therefore, we can evaluate the hydrogen fractionation factors (ε_D) between water bound to solute and free water in the lower concentration range up to 4 m, assuming that the added hydration number of alkali metal and halide ions is 8, 10 or 12. The ε_D values obtained are shown in Table 3. All the ε_D values are smaller than unity, indicating that the D/H ratio of the water bound in hydration spheres of solutes is lower than that of free water molecules, as shown in (8). The fractionation factors (ε_D) depend on the alkali halide salts and depend on both the cation and anion. This indicates a constant fractionation factor between the hydration water of the cation or anion and free water in the lower concentration range. On the assumption of a constant hydration number (n_h) for individual ions in aqueous alkali halide solutions, the values of the hydrogen isotope fractionation factor (ε_D) for the ions decrease from unity with an increase of the ionic radius of the solute in the order $Cs^+ > K^+ > Na^+ > Li^+$ for cation and $I^- > Br^- > Cl^-$ for anion, as shown in Table 3. Based on the ε_D values, the magnitude of the hydrogen isotope effect seems to be due to the contribution of anions rather than that of cations. In the following part of this paper we discuss the fractionation factors (ε_D) with respect to the ionic species of the alkali halides, based on the more reliable hydration numbers of individual ions.

Oxygen Isotope Fractionation in Aqueous Alkali Halide Solutions

In order to compare the hydrogen isotope effect in aqueous alkali halide solutions obtained in this work

Table 3. The hydrogen and oxygen fractionation factors (ε_D and $\varepsilon_{^{18}O}$) between the water molecules bound to solute and free water molecules, in aqueous alkali halide solutions at 25 °C. The sum of hydration numbers of solute is assumed with the hydration number of 4 or 6 for all alkali cations and halide anions.

Solute	$10^3(\beta_D - 1)/m$	ε_D			$10^3(\beta_{^{18}O} - 1)/m$*	$\varepsilon_{^{18}O}$		
		Sum of hydration numbers				Sum of hydration numbers		
		8	10	12		8	10	12
LiCl	−1.2	0.992	0.993	0.994	0.12	1.0008	1.0007	1.0006
NaCl	−2.3	0.984	0.987	0.989	0.00	1.0000	1.0000	1.0000
KCl	−2.7	0.981	0.985	0.988	−0.14	0.9990	0.9992	0.9994
CsCl	−3.0	0.979	0.983	0.986	−0.21	0.9985	0.9988	0.9990
NaBr	−2.9	0.980	0.984	0.987				
KBr	−3.4	0.976	0.981	0.984	−0.17	0.9988	0.9991	0.9992
NaI	−4.0	0.972	0.978	0.982	−0.08	0.9994	0.9996	0.9996
					−0.03	0.9998	0.9998	0.9999
KI	−4.2	0.971	0.977	0.981	−0.20	0.9986	0.9989	0.9991

* Calculated values from the data compiled by Bopp et al. [13].

with the oxygen isotope effects [3–6, 9–14], the oxygen isotope fractionation is analogously defined as

$$\beta_{^{18}O} = R(^{18}O)^{pw}_{V}/R(^{18}O)^{sol}_{V} = R(^{18}O)^{pw}_{CO_2}/R(^{18}O)^{sol}_{CO_2}, \quad (13)$$

where $R(^{18}O)$ is the $^{18}O/^{16}O$ ratio of oxygen specified by the indices V, CO_2, pw and sol, respectively. Negative $\beta_{^{18}O}-1$ values indicate that the $^{18}O/^{16}O$ ratio of water vapor and carbon dioxide equilibrated with aqueous solutions is higher than that of water vapor and carbon dioxide equilibrated with pure water. The values of $(\beta_{^{18}O}-1)/m$ calculated from the data compiled by Bopp et al. [13] at 25 °C are listed in Table 3. For alkali halide salts, $\beta_{^{18}O}-1$ was found to be positive for LiCl, nearly zero for NaCl, and negative for KCl, CsCl, KBr, NaI and KI. Assuming a constant hydration number (n_h), we can similarly evaluate the oxygen fractionation factors ($\varepsilon_{^{18}O}$). The $\varepsilon_{^{18}O}$ value of LiCl is higher than unity, which indicates that the $^{18}O/^{16}O$ ratio of the hydration water is higher than that of free water. The $\varepsilon_{^{18}O}$ values, except for LiCl and NaCl, are all smaller than unity, which means that $H_2{}^{18}O$ is depleted in the hydration water.

Comparison of the hydrogen and oxygen isotope effects in Table 3 shows that all the hydrogen isotope fractionation factors (ε_D) are smaller than unity, and that the $\varepsilon_{^{18}O}$ value of LiCl is larger than unity, the $\varepsilon_{^{18}O}$ value of NaCl is near unity, and the other values for alkali halides are smaller than unity. This indicates that the water molecules in the hydration spheres of alkali halide, except LiCl and NaCl, are enriched in lighter isotopes. Both the hydrogen and oxygen isotope effects are obviously dependent not only on the cations but also on the anions. While the hydrogen isotope effect seems to depend mainly on the anion rather than the cation, the oxygen isotope effect depends mainly on the cations rather than the anions [13, 14]. These results indicate that the mechanism of the hydrogen isotope fractionation between hydration water and free water is clearly different from that of oxygen isotope fractionation.

According to O'Neil [22], heavier molecules of water are enriched in ice rather than in liquid water at 0 °C. The hydrogen bonding network is more structured in ice than in liquid water, and D_2O is more structured than H_2O in the liquid state. If the energy of hydrogen bonding in ice or D_2O is larger than in liquid water or H_2O, then the heavier isotopes, D and ^{18}O, are enriched in the hydrogen bonded site, arising from the difference in the zero point energies. It is generally accepted that liquid water consists of hydrogen-bonded ice-like clusters of water molecules and non-hydrogen-bonded water molecules at equilibrium conditions (e.g., [23], [24]). The fractionation between hydration water and free water results from the energy difference of the hydration water and free water which is caused by a change in the structure of liquid water upon addition of solute. In the hydrogen and oxygen isotope effects caused by alkali halides, except LiCl and NaCl, the fact that free water molecules have the same structure as pure water, but are enriched in D and ^{18}O atoms, can be attributed to the increase in the energy of hydrogen-bonded clusters in free water, relative to pure water. Since heavier isotopes prefer to be incorporated into a site with a stronger bond, D and ^{18}O atoms are enriched in the hydrogen bonded sites. In addition, the fact that the hydrogen bonding site of water molecules in free water are enriched in D atoms, corresponds with the fact that the vapor pressure of D_2O is lower than that of H_2O, because the hydrogen bonded network of D_2O is stronger than that of H_2O.

Vapor Pressure Isotope Effect of Alkali Halide Solutions

The most important work in relation to the present study is the vapor pressure measurements in both H_2O and D_2O containing alkali halides, because they directly measure the isotopic free energy ratios of a solvent. The solvent vapor pressure isotope effect between H_2O and D_2O is determined in terms of

$$\Delta \ln R^{m}_{D_2O} = \ln(P^{0}_{H_2O}/P^{0}_{D_2O}) - \ln(P^{m}_{H_2O}/P^{m}_{D_2O}), \quad (14)$$

where the superscript 0 denotes pure water, and m represents the aquamolality which corresponds to the molality of the solute in 55.5 mol of solvent. Data of $\Delta \ln R^{m}_{D_2O}$ and $\ln \beta_D$ of alkali halide solutions at 25 °C are shown in Table 4. The values of $\Delta \ln R^{m}_{D_2O}$ for alkali halides and some salts were measured over a broad temperature- and concentration-range by Pupezin et al. [15] and Jakli et al. [16]. The measured values of $\Delta \ln R^{m}_{D_2O}$ are positive except for the value obtained for 2 m LiCl, and the values become larger if salts are added to both solvents. Positive $\Delta \ln R^{m}_{D_2O}$ means that the vapor pressure depression is smaller for D_2O than for H_2O.

The relationship between $\ln \beta_D$ and $\Delta \ln R^{m}_{D_2O}$ can be expressed as $\ln \beta_D = -1/2\, \Delta \ln R^{m}_{D_2O}$, if for an aqueous solution one assumes that the behavior of H_2O-HDO-D_2O mixing is ideal, and both equilibrium constants of the isotopic disproportionation reaction on liquid and gas phase are equal. In this case, the law of the geometric mean of vapor pressure, $P_{HDO} = (P_{H_2O} P_{D_2O})^{1/2}$, is always established. In the case of pure water, as mentioned in [8], the D/H fractionation factor between liquid and vapor is the same, within experimental error. Evidently, as a rule, the absolute values of $\ln \beta_D$ and $\Delta \ln R^m_{D_2O}$ become larger if an alkali halide is added to a liquid. This co-variation of $\ln \beta_D$ and $\Delta \ln R^m_{D_2O}$ can be interpreted as follows. The β_D measurements on H_2O-HDO mixtures show that HDO is less attracted by the solute than H_2O. Therefore, the degree of the vapor pressure depression of D_2O is smaller than that of the vapor pressure depression of H_2O when the solute is dissolved in the liquid phase. Although the qualitative trends with concentration of the alkali halides are the same in Table 4, the differences between the values of $\ln \beta_D$ and those of $1/2\ \Delta \ln R^m_{D_2O}$ are remarkably large at the various concentrations of alkali halide. This will be discussed in [25].

Table 4. Comparison of $10^3 \Delta \ln R^m_{D_2O}$ and $10^3 \ln \beta_D$ values for alkali halide salts at 25 °C.

Solute	Molality	$10^3 \Delta \ln R^m_{D_2O}$	$10^3 \ln \beta_D$
LiCl [1]	2.0 m	−0.1	−2.6*
	4.0 m	0.1	−4.7*
	6.0 m	0.8	−5.4*
NaCl [1]	2.0 m	0.3	−4.8
	4.0 m	1.0	−8.8
	6.0 m	2.3	−12.7
KCl [1]	2.0 m	0.4	−5.8
	4.0 m	1.8	−10.1
CsCl [1]	2.0 m	1.4	−6.2
	4.0 m	4.4	−12.0*
	6.0 m	7.1	−16.5*
NaBr [2]	2.0 m	0.0	−5.3
	4.0 m	0.9	−11.0*
	6.0 m	3.9	−15.6
	8.0 m	10.2	−21.9*
NaI [2]	2.0 m	0.3	−8.0
	4.0 m	1.6	−15.9
	6.0 m	4.7	−22.6
	8.0 m	10.1	−27.4

* Estimated values from this work.
[1] Pupezin et al. [15].
[2] Jakli et al. [16].

Free Energy Change of Transfer from H_2O to D_2O of Alkali Halide

The energy difference of solute in H_2O and D_2O is generally expressed as the free energy change of transfer from H_2O to D_2O. The free energy change can be related with the equilibrium constant of the isotopic exchange reaction between hydration water bound to alkali halide and free water as similar to (7):

$$H_2O(h) + D_2O(f) = D_2O(h) + H_2O(f). \qquad (15)$$

Table 5. Free energy (ΔG^0_t), enthalpy (ΔH^0_t) and entropy (ΔS^0_t) of transfer from H_2O to D_2O, and solubilities in H_2O and D_2O for alkali halide salts.

Solute	ΔG^0_t (cal/mol)	ΔH^0_t (cal/mol)	ΔS^0_t (cal/mol)	Solubilities [1]		X_{D_2O}/X_{H_2O} [2]
				H_2O	D_2O	
LiF	−58	−155	−0.33			1.15
LiCl	32	420	1.30	19.90	20.28	1.014
LiBr	67	560	1.65			
LiI	100	720	2.08			
NaF	−28	10	0.13			
NaCl	110	510	1.34	6.145	5.76	0.943
NaBr	170	650	1.61	9.20	9.07	0.988
NaI	230	810	1.95	12.34	12.18	0.989
KF	−3	60	0.21			
KCl	130	560	1.44	4.80	4.38	0.919
KBr	180	695	1.73	5.71	5.10	0.902
KI	240	865	2.09	8.90	8.07	0.919

[1] Solubilities are expressed as moles of solute per 55.5 moles of solvent.
[2] Solubility ratios are expressed as molar fraction ratios.

Greyson [17] measured the electromotive force (emf) of electrochemical cells of several alkali halide salts containing D_2O and H_2O solutions. The cell potentials were combined with available heat of solution data to determine the entropy of transfer of the salts between the isotopic solvents. The thermodynamic properties for the transfer from H_2O to D_2O, calculated from the emf data by Greyson [18] and for the solubilities of alkali halide at 25 °C in H_2O and D_2O from [26] are shown in Table 5. The change of free energy (ΔG^0_t) measured by electrochemical cells with dilute solutions suggests that alkali halide salts except LiF, NaF and KF have a higher standard free energy in D_2O than in H_2O, and the solubility suggest that alkali halide salts, except LiF and LiCl, are more soluble in H_2O than in D_2O. The enthalpy change (ΔH^0_t) for alkali halide salts correlates with the change in entropy (ΔS^0_t), as shown in Table 5.

Based on the data of the free energy change of transfer from H_2O to D_2O (ΔG^0_t) and those of the hydrogen isotope fractionation factors (ε_D), we can conclude that the water molecules bound to alkali halides, except

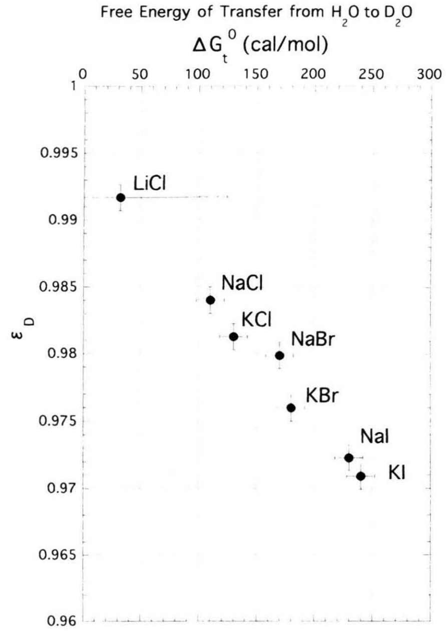


Fig. 3. Variation of the hydrogen fractionation factor (ε_D) between hydrated water and pure water molecules obtained by assuming the sum of hydration numbers of 8, versus the change of free energy for the transfer from H_2O to D_2O (ΔG_t^0) in aqueous alkali halide solutions at 25 °C obtained by Greyson [18].

LiF, NaF and KF, prefer H atom to D atom. The negative correlation of the hydrogen isotope fractionation factor (ε_D) obtained by assuming the sum of the hydration number 8 and the free energy change of transfer from H_2O to D_2O (ΔG_t^0) in aqueous alkali halide solutions at 25 °C are shown in Figure 3. Although the results of the free energy change of transfer are obtained for dilute solutions, these values have a linear correlation.

Krishnan and Friedman [27] estimated the free energy of transfer ($\Delta G_t^0(^{16}O \rightarrow {}^{18}O)$) from $H_2{}^{16}O$ to $H_2{}^{18}O$ for alkali metal ions at 25 °C, deduced from the data of Feder and Taube [9]. The $\Delta G_t^0(^{16}O \rightarrow {}^{18}O)$ values are apparently much smaller than the ΔG_t^0 values of the free energy of transfer from H_2O to D_2O.

Conclusions

1. The D/H ratios of hydrogen gas (the water vapor) in equilibrium with aqueous alkali halide solutions are higher than the D/H ratio of hydrogen gas (the water vapor) in equilibrium with pure water.
2. The D/H ratio of water molecules bound in the hydration sphere is estimated to be lower than that of free water for the alkali halide salts.
3. The magnitude of the hydrogen isotope effect of the alkali halide salts are in the order KI > NaI > KBr > CsCl ≧ NaBr > KCl > NaCl > LiCl.
4. The hydrogen isotope effect is markedly different from that of the oxygen isotope effect.
5. The hydrogen and oxygen isotope effects for alkali halides, except LiCl and NaCl, may be influenced by energy changes in hydrogen bonding in free water molecules.
6. The hydrogen isotope effect obtained in diluted solutions of HDO in H_2O is positively correlated with the change in the free energy of transfer from H_2O to D_2O calculated from the measurements of the electromotive force in H_2O and D_2O.

Acknowledgements

I wish to acknowledge the contribution of the graduate students at Gakushuin University, whose experimental work forms the basis for this study. I wish to thank Prof. H. Nagasawa (Gakushuin University) and Dr. K. Faure (Geological Survey of Japan) for critically reading the manuscript and for helpful comments. I am grateful to an anonymous competent reviewer for advise and comments.

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