Fractionation of Hydrogen Isotopes in Aqueous Lithium Chloride Solutions

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The D/H ratio of hydrogen gas in equilibrium with water vapor over aqueous lithium chloride solutions was measured at 25 °C, using a hydrophobic platinum catalyst. Experimental details are described. The hydrogen isotope effect between the solution 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 effect measured by Bopp et al. On the basis of these hydrogen and oxygen isotope effects it is concluded that $H_2{}^{18}O$ is enriched in the water molecules coordinated to Li^+ ions and $HD^{16}O$ is enriched in the free water molecules of the solution. The observed deviation from linearity for concentrations higher than ca. 12*m* is interpreted in terms of structural changes in the hydration sphere of the Li^+ ions.

Key words: Fractionation of hydrogen isotopes, Aqueous lithium chloride solution, Hydrophobic platinum catalyst, Dependence of D/H fractionation on molality, Comparison of hydrogen and oxygen isotope effects.

Introduction

In aqueous salt solutions, the water molecules coordinated to ions differ energetically from the 'free' water molecules of the solvent. This difference brings about an unequal partition of the hydrogen and oxygen isotopes between the coordinated and the free water. Because of this intra-solution isotope effect, the isotopic composition of water vapor or carbon dioxide equilibrated with pure water changes on dissolving a salt in the water [1–9]. Experimentally it is difficult to separate the vapor from the liquid under equilibrium conditions. Stewart and Friedman [1] measured the fractionation of the hydrogen isotopes by equilibrating a drop of the liquid with its vapor by means of a pump circulating the vapor. The fractionation factor, $(D/H)_{solution}/(D/H)_{vapor}$, which was larger than unity, became closer to unity as the salt concentration increased, except for Na_2SO_4 and K_2SO_2 solutions. Sofer and Gat [2] obtained similar results by circulating a given amount of air over the salt solutions. In both studies it was concluded that, except for the Na_2SO_4 and K_2SO_4 solutions, the D/H ratio of the water molecules bound to the ions is lower than that of the free water molecules.

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Kakiuchi and Matsuo [9] obtained the intra-solution fractionation factors of the hydrogen and oxygen isotopes of water molecules in aqueous urea solutions by the vapor-liquid equilibrium method. The concentration dependence of the fractionation factor was opposite to that found for the electrolyte solutions.

In the present study, the D/H ratio of water vapor in equilibrium with aqueous lithium chloride solutions is measured by means of hydrogen gas equilibrated with the water vapor. A novel hydrophobic platinum catalyst served for equilibrating the hydrogen gas with the water vapor [10]. The structural change of the solution on changing the salt concentration is discussed.

Experimental

The hydrophobic platinum catalyst consisting of dispersed platinum in styrene divinyl benzene copolymer is named "Hokko Beads" and is produced by Shoko Tsusho Co. Ltd. (porous resin doped with 3.0 wt% platinum, apparent specific gravity 0.2 g/cm^3, the bead diameter ranges from 125 to 250 μm). Because of the hydrophobicity of the porous resin, the surface of the doped platinum is not wetted. After equilibration, the hydrogen gas is subjected to D/H ratio analysis.

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Apparatus and Experimental Procedure

For the convenience of the D/H ratio measurements with a mass spectrometer designed for natural D/H ratios measurements, pure water having a deuterium content of about 600 ppm was prepared. The D/H fractionation factor between liquid pure water and hydrogen gas at 25 °C is 3.81 (Rolston et al. [11]). For each solution of lithium chloride with different concentration, the solvent with the high D/H ratio was prepared anew by mixing the heavy with natural water.

The hydrogen gas-liquid water equilibration system is shown in Figure 1. About 20 mg of platinum catalyst and about 5 ml of pure water or solution were introduced into the equilibration vessel (E) and frozen at liquid nitrogen temperature (or at dry ice-methanol temperature). The system was then evacuated. In order to ensure complete degassing of the liquid, a freezing-evacuation-thawing cycle was repeated twice. When the evacuation was completed, hydrogen gas was introduced from a tank. The quantity of hydrogen gas was measured manometrically, the volumes of E and V (the sampler) being known. The equilibration system was immersed in a thermostat kept at 25.0 ± 0.1 °C. In order to eliminate errors introduced by differences in the equilibrium conditions, mainly temperature, at least two pairs of a lithium chloride solution and pure water, usually even more such pairs, were treated in the same run.

The time necessary for the equilibration was checked by measuring the isotopic composition of the hydrogen gas collected from time to time. For pure water at 25.0 °C, several hours were sufficient to obtain a constant isotopoic composition. This finding agrees with that by Ohsumi and Fujino [12], who applied this method to D/H ratio measurements of natural waters. For aqueous lithium chloride solutions it was necessary to wait up to 500 hours (at 19.0 m) for the equilibration.

After the equilibration, the stopcock (S) was closed in the thermostat, and the hydrogen gas in the sampler was allowed to expand through the U-trap, where the coexisting water vapor was removed by freezing at liquid nitrogen temperature. The hydrogen gas was then subjected to the D/H analysis.

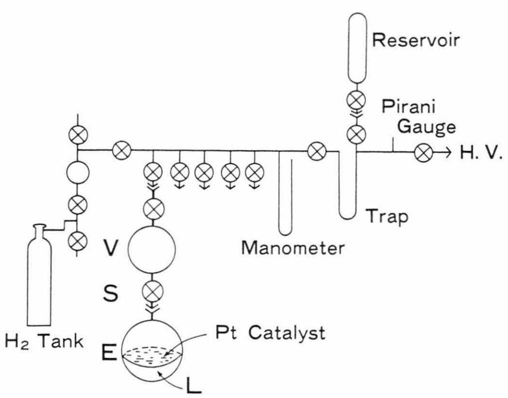

Fig. 1. The apparatus used for the hydrogen gas-liquid water equilibration. The equilibration system consists of the equilibration vessel (E) and the sampler (V), both having a volume of ca. 20 ml and being connected by a stopcock (S).

Isotopic Analysis

One uses pure water, p, and an aqueous solution, s, having the same isotope ratio, R_1, in the liquid state, l, and asks for the ratio, β_D, of the D/H ratios R_v^p and R_v^s of the vapors, v, in equilibrium with these liquids. β_D is found by measuring the D/H ratios R_g^p and R_g^s of hydrogen gas, g, in equilibrium with these vapors. This is possible because in equilibrium R_g^p/R_v^p equals R_g^s/R_v^s, so that β_D defined as

$$\beta_D = R_v^p/R_v^s \tag{1}$$

satisfies

$$\beta_D = R_g^p/R_g^s . \tag{2}$$

Measured hydrogen isotope ratios for rare isotopes are usually expressed in terms of δD values (the delta notation) defined as

$$\delta D\,(‰) = [(R/R_{st}) - 1] \cdot 10^3 , \tag{3}$$

where R_{st} is the D/H ratio of some standard. We have used Tokyo Institute of Technology standard for deuterium, for which $R_{st} = 1.47 \cdot 10^{-4}$.

We can rewrite (2) as follows using the delta notation:

$$\beta_D = (1 + 10^{-3}\,\delta D_g^p)/(1 + 10^{-3}\,\delta D_g^s), \tag{4}$$

where δD_g^p and δD_g^s are the measured delta values of hydrogen gas for pure water and aqueous solution, respectively.

The equilibrium value R_1 can be evaluated from the approximated material balance,

$$n_l\,R_l^i + n_g\,R_g^i = n_l\,R_l + n_g\,R_g , \tag{5}$$

where R_l^i and R_g^i are the D/H ratios of the initial state, i, input water and input hydrogen gas, and n_l and n_g are the respective molar amounts of water and hydrogen gas. In this approximation the amount of vapor was neglected and D/(H + D) was put equal to D/H. With use of the known equilibrium ratio at 25 °C [11],

$$R_l^p/R_g^p = 3.81\,, \tag{6}$$

one obtains

$$R_l = \left[\left(1 + \frac{n_g}{n_l}\frac{R_g^i}{R_l^i}\right)\bigg/\left(1 + \frac{n_g}{n_l}\cdot\frac{1}{3.81}\right)\right] R_l^i\,. \tag{7}$$

In sufficient accuracy this relation also holds for the aqueous solutions. We have input water with $R_l^i = 60 \cdot 10^{-5}$ for the experimental reasons already mentioned, and input hydrogen gas with $R_g^i = 3 \cdot 10^{-5}$. We also had typically $n_g = 0.5$ mmol and $n_l = 0.2$ mol (corresponding to ca. 5 cm^3 aqueous solution for 19 m) to 0.3 mol (corresponding to ca. 5 cm^3 pure water). For these values one obtains

$$R_l^s = 0.9994\, R_l^i \text{ (for } 19m \text{ solution)},$$
$$R_l^p = 0.9997\, R_l^i \text{ (for pure water)}. \tag{8}$$

The errors based on this material balance are estimated to be smaller than ± 0.3 in terms of $10^3(\beta_D - 1)$.

The obtained ratio β_D relates to this isotope ratio $R_l = R_l^p = R_l^s$ in the liquid state.

Results and Discussion

The results of the β_D determinations at 25 °C for various lithium chloride concentrations are presented in Table 1. The overall errors are estimated to be smaller than ± 3 in terms of $10^3(\beta_D - 1)$. The β_D's defined by (1), (2) and (4) are exactly the same.

In Fig. 2, $10^3(\beta_D - 1)$ is plotted against the molality of lithium chloride, and Fig. 3 shows the results on the D/H fractionation between water vapor and aqueous alkali halide solutions at concentrations up to 6 m. The negativity of the $\beta_D - 1$ values indicates that the D/H ratio of water vapor equilibrated with aqueous alkali halide solutions is higher than that of water vapor equilibrated with pure water. This means that HDO is depleted in the hydration spheres of alkali halides.

From Fig. 3 it becomes evident that the present technique gives more reliable data than the previous methods [1, 2]. On ignoring the data on sodium chloride by Sofer and Gat [2], it is concluded that at concentrations up to 6m the β_D values of alkali chlorides decrease with increasing radius of the cation. Although this study on lithium chloride was carried out at 25 °C, the temperature difference of 5 °C does not affect significantly the values of $\beta_D - 1$.

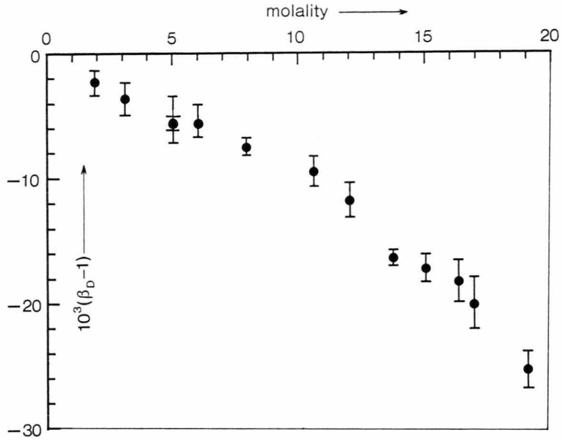

Fig. 2. The concentration dependence of the measured $10^3(\beta_D - 1)$ values for aqueous lithium chloride solutions at 25 °C. The errors are indicated by the vertical bars.

Table 1. Measured values of δD_g^s and δD_g^p for various molalities of lithium chloride, and obtained values of β_D calculated by (4) at 25 °C.

Molality of LiCl	δD_g^s (‰)	δD_g^p (‰)	β_D	$10^3(\beta_D - 1)$
1.9	66.6 ± 1.6 (7)	64.2 ± 1.9 (6)	0.9977	−2.3 ± 1.0
3.1	72.1 ± 2.6 (9)	68.3 ± 1.9 (4)	0.9965	−3.5 ± 1.3
5.0	85.4 ± 2.6 (2)	79.7 ± 2.0 (5)	0.9947	−5.3 ± 2.0
5.0	3.8 ± 0.4 (5)	−1.5 ± 0.5 (4)	0.9947	−5.3 ± 0.3
6.0	75.5 ± 1.7 (3)	69.8 ± 1.6 (3)	0.9947	−5.3 ± 1.3
7.9	75.3 ± 1.1 (5)	67.2 ± 1.2 (6)	0.9925	−7.5 ± 0.7
10.6	90.4 ± 0.1 (2)	79.7 ± 2.0 (5)	0.9902	−9.8 ± 0.9
12.0	75.0 ± 2.8 (9)	62.5 ± 1.8 (3)	0.9884	−11.6 ± 1.4
13.7	51.6 ± 1.0 (5)	34.4 ± 0.5 (7)	0.9836	−16.4 ± 0.5
15.0	82.9 ± 1.8 (6)	64.2 ± 1.9 (6)	0.9827	−17.3 ± 1.1
16.3	88.6 ± 1.8 (5)	69.0 ± 3.3 (5)	0.9820	−18.0 ± 1.7
16.9	91.5 ± 1.8 (4)	69.8 ± 3.7 (4)	0.9801	−19.9 ± 2.1
19.0	50.7 ± 2.3 (9)	24.0 ± 2.8 (4)	0.9746	−25.4 ± 1.6

The ranges indicate the standard deviations, and the numbers in the bracket the number of measurements. The hydrogen isotope ratios of hydrogen gas, δD_g^s and δD_g^p, were expressed by δD values relative to the laboratory standard at Tokyo Institute of Technology, the D/H ratio of which is $1.47 \cdot 10^{-4}$. The values of δD_g^p are scattered because the pure water used as solvent for the LiCl solutions was prepared by diluting the heavy water independently for each concentration.

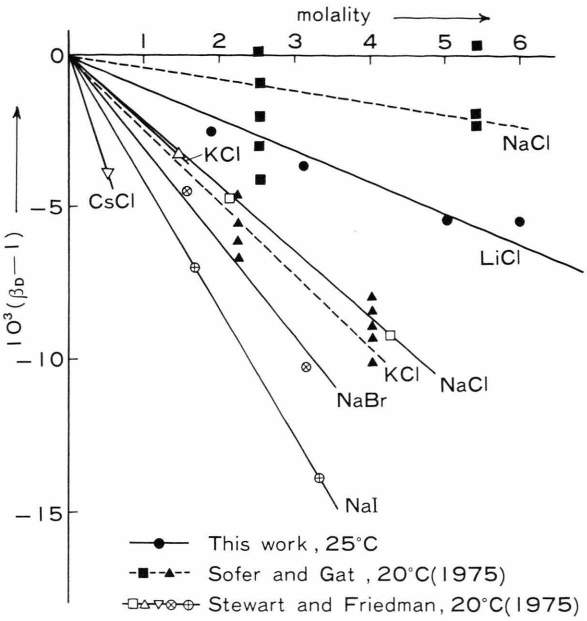

Fig. 3. $10^3(\beta_D - 1)$ values for various alkali halide solutions at low concentrations up to $6m$. The lines for 20 °C were taken from Stewart and Friedman [1], and Sofer and Gat [2].

Table 2. The values of β_D^* according to (9) at 25 °C for alkali chloride solutions by Pupezin et al. [13].

Salt	Molality	$10^3(\beta_D^* - 1)$
LiCl	2	0.1 ± 0.2
	4	-0.1 ± 0.2
	6	-0.8 ± 0.2
	10	-5.9 ± 0.2
	15	-23.6 ± 0.3
NaCl	2	-0.3 ± 0.2
	4	-1.0 ± 0.2
	6	-2.3 ± 0.2
KCl	2	-0.4 ± 0.2
	4	-1.8 ± 0.2
CsCl	2	-1.4 ± 0.2
	4	-4.4 ± 0.6
	6	-7.1 ± 1.1

Pupezin et al. [13] measured and compared the vapor pressures of solutions of alkali chlorides in H_2O and D_2O. Some of their results are listed in Table 2 in terms of

$$\beta_D^* = \left(\frac{P_{D_2O}}{P_{H_2O}}\right)^p \Bigg/ \left(\frac{P_{D_2O}}{P_{H_2O}}\right)^s, \qquad (9)$$

where p refers to the pure solvents and s to the solutions, and where P_{D_2O} and P_{H_2O} are the D_2O and H_2O vapor pressures, respectively. Evidently, as a rule both the $(D/H)_v$ mixing ratio of the vapor (Fig. 3) and the P_{D_2O}/P_{H_2O} ratio of the vapor pressures (Table 2) become larger if alkali chloride is added to the respective liquids. The only exception is the behavior of P_{D_2O}/P_{H_2O} in case of LiCl at the concentration of $2m$. This parallelism of β_D and β_D^* can be interpreted as follows: The measurements on the H_2O-HDO mixtures show that HDO is less attracted by the cations than H_2O. Therefore also the vapor pressure of D_2O is less reduced by the addition of cations to the liquid than the vapor pressure of H_2O.

The intra-solution oxygen isotope effect can be studied by the CO_2 equilibration technique. Analogously to (1) and (2) one defines

$$\beta_{^{18}O} = R(18)_v^p / R(18)_v^s = R(18)_{CO_2}^p / R(18)_{CO_2}^s, \qquad (10)$$

where $R(18)$ is the $^{18}O/^{16}O$ ratio of oxygen specified by the indexes v, CO_2, p and s, respectively. As to the alkali chlorides at 25 °C, $\beta_{^{18}O} - 1$ was found to be positive for LiCl [3, 4, 8], nearly zero for NaCl [4], and negative for KCl [5, 6] and CsCl [4, 8]. Positive and negative values of $\beta_{^{18}O} - 1$ indicate that $H_2{}^{18}O$ is enriched in the hydration water and free water, respectively.

In Fig. 4, the molality dependence of $\beta_D - 1$ and $\beta_{^{18}O} - 1$ for LiCl solutions at 25 °C are shown together. At concentrations up to ca. $12m$, both $\beta_D - 1$ and $\beta_{^{18}O} - 1$ depend linearly on molality. In the concentration range from ca. $12m$ up to saturation both values deviate from this linearity.

Based on X-ray and neutron diffraction measurements by Narten et al. [14], which showed that the coordination number of Li^+ is 4 up to very high concentrations, Bopp et al. [8] argued that at $13.9m$ all water molecules are coordinated to Li^+ ions, and that the $Li(H_2O)_4^+$ groups do not share water molecules.

Recently, a molecular dynamics (MD) simulation of a $LiCl \cdot 4H_2O$ ($m = 13.9$) solution was performed by Bopp et al. [15]. They found that the number of first neighbor water molecules around Li^+ is about 5, and that this number around Cl^- ranges from 6 to 8, there being no clear-cut structure of the hydration sphere of Cl^-. Therefore the first neighbor water molecules around Cl^- should be energetically similar to the free water molecules, and there should be almost no isotope fractionation between the two. Bopp et al. [15] also concluded that the extent of ion pairing is very small.

The dependencies of the β-values on the LiCl concentration can thus be interpreted as follows: At con-

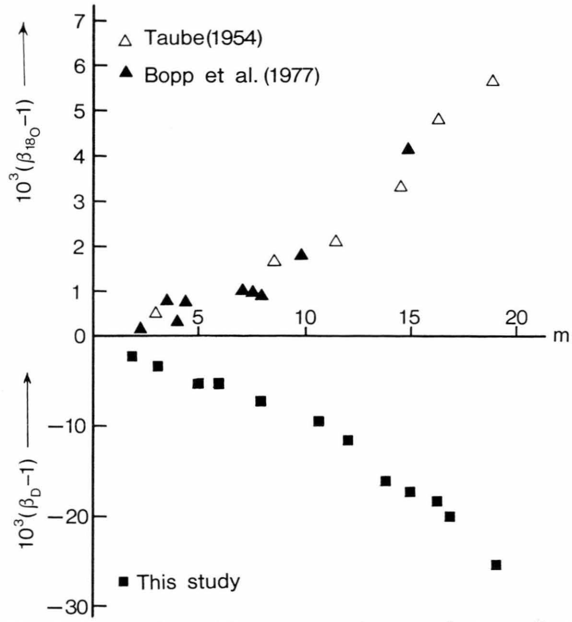

Fig. 4. Comparison of hydrogen and oxygen isotope effects, $10^3(\beta_D - 1)$ and $10^3(\beta_{^{18}O} - 1)$, for aqueous lithium chloride solutions at 25 °C. For the oxygen isotope effect, the open triangles in the plot were taken from Taube [4], and the solid triangles from Bopp et al. [8].

centrations up to about 12 *m* the hydration sphere of the Li^+ ions do not share water molecules, and there are free water molecules and energetically similar water molecules near Cl^- ions left. Therefore $\beta_D - 1$ and $\beta_{^{18}O} - 1$ are proportional to the LiCl molality. At LiCl concentrations higher than about 14 *m* the structures existing in the low concentration range have disappeared. All the water molecules are coordinated to Li^+, and more and more are coordinated to several Li^+ ions. The structure becomes more solid like, and since the structural and energetical differences between solid and vapor are larger than those between liquid and vapor, the β_D and $\beta_{^{18}O}$ values deviate even more from those expected from the linear relationship between the β values and the molality prevailing at low LiCl concentrations.

Deviations from a linear relationship at LiCl concentrations higher than about 12 *m* have also been observed for other properties of these aqueous solutions, thus for the relative viscosity [16] and the vapor pressure depression [17]. These facts suggest that a chain or sheet structure emerges at concentrations higher than about 12 *m*.

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