Hydrogen Isotope Fractionation in Aqueous Alkaline Earth Chloride Solutions

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The D/H ratio of hydrogen gas in equilibrium with aqueous alkaline earth (Mg, Ca, Sr or Ba) chloride solutions measured at 25 °C using a hydrophobic platinum catalyst, was found to be higher than the D/H ratio equilibrated with the applied pure water. The hydrogen isotope effect between such solutions and pure water changes with the molality of the solutions. The order of the D/H ratios in alkaline earth chlorides is found to be $BaCl_2 > SrCl_2 \geq CaCl_2 \geq MgCl_2$. The hydrogen isotope effect in the aqueous chloride solutions of Mg, Ca, Sr or Ba ions is significantly larger than that in the aqueous chloride solutions of Li, Na, K or Cs ions. For $MgCl_2$ and $CaCl_2$ solutions, the hydrogen isotope effect is opposite to the oxygen isotope effect. The results are compared with the free energy change of transfer from H_2O to D_2O, and are discussed for the vapour pressure ratio of H_2O and D_2O of $CaCl_2$ solutions.

Key words: Hydrogen Isotopes; Alkaline Earth Chloride; D/H Fractionation; Isotope Effect in Aqueous Salt Solutions; Hydrated Water Molecules.

1. Introduction

In aqueous salt solutions, the water molecules hydrating the ions differ energetically from the water molecules of the bulk of the solvent. This difference brings about an unequal partition of the hydrogen and oxygen isotopes between the hydrated water molecules and the bulk water molecules, and thereby an isotope fractionation of hydrogen and oxygen occures between aqueous solutions and water vapour or of oxygen isotopes between aqueous solutions and carbon dioxide.

Since Feder and Taube [1] first applied the CO_2 equilibration technique to the oxygen isotope effect of aqueous salt solutions, various workers have measured the oxygen isotope composition of CO_2 in equilibrium with aqueous solutions [1 – 6]. In addition, Kakiuchi and Matsuo [7], Horita et al. [8 – 10], and Driesner and Seward [11] have measured the oxygen isotope composition of water vapour in equilibrium with aqueous solutions.

On the other hand, the hydrogen isotope effect of various aqueous solutions has been measured by the water vapour-liquid water equilibration technique (vapour-liquid equilibration technique) [7 – 13]. As a new method to obtain the hydrogen isotope effect, the hydrogen gas-liquid water equilibration technique (H_2 equilibration technique) was developed [14]. In this method the D/H ratios of hydrogen gas equilibrated with water vapour over aqueous LiCl and pure water at 25 °C [14] and those over aqueous NaCl and pure water from 10 to 95 °C were measured [15]. The effect of hydrogen isotopes in aqueous alkali halide solutions at 25 °C also measured [16], and the hydrogen isotope effect of alkali metal and halide ions on hydration was interpreted [17].

The studies reported in this paper were performed as a continuation of the study on the hydrogen isotope effect in aqueous alkali halide solutions obtained by the H_2 equilibration technique [16].

2. Experimental

2.1. Basic Equations

The D/H fractionation factor between liquid water (L) of an aqueous solution and water vapour (V) is defined as

$$\alpha_{\mathrm{sol-V}} = (\mathrm{D/H})_{\mathrm{L}}{}^{\mathrm{sol}} / (\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{sol}}, \quad (1)$$

where the superscript sol means the aqueous solution.

In the case of pure water, the D/H fractionation factor is defined as

$$\alpha_{\mathrm{pw-V}} = (\mathrm{D/H})_{\mathrm{L}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{pw}}, \quad (2)$$

where the superscript pw means pure water. The value of $\alpha_{\mathrm{pw-V}}$ at 25 °C is 1.078 [18].

In order to compare $\alpha_{\mathrm{sol-V}}$ with $\alpha_{\mathrm{pw-V}}$, the hydrogen isotope effect β_{D}, which is the ratio of the fractionation factors, is introduced as

$$\begin{aligned}\beta_{\mathrm{D}} &= \alpha_{\mathrm{sol-V}}/\alpha_{\mathrm{pw-V}} \\ &= [(\mathrm{D/H})_{\mathrm{L}}{}^{\mathrm{sol}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{sol}}] \\ &\quad /[(\mathrm{D/H})_{\mathrm{L}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{pw}}].\end{aligned} \quad (3)$$

When identical water is used for pure water and the aqueous solutions, $(\mathrm{D/H})_{\mathrm{L}}{}^{\mathrm{sol}}$ and $(\mathrm{D/H})_{\mathrm{L}}{}^{\mathrm{pw}}$ in (3) are equal. In this case, (3) becomes

$$\beta_{\mathrm{D}} = (\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{sol}}. \quad (4)$$

The value of β_{D} can be obtained by measuring the D/H ratio of water vapour equilibrated with pure water and that of water vapour equilibrated with the aqueous solution of different molality.

In this study, the hydrogen gas-liquid water equilibration technique (H_2 equilibration technique) was applied as mentioned below. The ratio β_{D} of $(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{pw}}$ and $(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{sol}}$ of water vapours in equilibrium with these liquid waters is determined by measuring the D/H ratios of hydrogen gas in equilibrium with these water vapours. This is possible because at equilibrium $(\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{pw}}$ is equal to $(\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{sol}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{sol}}$, so that β_{D} in (4) can be defined as

$$\beta_{\mathrm{D}} = (\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{V}}{}^{\mathrm{sol}} = (\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{sol}}, \quad (5)$$

where the subscript g represents hydrogen gas equilibrated with the liquid phase.

The relative deviation of the D/H ratio from the standard is given by the delta notation and is defined as

$$\delta\,\mathrm{D}\,(‰) = [\{(\mathrm{D/H})_{\mathrm{sample}}/(\mathrm{D/H})_{\mathrm{standard}}\} - 1]\cdot 10^3. \quad (6)$$

The standard used is the laboratory standard of a deuterium content of about 155 ppm. Equation (5) can be rewritten as follows, using the delta notation:

$$\begin{aligned}\beta_{\mathrm{D}} &= (\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{pw}}/(\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{sol}} \\ &= (1 + 10^{-3}\,\delta\,\mathrm{D_c}{}^{\mathrm{pw}})/(1 + 10^{-3}\,\delta\,\mathrm{D_c}{}^{\mathrm{sol}}),\end{aligned} \quad (7)$$

where $\delta\,\mathrm{D_c}{}^{\mathrm{pw}}$ and $\delta\,\mathrm{D_c}{}^{\mathrm{sol}}$ are the calculated $\delta\,\mathrm{D_c}$ values for the hydrogen gas in equilibrium with the initial pure water and the initial aqueous solution, respectively. The method of the $\delta\,\mathrm{D_c}$ value calculation has already been mentioned in previous papers [15, 16].

Then, using the value β_{D} and the fractionation factor between pure water and vapour, $\alpha_{\mathrm{pw-V}}$, we can obtain the fractionation factor between the aqueous solution and its water vapour as

$$\alpha_{\mathrm{sol-V}} = \beta_{\mathrm{D}}\,\alpha_{\mathrm{pw-V}}. \quad (8)$$

2.2. *Isotopic Analysis for β_D Determination*

The experimental method used here is essentially identical to that used and described for β_{D} determinations between pure water and aqueous solutions in previous papers [14 – 16]. The reagent grade anhydrous salts of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ used for this experiment 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 $5.8 \cdot 10^{-4}$. The D/H ratio of hydrogen gas in equilibrium with the deuterium-doped water was about $1.5 \cdot 10^{-4}$, as indicated by the fractionation factor 3.81 between liquid pure water and hydrogen gas at 25 °C [19].

The equilibration apparatus, in which the hydrogen gas and liquid water sample were stored, was immersed in a water bath maintained at (25.0 ± 0.1) °C, regulated using a thermostat. The time necessary for the equilibration was checked by measuring the $(\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{sol}}$ and $(\mathrm{D/H})_{\mathrm{g}}{}^{\mathrm{pw}}$ ($\delta\,\mathrm{D_c}{}^{\mathrm{sol}}$ and $\delta\,\mathrm{D_c}{}^{\mathrm{pw}}$) values of the hydrogen gas of samples from time to time. Pure water required several hours for a constant isotopic composition. Especially, in order to examine the attainment to the equilibrium conditions of aqueous solutions, the concentrated aqueous solutions were carefully checked in the same run. To attain solutions near saturation several days were necessary.

After equilibration, the hydrogen gas was separated from the liquid phase and the catalyst, followed by removal of the water vapour by cooling the sample with liquid nitrogen. The hydrogen gas was collected, using a Toepler pump, and subsequently analyzed for the D/H ratio using a mass spectrometer.

Table 1. Values of δD_c^{sol} and δD_c^{pw} (± standard deviation) as functions of the molality of aqueous alkaline earth chloride solutions, and values of β_D calculated by (7) at 25 °C. Values in parenthesis are the number of measurements.

Salt	Molality	δD_c^{sol} (‰)	δD_c^{pw} (‰)	β_D	$10^3(\beta_D-1)$
$MgCl_2$	1.0	-22.5 ± 0.4 (5)	-27.3 ± 0.4 (14)	0.9951	-4.9 ± 0.6
	2.0	-17.6 ± 0.5 (7)	-27.3 ± 0.4 (14)	0.9901	-9.9 ± 0.6
	4.0	-8.6 ± 0.4 (8)	-27.3 ± 0.4 (14)	0.9811	-18.9 ± 0.6
	5.7*	25.4 ± 1.0 (4)	-0.9 ± 0.3 (4)	0.9744	-25.6 ± 1.0
$CaCl_2$	1.0	6.4 ± 1.8 (5)	0.8 ± 0.9 (7)	0.9944	-5.6 ± 2.0
		5.2 ± 1.1 (4)	0.8 ± 0.8 (10)	0.9956	-4.4 ± 1.4
	2.0	-15.8 ± 0.6 (9)	-26.8 ± 0.7 (5)	0.9888	-11.2 ± 0.9
	4.0	-7.0 ± 0.2 (3)	-26.7 ± 0.3 (7)	0.9802	-19.8 ± 0.4
$SrCl_2$	1.0	5.8 ± 0.5 (7)	1.0 ± 0.5 (14)	0.9952	-4.8 ± 0.7
	2.0	10.2 ± 0.7 (5)	-0.8 ± 0.6 (7)	0.9891	-10.9 ± 0.9
	3.5*	16.3 ± 0.6 (6)	1.0 ± 0.5 (14)	0.9849	-15.1 ± 0.8
$BaCl_2$	0.9	-9.4 ± 0.2 (6)	-16.1 ± 0.4 (7)	0.9932	-6.8 ± 0.4
	1.7*	-4.1 ± 0.3 (5)	-16.1 ± 0.4 (7)	0.9880	-12.0 ± 0.5

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.
* Near the saturation.

Table 2. Calculated values of the slope of the line $10^3(\beta_D-1)$ versus molality (b) and ionic strength (I), $b_D = 10^3(\beta_D-1)/b$ and $b'_D = 10^3(\beta_D-1)/I$ for alkaline earth chloride solutions at 25 °C from our works in Table 1. The slopes b_D and b'_D are calculated by the values up to each molality from the lowest molality.

Salt	b (m)	$10^3(\beta_D-1)/b$	Slope b_D	$10^3(\beta_D-1)/I$	Slope b'_D
$MgCl_2$	1.0	-4.9 ± 0.6	-4.9	-1.6 ± 0.2	-1.6
	2.0	-5.0 ± 0.3	-5.0	-1.7 ± 0.1	-1.7
	4.0	-4.7 ± 0.2	-4.9	-1.6 ± 0.1	-1.6
	5.7*	-4.5 ± 0.2	-4.8	-1.5 ± 0.1	-1.6
$CaCl_2$	1.0	-5.0 ± 1.7	-5.0	-1.7 ± 0.6	-1.7
	2.0	-5.6 ± 0.5	-5.3	-1.9 ± 0.2	-1.8
	4.0	-5.0 ± 0.1	-5.2	-1.6 ± 0.1	-1.7
$SrCl_2$	1.0	-4.8 ± 0.7	-4.8	-1.6 ± 0.2	-1.6
	2.0	-5.5 ± 0.5	-5.2	-1.8 ± 0.2	-1.7
	3.5*	-4.3 ± 0.2	-4.9	-1.4 ± 0.1	-1.6
$BaCl_2$	0.9	-7.6 ± 0.4	-7.6	-2.5 ± 0.1	-2.5
	1.7*	-7.1 ± 0.3	-7.4	-2.4 ± 0.1	-2.5

* Near the saturation.

3. Results

In this study, the hydrogen isotope effect at 25 °C according to (7), β_D, which is the D/H ratio of hydrogen gas in equilibrium with pure water and the aqueous solutions of alkaline earth chloride, was obtained. Results of the β_D determination of the $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ solutions with concentrations up to the saturation point are presented in Table 1. Each point represents the average value of several measurements. The overall error is estimated to be smaller than ±1 except

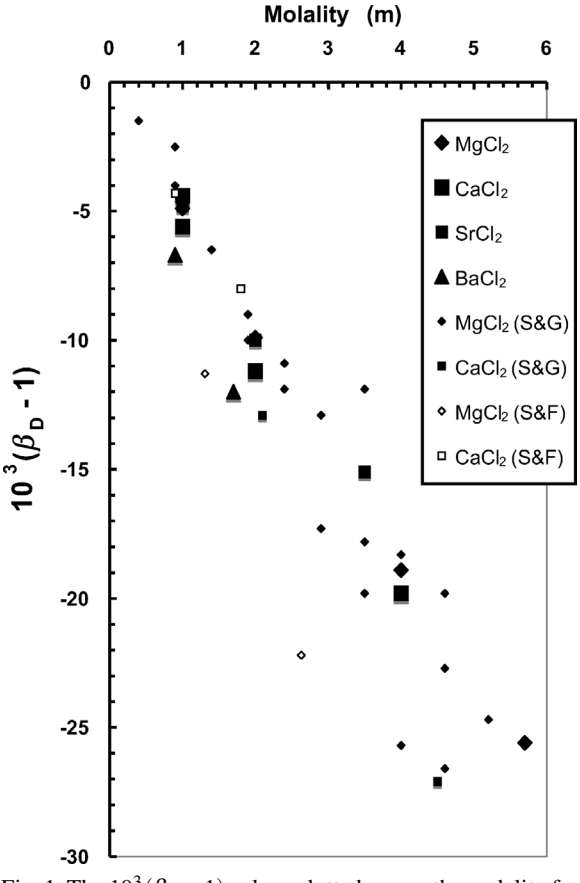

Fig. 1. The $10^3(\beta_D-1)$ values plotted versus the molality for alkaline earth chloride solutions at 25 °C up to a content of 5.7 m. The data of S&G (smaller symbols) were taken from Sofer and Gat [12] at 20 °C. The data of S&F (blank symbols) were calculated from the values obtained by Stewart and Friedman [13] at 20 °C.

1.0 m of $CaCl_2$ 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}. This indicates that the D/H ratios of hydrogen gas (water vapour), equilibrated with aqueous solutions of alkaline earth chloride, are higher than those of the hydrogen gas (water vapour) equilibrated with pure water. The order of the hydrogen isotope effects in alkaline earth chloride solutions is found to be $BaCl_2 > SrCl_2 \geq CaCl_2 \geq MgCl_2$. The magnitude of the hydrogen isotope effect of $MgCl_2$, $CaCl_2$ and $SrCl_2$ solutions is within experimental error.

In Fig. 1, the $10^3(\beta_D-1)$ values at 25 °C are plotted versus the molality (b) of the alkaline earth chloride solutions. For comparison with other workers, the $10^3(\beta_D-1)$ values at 20 °C calculated from the results of Sofer and Gat [12] and Stewart and Fried-

Table 3. Comparison of the hydrogen and oxygen isotope effects, β_D and $\beta(^{18}O)$, for the $MgCl_2$ and $CaCl_2$ solutions at 25 °C, obtained by this work and by O'Neil and Truesdell [6]. The values of the slopes of the lines, $b_D = 10^3(\beta_D - 1)/b$ and $b(^{18}O) = 10^3\{\beta(^{18}O) - 1\}/b$ were calculated from these data. The slopes b_D and $b(^{18}O)$ were calculated by the values up to each molality from the lowest molality.

Salt	Hydrogen isotope effect				Oxygen isotope effect			
	b	β_D	$10^3(\beta_D - 1)/b$	Slope b_D	b	$\beta(^{18}O)$	$10^3\{\beta(^{18}O) - 1\}/b$	Slope $b(^{18}O)$
$MgCl_2$	1.0	0.9951	−4.9	−4.9	2.0	1.00182	0.91	0.91
	2.0	0.9901	−5.0	−5.0	3.0	1.00300	1.00	0.96
					3.5	1.00366	1.05	0.99
	4.0	0.9811	−4.7	−4.9	4.0	1.00451	1.13	1.02
	5.7	0.9744	−4.5	−4.8	5.0	1.00521	1.04	1.03
$CaCl_2$	1.0	0.9950	−5.0	−5.0				
	2.0	0.9888	−5.6	−5.3				
	4.0	0.9802	−5.0	−5.2	4.0	1.00163	0.41	0.41

man [13] are also plotted in Figure 1. The difference in $10^3(\beta_D - 1)$ values based on the temperature difference of 5 °C is estimated to be within the experimental error. The data obtained in this study show very good agreement with the data of $MgCl_2$ by Sofer and Gat [12], though their values were considerably scattered. The absolute values of $10^3(\beta_D - 1)$ obtained by this study and Sofer and Gat [12] are in the order $CaCl_2 \geq MgCl_2$. However, the absolute values of $10^3(\beta_D - 1)$ calculated from the data by Stewart and Friedman [13] are in the order $MgCl_2 > CaCl_2$.

For aqueous alkaline earth chloride solutions at 25 °C, the ratio of $10^3(\beta_D - 1)$ and molality (b), $10^3(\beta_D - 1)/b$, and the ratio of $10^3(\beta_D - 1)$ and ionic strength (I), $10^3(\beta_D - 1)/I$, are listed in Table 2. We obtained the slopes, $b_D = 10^3(\beta_D - 1)/b$ and $b'_D = 10^3(\beta_D - 1)/I$, which were calculated by the values up to each molality from the lowest molality. Those are the best fit straight lines. As mentioned above, the slopes of aqueous solutions of $MgCl_2$, $CaCl_2$ and $SrCl_2$ for b_D and b'_D in the concentration range in this work are equal within the experimental error. The slopes of $BaCl_2$ are obviously larger than those of the other alkaline earth chlorides.

4. Discussion

4.1. Comparison with the Oxygen Isotope Effect in Aqueous Alkaline Earth Chloride Solutions

In order to compare the hydrogen isotope effect in aqueous alkaline earth chloride solutions obtained in this work at 25 °C with the oxygen isotope effect obtained by several workers [1 – 11], the ratio of the oxygen isotope fractionation factors between pure water and the aqueous solution, $\beta(^{18}O)$, is analogously defined for the vapour-solution or CO_2-solution equilibration technique as

$$\begin{aligned}\beta(^{18}O) &= \alpha(^{18}O)_{sol-V}/\alpha(^{18}O)_{pw-V} \\ &= (^{18}O/^{16}O)_V{}^{pw}/(^{18}O/^{16}O)_V{}^{sol} \\ &= \alpha(^{18}O)_{sol-CO_2}/\alpha(^{18}O)_{pw-CO_2} \\ &= (^{18}O/^{16}O)_{CO_2}{}^{pw}/(^{18}O/^{16}O)_{CO_2}{}^{sol},\end{aligned} \tag{9}$$

where the superscripts and subscripts are specified by the indices V, CO_2, pw and sol, respectively. Positive $(\beta(^{18}O) - 1)$ values indicate that the $^{18}O/^{16}O$ ratio of water vapour or carbon dioxide equilibrated with the aqueous solution is lower than that of water vapour or carbon dioxide equilibrated with pure water. For $MgCl_2$ and $CaCl_2$ solutions, the $\beta(^{18}O)$ values obtained by O'Neil and Truesdell [6] at 25 °C are presented in Table 3 in comparison with the β_D values. While the β_D values for the hydrogen isotope effect are smaller than unity, the $\beta(^{18}O)$ values for the oxygen isotope effect are larger than unity. The calculated values of $(\beta_D - 1)/b$ and $\{\beta(^{18}O) - 1\}/b$ are also listed in Table 3. We also obtained the slopes b_D and $b(^{18}O)$, which were calculated by the values up to each molality from the lowest molality. It seems that the slopes of $MgCl_2$ for b_D and $b(^{18}O)$ are constant up to the values 5.7 m and 5.0 m. It is shown that the structure of an aqueous $MgCl_2$ solution is not significantly changed up to the saturation point. While based on the hydrogen isotope effect the values of b_D for $MgCl_2$ and $CaCl_2$ are nearly equal, based on the oxygen isotope effect the value of $b(^{18}O)$ for $MgCl_2$ is significantly larger than that for $CaCl_2$.

4.2. Isotope Fractionation between Hydrated Water and Bulk Water Molecules

We chose to explain the observed hydrogen and oxygen isotope effects in terms of a separation of the avail-

able water into at least two different species: water molecules bound in the primary hydration sphere of a cation and an anion in an aquo complex, $H_2O(h)$, and remaining bulk water molecules, $H_2O(b)$.

Between these two species there are hydrogen and oxygen isotope exchange reactions such as

$$\begin{aligned} &H_2O(h) + HDO(b) = HDO(h) + H_2O(b), \\ &H_2{}^{16}O(h) + H_2{}^{18}O(b) = H_2{}^{18}O(h) + H_2{}^{16}O(b). \end{aligned} \tag{10}$$

The equilibrium constants for these isotope exchange reactions, ε, can be expressed as

$$\varepsilon = R_h/R_b, \tag{11}$$

where R_h is the D/H or $^{18}O/^{16}O$ ratio of water molecules bound in a hydration sphere and R_b is the D/H or $^{18}O/^{16}O$ ratio of remaining bulk water molecules. From mass-balance considerations we obtain

$$n_h b R_h + (55.5 - n_h b) R_b = 55.5 R_L{}^{sol}, \tag{12}$$

where n_h is the total hydration number which, in case of alkaline earth chloride solutions, adds the hydration number of a cation and duplicates the hydration number of a chloride ion; b is the molality of the solute, and $R_L{}^{sol}$ are the D/H and $^{18}O/^{16}O$ 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 vapour and bulk water is equal to that between water vapour (carbon dioxide) and pure water, i. e.

$$\begin{aligned} &R_L{}^{pw}/R_V{}^{pw} = R_b/R_V{}^{sol} \\ &(R_L{}^{pw}/R_{CO_2}{}^{pw} = R_b/R_{CO_2}{}^{sol}) \end{aligned} \tag{13}$$

and $R_L{}^{sol}/R_b$ is equal to $(R_L{}^{sol}/R_V{}^{sol})(R_V{}^{sol}/R_b)$ and $(R_L{}^{sol}/R_{CO_2}{}^{sol})(R_{CO_2}{}^{sol}/R_b)$ which are the same as β, according to (4) and (9) and $R_L{}^{sol} = R_L{}^{pw}$. Therefore, (12) can be rewritten as follows, using β [β_D or $\beta(^{18}O)$]:

$$n_h b\varepsilon + (55.5 - n_h b) = 55.5\beta. \tag{14}$$

Re-arranging (14):

$$\beta - 1 = n_h(\varepsilon - 1)b/55.5. \tag{15}$$

Equation (15) requires a linear variation of $(\beta - 1)$ with the molality of solute, if the total hydration numbers, n_h, are constant, and the equilibrium constants, ε, depend only on the temperature and not on the molality. Assuming a constant total hydration number for all the alkaline earth ions and the chloride ion (n_h) in (15), the values of $(\beta - 1)$ vary linearly with the molality. Though at the higher concentrations the bulk water does not exist, it seems that the values of $(\beta_D - 1)/b$ and $(\beta_D - 1)/I$ of the alkaline earth chloride solutions are constant, as shown in Table 2.

Comparison of the hydrogen and oxygen isotope effects in aqueous alkaline earth chloride solutions in Table 3 shows that for the hydrogen isotope effect the β_D values are smaller than unity and for the oxygen isotope effect the $\beta(^{18}O)$ values are larger than unity. This indicates that the hydration spheres of $MgCl_2$ and $CaCl_2$ solutions are enriched with the lighter isotope (H) and the heavier isotope (^{18}O).

4.3. Comparison with the Hydrogen Isotope Effect in Aqueous Alkali Chloride Solutions

In Fig. 2, the $10^3(\beta_D - 1)$ values at 25 °C of aqueous alkaline earth chloride solutions are compared with

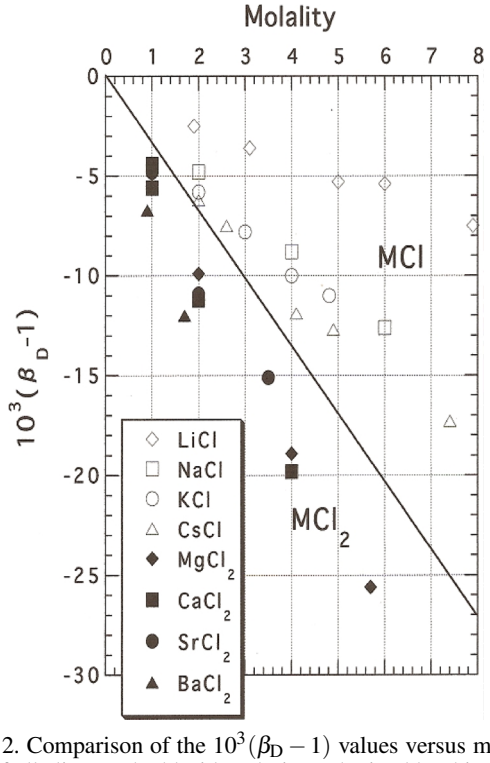

Fig. 2. Comparison of the $10^3(\beta_D - 1)$ values versus molality of alkaline earth chloride solutions obtained by this work and of alkali chloride solutions obtained by previous works [14, 16] at 25 °C up to 6 m.

those of aqueous alkali chloride solutions obtained in previous works [14–16]. The $10^3(\beta_D - 1)$ values of the alkaline earth chlorides indicate a larger hydrogen isotope effect than those of the alkali chlorides. This fact indicates that, depending on the contribution of the hydrogen isotope effect on hydration, the influence of the chloride ion might be larger than that of the alkali and alkaline earth cations in aqueous chloride solutions. However, if we consider the solvation of any solute in H_2O and D_2O, we recognize that D_2O will be a poorer solvent due to the greater strength of the hydrogen bonds in D_2O. Anions as chloride ions, which are capable of forming hydrogen bonds, are more strongly solvated in D_2O than H_2O. If so, this means that chloride ions prefer the heavier hydrogen atom (D) in comparison with the lighter hydrogen atom (H) in their hydration. Judging from the data of the hydrogen isotope effect, the alkali and alkaline earth metal ions are enriched in H atoms in hydration, and water molecules in the hydration sphere of alkaline earth metal ions are significantly enriched in H atoms in comparison with those of alkali metal ions.

4.4. Free Energy Change of Transfer from H_2O to D_2O

The energy difference of a 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 isotope exchange reaction between hydration water molecules bound to a cation and/or anion and bulk water molecules. The electromotive force (emf) of several alkali halides [20, 21] and alkaline earth chlorides [22] solutions containing D_2O and H_2O was measured with dilute solutions using electrochemical cells, and the calculated change in the free energy ($\Delta G_t{}^0H_2O$-D_2O) suggests that alkaline earth chloride salts have a higher standard free energy in D_2O than in H_2O. The magnitude of the change in free energy of transfer from H_2O to D_2O for chloride salts is in the order $LiCl < NaCl < KCl < MgCl_2 < CaCl_2 \leq SrCl_2 < BaCl_2$.

The data of the free energy change of transfer from H_2O to D_2O ($\Delta G_t{}^0H_2O$-D_2O) and the values of the slope of $b_D = 10^3(\beta_D - 1)/b$ at the content of 2 m at 25 °C are plotted in Figure 3. Judging from the negative correlation of the slope b_D and the free energy change of transfer from H_2O to D_2O in these solutions, we can conclude that the water molecules bound to these alkali halides and alkaline earth chlorides prefer

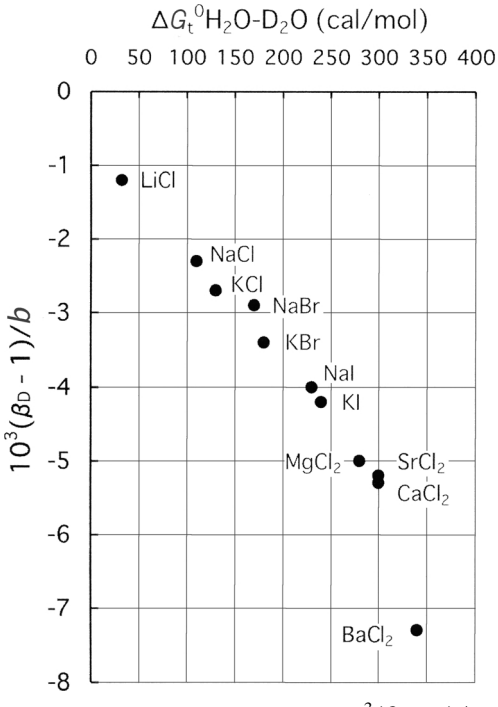

Fig. 3. Correlation of the slope of $b_D = 10^3(\beta_D - 1)/b$ at 2 m versus the change of free energy ($\Delta G_t{}^0H_20 - D_20$) obtained by electromotive force (emf) measurement [20–22] for alkali halides and alkaline earth chlorides at 25 °C.

the H atom to the D atom. Although the results of the free energy change of transfer are obtained for dilute solutions of salts, these values have a linear correlation. This fact indicates that the change of the isotopic composition of water vapour in equilibrium with liquid water, when a salt is added, reflects the phenomenon of the hydration of ions correctly. It is concluded that water molecules of the lighter hydrogen isotope (H) are enriched in the hydration sphere of these salts.

4.5. Vapour Pressure Isotope Effect

The distribution of the isotopic water molecules, H_2O, HDO and D_2O, in the vapour and liquid phase is related to the D/H fractionation factor between the liquid and vapour phase, $\alpha_{L\text{-}V}$, and the vapour pressure ratio between pure H_2O and D_2O, P_{H_2O}/P_{D_2O}. The vapour pressure ratio measurements of separated isotopes in aqueous solutions are particularly useful because they directly give the isotopic free energy ratios of the solvent. The solvent vapour pressure isotope effect between pure H_2O and D_2O has been determined

Table 4. Comparison of $10^3 \ln \beta_D$ and $10^3 \Delta \ln R^m{}_{D_2O}$ values for aqueous $CaCl_2$ solutions at 25 °C. The γ_m values were evaluated from the $10^3 \ln \beta_D$ and $10^3 \Delta \ln R^m{}_{D_2O}$ values using the value of $\gamma_0 = 1.92$ in pure water obtained by Kakiuchi [24] and the value of $10^3 \ln(P^0{}_{H_2O}/P^0{}_{D_2O})$ in pure water taken to be 145.6 by Pupezin et al. [25].

Aquamolality	$10^3 \ln \beta_D$	$10^3 \Delta \ln R^m{}_{D_2O}$ *	γ_m
2.0	-11.3 ± 0.9	7.9 ± 2.0	2.13 ± 0.01
4.0	-20.0 ± 0.4	28.3 ± 2.0	2.10 ± 0.01

* Obtained by Jakli et al. [23].

in terms of

$$\Delta \ln R^m{}_{D_2O} = \ln(P^0{}_{H_2O}/P^0{}_{D_2O}) - \ln(P^m{}_{H_2O}/P^m{}_{D_2O}), \quad (16)$$

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.

Only the data of $\Delta \ln R^m{}_{D_2O}$ of $CaCl_2$ measured by Jakli et al. [23] are available for the comparison with the results of β_D values obtained in this work, and are shown in Table 4. The measured values of $\Delta \ln R^m{}_{D_2O}$ are positive and become larger if $CaCl_2$ is added to both solvents. Positive $\Delta \ln R^m{}_{D_2O}$ means that the vapour pressure depression is smaller for D_2O than for H_2O. Evidently the absolute values of $\ln \beta_D$ and $\Delta \ln R^m{}_{D_2O}$ become larger when $CaCl_2$ is added to the 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 vapour pressure depression of D_2O is smaller than that of the vapour pressure depression of H_2O.

As pure HDO does not exist, it is complicated to compare the experimental data of the vapour pressure ratio of pure H_2O and D_2O with those of a D/H fractionation factor between the liquid and vapour phase directly. In order to connect both values, the vapour pressure ratio and the D/H fractionation factor, Kakiuchi [24] proposed the γ value with the assumption that the experimental data of the D/H fractionation factor, α_{L-V}, are equal to the vapour pressure ratio between H_2O and hypothetical HDO, P_{H_2O}/P_{HDO}:

$$\alpha_{L\text{-}V} = P_{H_2O}/P_{HDO}. \quad (17)$$

Thus for pure water,

$$\gamma_0 = \ln(P^0{}_{H_2O}/P^0{}_{D_2O})/\ln(P^0{}_{H_2O}/P^0{}_{HDO}) = \ln(P^0{}_{H_2O}/P^0{}_{D_2O})/\ln \alpha_{pw-V}. \quad (18)$$

And for an aqueous solution of aquamolality m,

$$\gamma_m = \ln(P^m{}_{H_2O}/P^m{}_{D_2O})/\ln(P^m{}_{H_2O}/P^m{}_{HDO}) = \ln(P^m{}_{H_2O}/P^m{}_{D_2O})/\ln \alpha_{sol-V}(m). \quad (19)$$

When the aquamolality is m, the definition of β_D in (3) is

$$\ln \beta_D(m) = \ln \alpha_{sol-V}(m) - \ln \alpha_{pw-V}. \quad (20)$$

Based on the values of $\gamma_0 = 1.92$ at 25 °C in pure water [24], we would attempt to evaluate the γ_m values for $CaCl_2$ solutions from the data of $\ln \beta_D$ and those of $\Delta \ln R^m{}_{D_2O}$ at 25 °C, using (16), (18), (19) and (20). The γ_m values are larger than the γ_0 value in pure water and are given in Table 4. It is concluded that the equilibrium constants for the $H_2O + D_2O = 2HDO$ reaction in the liquid phase of $CaCl_2$ solutions are smaller than the equilibrium constant of pure water.

5. Conclusions

1. The D/H ratios of hydrogen gas (water vapour) in equilibrium with aqueous alkaline earth chloride solutions are higher than the D/H ratio of hydrogen gas (water vapour) in equilibrium with pure water.

2. The order of the hydrogen isotope effect in aqueous alkaline earth chloride solutions is found to be $BaCl_2 > SrCl_2 \geq CaCl_2 \geq MgCl_2$.

3. The D/H ratio of water molecules bound in the hydration sphere is estimated to be lower than that of bulk water for aqueous chloride solutions of alkali and alkaline earth metals.

4. The magnitudes of the hydrogen isotope effect of the chloride solutions are in the order, alkaline earth chloride > alkali chloride.

5. For $MgCl_2$ and $CaCl_2$ solutions, the β_D values on the hydrogen isotope effect are smaller than unity, while the $\beta(^{18}O)$ values on the oxygen isotope effect are larger than unity.

6. The slopes of the hydrogen isotope effect for aqueous solutions obtained at 2 m in diluted solutions of HDO in H_2O, $b_D = 10^3(\beta_D - 1)/b$, are evidently correlated with the change of free energy of transfer from H_2O to D_2O, calculated from the measurements of the electromotive force in H_2O and D_2O.

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