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A Thermodynamic Study on the Hydrolysis of Beryllium Ion in Dioxane–Water Mixed Solvents

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The hydrolytic reactions of beryllium(II) ions were calorimetrically studied at 25 °C in aqueous solution and dioxane–water mixtures, both containing 3.0 mol dm^{-3} (Li)ClO$_4$ as a constant ionic medium. On the basis of the formation constants previously determined,[10–12] the enthalpy and entropy changes for the reaction, $q\mathrm{Be}^{2+}+p\mathrm{H_2O}=\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}+p\mathrm{H}^+$, were estimated for the $\mathrm{Be_2OH^{3+}}$ and $\mathrm{Be_3(OH)_3{}^{3+}}$ complexes in aqueous solution and 0.1 mole fraction dioxane–water mixture and for $\mathrm{Be_2OH^{3+}}$, $\mathrm{Be_3(OH)_3{}^{3+}}$, and $\mathrm{Be_2(OH)_2{}^{2+}}$ complexes in 0.2 mole fraction dioxane–water mixture. The enthalpy and entropy changes of formation of the $\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}$ complex obtained in solutions of various mole fractions of dioxane were as follows: $2\mathrm{Be}^{2+}+\mathrm{H_2O}=\mathrm{Be_2OH^{3+}}+\mathrm{H}^+$; ΔH_{12} (mole fraction: 0.0)$=18.6\pm0.2$ kJ mol^{-1}, $T\Delta S_{12}$(mole fraction: 0.0)$=1.3\pm0.2$ kJ mol^{-1}, ΔH_{12} (0.1)$=15.2\pm0.2$ kJ mol^{-1}, $T\Delta S_{12}(0.1)=-3.4\pm0.2$ kJ mol^{-1}, $\Delta H_{12}(0.2)=8.4\pm0.4$ kJ mol^{-1}, $T\Delta S_{12}(0.2)=-12.4\pm0.4$ kJ mol^{-1}, $3\mathrm{Be}^{2+}+3\mathrm{H_2O}=\mathrm{Be_3(OH)_3{}^{3+}}+3\mathrm{H}^+$; $\Delta H_{33}(0.0)=61.7\pm0.2$ kJ mol^{-1}, $T\Delta S_{33}(0.0)=12.2\pm0.2$ kJ mol^{-1}, $\Delta H_{33}(0.1)=59.4\pm0.2$ kJ mol^{-1}, $T\Delta S_{33}(0.1)=10.0\pm0.2$ kJ mol^{-1}, $\Delta H_{33}(0.2)=59.0\pm0.4$ kJ mol^{-1}, $T\Delta S_{33}$-$(0.2)=9.1\pm0.4$ kJ mol^{-1}, $2\mathrm{Be}^{2+}+2\mathrm{H_2O}=\mathrm{Be_2(OH)_2{}^{2+}}+2\mathrm{H}^+$; $\Delta H_{22}(0.2)=42.3\pm0.4$ kJ mol^{-1}, $T\Delta S_{22}(0.2)=1.3\pm0.4$ kJ mol^{-1}. The enthalpy and entropy changes of the reaction, $\mathrm{H_2O}=\mathrm{H}^++\mathrm{OH}^-$, in the solutions of the same compositions were also determined as $\Delta H_\mathrm{w}(0.0)=56.6\pm0.1$ kJ mol^{-1}, $T\Delta S_\mathrm{w}(0.0)=-22.6\pm$ 0.1 kJ mol^{-1}, $\Delta H_\mathrm{w}(0.1)=58.1\pm0.1$ kJ mol^{-1}, $T\Delta S_\mathrm{w}(0.1)=-25.3\pm0.1$ kJ mol^{-1}, $\Delta H_\mathrm{w}(0.2)=61.2\pm0.1$ kJ mol^{-1}, $T\Delta S_\mathrm{w}(0.2)=-26.6\pm0.1$ kJ mol^{-1}. These results were discussed in connection with interactions between the hydroxo complexes and the solvent molecules and with those between solvent molecules in the mixed solvents.

It has been said that the thermodynamic parameters of transfer of electrolytes from aqueous to aqueous organic mixed solvents would be a measure of solute–solvent and solvent–solvent interactions.[1–4] The change in strength of carboxylic acids in mixed solvents may be a typical example, where the acidity usually decreases with increasing mole fraction of organic component.[5,6] On the other hand, the acidity of ammonium ion and its homologues increases with the concentration of an organic solvent and then sharply decreases after passing through a maximum.[7–9] In the preceding studies of hydrolytic reactions of metal ions in mixed solvents,[10–12] we pointed out that hydrated metal ions behave in different manner from these two types of acids, that is, the acid dissociation (*i.e.*, hydrolysis) constant of a hydrated metal ion is not practically influenced by the solvent composition of aqueous organic mixtures.

Since no data have been available for the enthalpy and entropy changes of hydrolytic reactions of metal ions in aqueous organic mixtures, we carried out calorimetric measurements of hydrolytic reactions of metal ions in order to investigate solute–solute and solute–solvent interactions in the reactions. Beryllium ion was first chosen as a target of the aim, because it has been investigated in detail in aqueous and aqueous organic mixtures containing various ionic media.[10–12] Since the complex formation proceeds rather slowly at a high pH range,[12] the experiments in this study were carried out in the range pH≤4.

Experimental

Reagents and Analysis. *Beryllium Perchlorate*: Beryllium oxide of reagent grade was heated for several hours with an excess of perchloric acid. Residual beryllium oxide was filtered off with a glass filter and beryllium perchlorate thus prepared was recrystallized three times from water. The concentration of beryllium ions in the stock solution was determined gravimetrically.[13]

Lithium Perchlorate: Lithium perchlorate was prepared as described in Ref. 14. Crystals of lithium perchlorate were dried at about 200 °C in an electric oven.

Lithium Hydroxide: A lithium hydroxide solution was prepared by electrolysis of an aliquot of the lithium perchlorate stock solution under an atmosphere of nitrogen in a polyethylene bottle. The concentration of hydroxide ions thus prepared was determined by Gran's method[15] by titrating with a standard perchloric acid solution.

Perchloric Acid: Perchloric acid of super special grade was used without further purification.

Dioxane: Dioxane was purified by the method described in Ref. 10.

The concentrations of hydrogen ions contained in the stock solutions were coulometrically determined by Gran's method.[15]

Preparation of Test Solutions. Test solutions were contained 3.0 mol dm^{-3} perchlorate ions as a constant ionic medium. In each titration, two test solutions were prepared, both containing the same total concentration of beryllium ion at a given concentration of dioxane in the solutions. One (Solution S) contained hydrolyzed beryllium ions and the other (Solution T) contained unhydrolyzed beryllium ions and a known concentration of perchloric acid, and the former was titrated by the latter. The total concentration of beryllium ion was kept practically constant during the titration.

The Method of Measurements. The measurements were carried out in a thermostated room at 25.0±0.5 °C. All the cells used were Dewar vessels, which were immersed in a thermostated water bath. The temperature fluctuated by ±0.0007 °C at 25.00±0.05 °C. First, about 150 cm^3 of test solution S was placed in a titration vessel. The temperature change in the titration vessel was detected by use of a micro volt meter (Model AM-1001, Ohkura Electric Co., Ltd.) and a couple of thermisters which were introduced into the titration and reference vessels. Temperature in

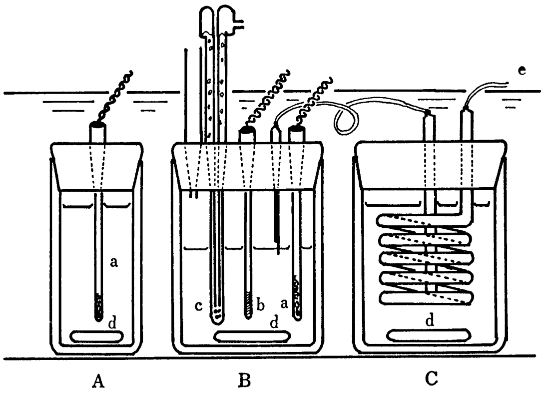


Fig. 1. The cell arrangement used for the enthalpy titration. A: The reference vessel, B: the titration vessel, C: the cell used as a heat exchanger, a: thermister, b: heater, c: cooler which is filled with methanol and is connected with an air pump, d: stirring bar, e: titrant from a piston buret.

the reference vessel, to which the temperature change in the titration vessel was referred, was kept constant throughout the titration. At the thermal equilibrium, temperature in the titration vessel was usually slightly higher than that in the thermostated water bath because of joule heat by agitation. Therefore, in order to keep temperature of the titrant practically the same as that of the test solution, another cell was used as a heat exchanger through which the titrant T was introduced into the titration vessel. The heat exchanger was also agitated with a stirring bar to keep the same temperature in the heat exchanger with that in the titration vessel. The cell arrangement was depicted in Fig. 1. Heat evolved per addition of the titrant was about 6—20 J, which corresponded to the change of about 200—700 μV. The estimated uncertainty (σ) of the heat measurements was about ±0.4 μV or ±0.00005 °C. The on-line controlled enthalpy titration system was developed in order to make precise determinations of heat evolved and to spare time for measurements.

The On-line Controlled Enthalpy Titration System. The on-line controlled enthalpy titration system is schematically shown in Fig. 2. The temperature change in the titration vessel was monitored by a JEC-6 spectrum computer (JEOL Co., Ltd.) through a micro volt meter and a 10-bit AD converter. Throughout the measurements, time was controlled by means of a pulse generator.

The procedure of a heat measurement per addition of the titrant consisted of four steps, A through D, as is shown in Fig. 3.

A Region: Before addition of the titrant, the temperature difference between the titration and reference vessels was measured every 10 seconds and a set of continued 50 data was analyzed to give the temperature gradient G ($=\mathrm{d}\theta/\mathrm{d}t$) by assuming the temperature (θ) changing linearly with time, and, at the same time, the uncertainty δG was estimated. If G and δG obtained did not fall within specified ranges, one more temperature-difference was measured, and the same procedure was repeated using a new set of 50 data. When G and δG fell within given ranges, and thus the test solution was reached the thermal equilibrium with the thermostated bath, the temperature at the equilibrium θ_0 and its uncertainty $\delta\theta_0$ were recorded.

B Region: When the test solution was reached the thermal equilibrium with the thermostated bath, the titrant T was added from a piston buret to the test solution. The operation of adding the titrant usually took a few minutes. When the temperature in the titration vessel rose over a level of $10\delta\theta_0$, the temperature change was read every second. The procedure was continued until the temperature in the titration vessel started to decrease, and the time (t_{max}) when the temperature reached the maximum was determined (the maximum temperature: θ_{max}).

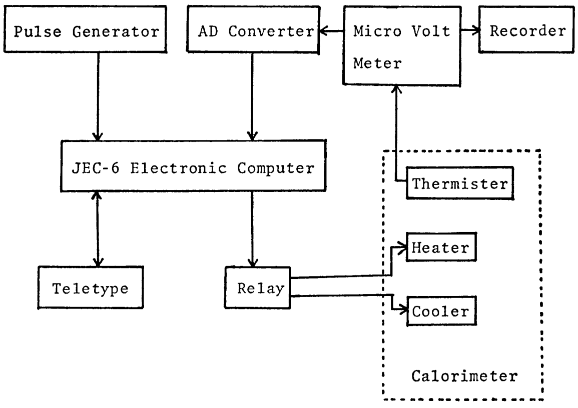


Fig. 2. The on-line controlled enthalpy titration system. The arrows indicate the direction of signals.

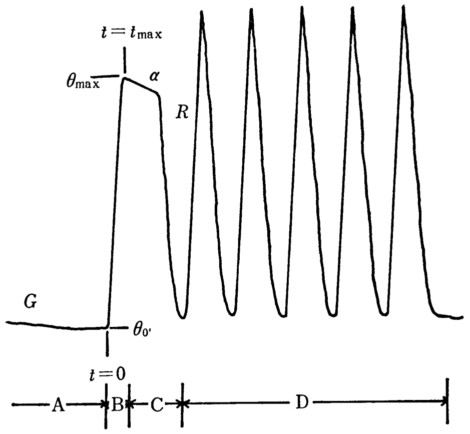


Fig. 3. Determination of heat evolved per addition of the titrant.

C Region: The temperature in the titration vessel decreased approximately linearly after passing through the maximum. The temperature change in the C region could be expressed by the following equation:

$$\theta(t) = (\theta_{\mathrm{max}}-\theta_0)\{1-\alpha(t-t_{\mathrm{max}})\} \tag{1}$$

where α denotes a constant. The values of θ_{max} and α were determined using a set of 100 data in this region which were measured every second. Then, a cooler was operated to cool the test solution to approximately the same temperature as θ_0.

D Region: When the cooling of the test solution was finished, the test solution was heated by using a standard heater which evolved a constant joule heat q. During the evolution of heat, the temperature change was read every second. The heating of the test solution was continued until a set of 100 data was recorded, then the cooler was again operated. The set of 100 data was analyzed by assuming that temperature rose with a constant rate, and the rate R ($=\mathrm{d}\theta/\mathrm{d}t$) was determined. The determination of R was repeated five times and the mean value was used to estimate the heat capacity C_p of the test solution $C_p=q/RV$, where V denotes the volume of the test solution. The uncertainty in R was usually within $\pm 0.3\%$. Thus, the heat evolved in the course of one titration q was determined by the following equation:

$$q = k_1 C_p V f(\theta_{\max} - \theta_0) + k_2 \tag{2}$$

where f stands for a correction of heat escaped from the titration vessel until temperature reached the maximum in the B region,

$$f = 1/(1 - \alpha t_{\max}/2 + \alpha^2 t_{\max}^2/3) \tag{3}$$

and k_1 and k_2 represent empirical constants (k_1 was nearly unity and k_2 was nearly zero) which had been determined by separate experiments using a standard heater.

All procedures were automatically operated under the controll by the JEC-6 electronic computer. A least-squares method was employed for the analysis of the sets of data obtained. One procedure of the measurement from A to D usually finished within 40 min. In one run of the whole titration, ten experimental points were usually measured with the total volume of the titrant of about 20 cm³.

Results

The Enthalpy Change for the Autoprotolysis Reaction of Solvents. The enthalpy change for the autoprotolysis reaction of the solvents were measured by titrating a standard lithium hydroxide solution with perchloric acid in mixed solvents containing 3.0 mol dm^{-3} perchlorate ions. The enthalpy change ΔH_w for the reaction, $H_2O = H^+ + OH^-$, is given by the equation:

$$Q = \sum q = \Delta H_w c_H v \tag{4}$$

where Q, q, c_H, and v stand for the total heat evolved, the heat evolved per addition of the titrant, the concentration of hydrogen ions in the titrant and the total volume of the titrant added, respectively. A plot of Q/c_H against v might give a straight line. The plots in various solvents are shown in Fig. 4, and ΔH_w was given as the slope of the straight line.

The Enthalpy Changes of Formation of the Hydroxo Complexes of Beryllium(II). In aqueous solution and 0.1 mole fraction dioxane–water mixture, the only Be_2OH^{3+} and $Be_3(OH)_3^{3+}$ complexes were formed in the pH range examined (pH$\leq$4). Therefore, the heat evolved was expressed as follows:

$$Q = \sum q = \Delta H_{12}\delta n_{12} + \Delta H_{33}\delta n_{33} \tag{5}$$

where δn_{pq} denotes the total change in the number of moles of the $Be_q(OH)_p^{(2q-p)+}$ complex when the titrant was added. The δn_{pq} was calculated on the basis of the formation constants previously determined.[10–12] Plots of $Q/\delta n_{33}$ against $\delta n_{12}/\delta n_{33}$ gave a straight line with the slope of ΔH_{12} and the intercept of ΔH_{33}. The plots are shown in Fig. 5.

In 0.2 mole fraction dioxane–water mixture, the $Be_2(OH)_2^{2+}$ complex was formed together with the Be_2OH^{3+} and $Be_3(OH)_3^{3+}$ complexes. Therefore, the heat evolved was expressed as follows:

$$Q = \Delta H_{12}\delta n_{12} + \Delta H_{33}\delta n_{33} + \Delta H_{22}\delta n_{22} \tag{6}$$

When we applied a least-squares method to Eq. 6 in order to evaluate the values ΔH_{12}, ΔH_{33}, and ΔH_{22}, reasonable values were not obtained. A possible reason may be that δn_{22} was approximately proportional to δn_{33} under the experimental conditions examined. Since the formation of the $Be_2(OH)_2^{2+}$ complex was small (about 20%) compared with that of the $Be_3(OH)_3^{3+}$ complex, we assumed at a first step of approch that the only Be_2OH^{3+} and $Be_3(OH)_3^{3+}$ complexes were present. Thus, the same plots as those demonstrated for the aqueous solution and 0.1 mole fraction dioxane–water mixture were possible and are shown in Fig. 6. A relatively good straight line was obtained to give approximate values of ΔH_{12} and ΔH_{33}. Using the value of ΔH_{12} thus obtained, the values of ΔH_{33} and ΔH_{22} were estimated by Eq. 7:

$$(Q - \Delta H_{12}\delta n_{12})/\delta n_{33} = \Delta H_{33} + \Delta H_{22}(\delta n_{22}/\delta n_{33}) \tag{7}$$

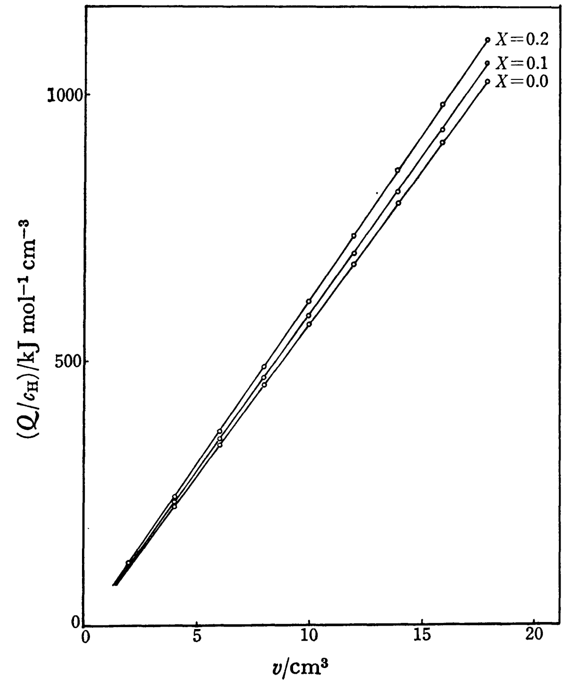


Fig. 4. Determination of the enthalpy change for the autoprotolysis reaction of water in dioxane–water mixture. X represents mole fraction of dioxane in the mixture.

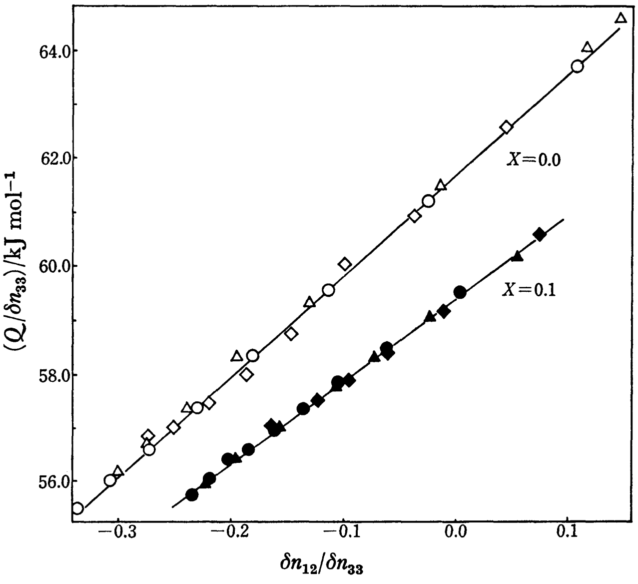


Fig. 5. Determinations of the enthalpy changes of formation of the Be_2OH^{3+} and $Be_3(OH)_3^{3+}$ complexes in aqueous solution and 0.1 mole fraction dioxane–water mixture. Total concentration of beryllium ions c_{Be} (mol dm^{-3}): ○ 0.1620, △ 0.0967, ◇ 0.0506 ▲ 0.0995, ◆ 0.0831, ● 0.0652. X represents mole fraction of dioxane in the mixture.

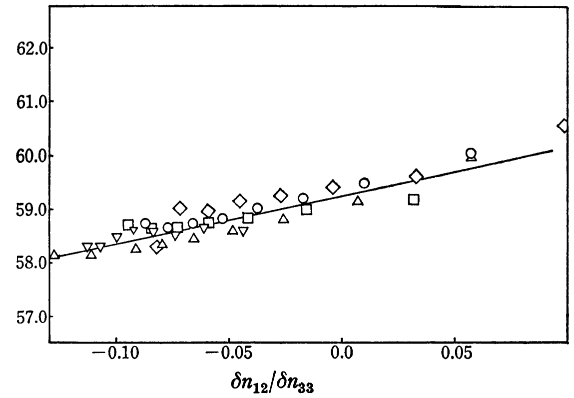


Fig. 6. Determination of the enthalpy changes of formation of the Be_2OH^{3+} and $Be_3(OH)_3{}^{3+}$ complexes in 0.2 mole fraction dioxane–water mixture. Total concentration of beryllium ions c_{Be} (mol dm^{-3}): ○ 0.1183, △ 0.0855, □ 0.0847, ▽ 0.0646, ◇ 0.0390.

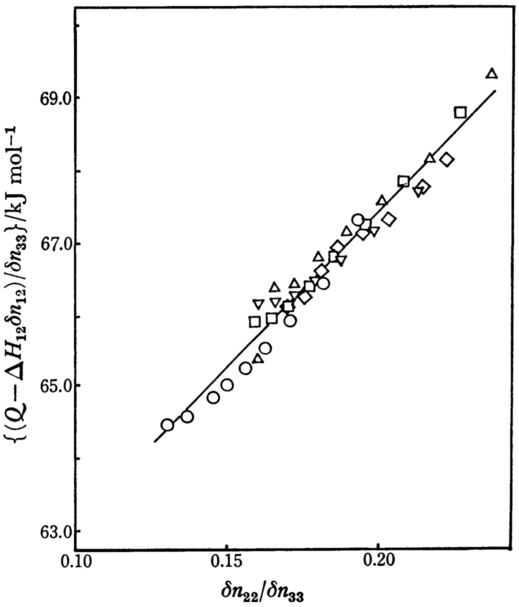


Fig. 7. Determination of the enthalpy changes of formation of the $Be_2(OH)_2{}^{2+}$ and $Be_3(OH)_3{}^{3+}$ complexes in 0.2 mole fraction dioxane–water mixture. Total concentration of beryllium ions c_{Be} (mol dm^{-3}): ○ 0.1183, △ 0.0855, □ 0.0847, ▽ 0.0646, ◇ 0.0390.

The plots of $(Q-\Delta H_{12}\delta n_{12})/\delta n_{33}$ against $\delta n_{22}/\delta n_{33}$ for a given total concentration of beryllium ions gave a straight line with the slope of ΔH_{22} and the intercept of ΔH_{33}. By changing ΔH_{12} around the value firstly obtained, the procedure was repeated until the plots for all given total concentrations of beryllium ions examined were converged on the same line. The plots are shown in Fig. 7. The value of ΔH_{33} finally obtained was 59.0 kJ mol^{-1}, which was in good agreement with the value of 59.2 kJ mol^{-1} firstly approximated. The thermodynamic parameters for the formation of the hydroxo complexes of beryllium ions and for the autoprotolysis reaction of the solvents thus obtained are summarized in Table 1. The results obtained in aqueous solution are in good agreement with those obtained previously.[16,17)]

Discussion

Ion–solvent and solvent–solvent interactions in dioxane–water mixtures have so far been studied by using various methods and the following conclusions are generally accepted. 1) The hydrogen bonded structure of water is broken down by the addition of dioxane (it has also been reported that the structure of water may be enhanced by the addition of dioxane less than 0.05 mole fraction[18)]). The fact is directly confirmed by means of NMR. The PMR signal of the water molecules shifts to the higher magnetic field on dilution with dioxane.[19)] 2) The interaction between cations and solvent molecules is enhanced as the dioxane content of the solvent increases, while the reverse is the case for the interaction between anions and solvent molecules. The cation–solvent interaction is usually larger than the anion–solvent interaction. It has been shown that the enthalpy changes of transfer of most electrolytes from aqueous solution to dioxane–water mixture are negative (exothermic) and become more negative as the dioxane content of the mixtures increases.[20–22)] The results are explained as follows: Solvent structure plays an important role in determining the thermodynamic parameters of transfer of electrolytes.[23,24)] A dioxane–water mixture is less structured than an aqueous solution, and therefore, ions have a larger solvent-ordering effect (or an enhanced solvation structure of ions) in the dioxane–water mixture. 3) The inner-sphere structure of a complex ion is not practically influenced by the addition of dioxane. It has been found that metal ions are primarily solvated with water molecules in water-rich dioxane–water mixtures (*e.g.*, the dioxane content less than 0.5 mole fraction).[25,26)]

On the basis of these facts, the solvent effects on the autoprotolysis of water and the formation of hydroxo complexes of beryllium ion are discussed in the following sections.

Autoprotolysis Reaction of the Solvents. The difference between the enthalpy changes for the autoprotolysis reaction of water, $H_2O=H^++OH^-$, in a dioxane–water mixture and an aqueous solution is represented as follows:

$$\begin{aligned}\Delta H_{\mathrm{w}}^{\mathrm{t}} &= \Delta H_{\mathrm{w}}(\text{mixed}) - \Delta H_{\mathrm{w}}(\text{aqueous})\\ &= \Delta h_{\mathrm{H}}^{\mathrm{t}} + \Delta h_{\mathrm{OH}}^{\mathrm{t}} - \Delta h_{\mathrm{H_2O}}^{\mathrm{t}} \qquad (1)\end{aligned}$$

where $\Delta h_{\mathrm{i}}^{\mathrm{t}}$ stands for the partial molar enthalpy change of transfer of species i from aqueous solution to a dioxane–water mixture. As is seen from Table 1, the enthalpy changes in both aqueous solution and dioxane–water mixtures were positive. $\Delta H_{\mathrm{w}}^{\mathrm{t}}$ was also positive and became more positive with increasing concentration of dioxane. This result for $\Delta H_{\mathrm{w}}^{\mathrm{t}}$ is in contrast to those of dissociation reactions of weak acids (*e.g.*, acetic acid), in which $\Delta H_{\mathrm{w}}^{\mathrm{t}}$ is usually negative.[5)] Since the sum of the partial molar enthalpy changes of transfer of H^+ and OH^- ions from water to a dioxane–water mixture is negative,[20)] the positive $\Delta H_{\mathrm{w}}^{\mathrm{t}}$ obtained indicated that $\Delta h_{\mathrm{H_2O}}^{\mathrm{t}}$ must be more negative than the sum of $\Delta h_{\mathrm{H}}^{\mathrm{t}}$ and $\Delta h_{\mathrm{OH}}^{\mathrm{t}}$. Since the hydrogen bonded structure of water is broken down by the addition of dioxane, the negative $\Delta h_{\mathrm{H_2O}}^{\mathrm{t}}$ may be caused by enhancement of the intramolecular interaction of a water molecule (*i.e.*, the strength of the O–H bond) in dioxane–water mixtures.

Formation of Hydroxo Complexes of Beryllium Ion. A hydrolytic reaction of beryllium ions may be expressed as follows:

$$q\mathrm{Be}^{2+} + p\mathrm{H_2O} = \mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+ \qquad (2)$$

Similar to Eq. 1, Eq. 3 can be represented as follows:

$$\Delta H^{t}_{pq} = \Delta H_{pq}(\text{mixed}) - \Delta H_{pq}(\text{aqueous})$$
$$= \Delta h^{t}_{pq} + p\Delta h^{t}_{\mathrm{H}} - q\Delta h^{t}_{\mathrm{Be}} - p\Delta h^{t}_{\mathrm{H_2O}} \qquad (3)$$

In order to estimate the extent of the direct beryllium–dioxane interaction, Raman spectra of aqua beryllium ions in dioxane–water mixtures were measured. Raman bands of aqua beryllium ions in aqueous solution were held at the same frequencies in dioxane–water mixtures examined, and therefore, beryllium ions may be preferentially solvated with water molecules in the mixtures. Although no direct evidence has been given for hydroxo complexes, beryllium ions within the hydroxo complexes may also be preferentially solvated with water molecules in water-rich dioxane–water mixtures, and the structure of the skeleton (*i.e.*, –Be–OH– bonds) of the hydroxo complexes may not be appreciably influenced by the solvent composition. Therefore, we assumed that Δh^{t}_{pq}, as well as those of simple ions, reflected the change in the solvation structure of the $\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}$ complex when the hydroxo complex was transferred from water to a dioxane–water mixture. Solvation of the hydroxo complex may occur at the beryllium ions within the complex. Charges of beryllium ions within the $\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}$ complex may partially be compensated with those of hydroxide ions, and therefore, the charge per beryllium ion of the $\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}$ complex may be smaller than +2. Thus, the relation $\Delta h^{t}_{pq} > q\Delta h^{t}_{\mathrm{Be}}$ may generally be held.

As is seen from Table 1, the enthalpy changes of formation of the $\mathrm{Be_2OH^{3+}}$ complex in aqueous solution and dioxane–water mixtures were both positive, but ΔH^{t}_{12} became negative with the increase in the concentration of dioxane. On the contrary, the enthalpy changes of the $\mathrm{Be_3(OH)_3{}^{3+}}$ complex was practically independent of the concentration of dioxane, and ΔH^{t}_{33} was approximately zero. The different tendencies in ΔH^{t}_{pq} between $\mathrm{Be_2OH^{3+}}$ and $\mathrm{Be_3(OH)_3{}^{3+}}$ complexes may be caused by the difference in Δh^{t}_{pq}, or in other words, the different solvation structures of the complexes.

Table 1. The formation constants and the changes in enthalpy (ΔH_{pq}/kJ mol^{-1}) and entropy ($T\Delta S_{pq}$/kJ mol^{-1}) of the hydrolytic reaction of beryllium ion in dioxane–water mixtures

$$q\mathrm{Be}^{2+} + p\mathrm{H_2O} = \mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+$$
$$\beta^{*}_{pq} = [\mathrm{Be}_q(\mathrm{OH})_p{}^{(2q-p)+}][\mathrm{H}^+]^p/[\mathrm{Be}^{2+}]^q$$

		Mole fraction of dioxane		
		0.0	0.1	0.2
$\mathrm{Be_2OH^{3+}}$	$-\log\beta^{*}_{12}$	3.04[11]	3.29[11]	3.64[10]
	ΔH_{12}	18.6	15.2	8.4
	$T\Delta S_{12}$	1.3	−3.4	−12.4
$\mathrm{Be_3(OH)_3{}^{3+}}$	$-\log\beta^{*}_{33}$	8.671[11]	8.65[11]	8.763[10]
	ΔH_{33}	61.7	59.4	59.0
	$T\Delta S_{33}$	12.2	10.0	9.1
$\mathrm{Be_2(OH)_2{}^{2+}}$	$-\log\beta^{*}_{22}$	—	—	7.11
	ΔH_{22}	—	—	42.3
	$T\Delta S_{22}$	—	—	1.3
$\mathrm{H_2O = H^+ + OH^-}$	$\mathrm{p}K_{\mathrm{w}}$	13.867[6]	14.610[6]	15.376[6]
	ΔH_{w}	56.6	58.1	61.2
	$T\Delta S_{\mathrm{w}}$	−22.6	−25.3	−26.6

In order to compare Δh^{t}_{12} and Δh^{t}_{33} with $\Delta h^{t}_{\mathrm{Be}}$, the values of $\Delta H^{t}_{\mathrm{A}}$ and $\Delta H^{t}_{\mathrm{B}}$ of the following reactions were calculated, where the contributions of hydrogen ions and water molecules to the reactions are same.

$$6\mathrm{Be}^{2+} + 3\mathrm{H_2O} = 3\mathrm{Be_2OH^{3+}} + 3\mathrm{H}^+;\quad \Delta H^{t}_{\mathrm{A}} = 3\Delta H^{t}_{12} \qquad (4)$$

$$3\mathrm{Be_2OH^{3+}} + 3\mathrm{H_2O} = 2\mathrm{Be_3(OH)_3{}^{3+}} + 3\mathrm{H}^+;$$
$$\Delta H^{t}_{\mathrm{B}} = 2\Delta H^{t}_{33} - 3\Delta H^{t}_{12}. \qquad (5)$$

The values of $\Delta H^{t}_{\mathrm{A}}$ and $\Delta H^{t}_{\mathrm{B}}$ from water to 0.2 mole fraction dioxane–water mixture were −30.6 and 25.2 kJ mol^{-1}, respectively. Equations 6 and 7 can be derived by using partial molar enthalpy changes of transfer of the relevant species as follows:

$$\Delta H^{t}_{\mathrm{A}} = 3(\Delta h^{t}_{12} - 2\Delta h^{t}_{\mathrm{Be}}) + 3(\Delta h^{t}_{\mathrm{H}} - \Delta h^{t}_{\mathrm{H_2O}}) \qquad (6)$$

$$\Delta H^{t}_{\mathrm{B}} = (2\Delta h^{t}_{33} - 3\Delta h^{t}_{12}) + 3(\Delta h^{t}_{\mathrm{H}} - \Delta h^{t}_{\mathrm{H_2O}}) \qquad (7)$$

and

$$\Delta H^{t}_{\mathrm{A}} < \Delta H^{t}_{\mathrm{B}} \qquad (8)$$

Therefore, the relation

$$2\Delta h^{t}_{33} - 3\Delta h^{t}_{12} > 3\Delta h^{t}_{12} - 6\Delta h^{t}_{\mathrm{Be}} \qquad (9)$$

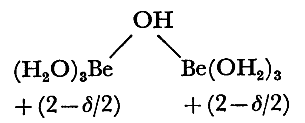
or

$$0 > 2\Delta h^{t}_{33} \gg 3\Delta h^{t}_{12} > 6\Delta h^{t}_{\mathrm{Be}} \qquad (10)$$

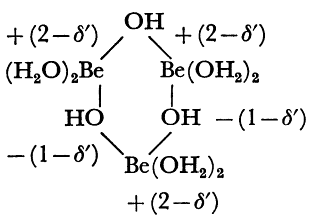
was readily obtained.

As has been pointed out by earlier workers,[18–26] the enthalpy change of transfer of an ion from water to dioxane–water is due to the change in secondary or more hydration spheres of the ion and the enthalpy change of transfer becomes large for ions having a large charge density. Therefore, the relationship given in Eq. 10 leads to the charge density per metal ion of aqua and hydroxo complexes of beryllium ions decreasing in the order of $\mathrm{Be^{2+}}$, $\mathrm{Be_2OH^{3+}}$, and $\mathrm{Be_3(OH)_3{}^{3+}}$. Although the formal charges calculated on the beryllium atoms within the aqua and hydroxo complexes are +2, +1.5, and +1 for $\mathrm{Be^{2+}}$, $\mathrm{Be_2OH^{3+}}$, and $\mathrm{Be_3(OH)_3{}^{3+}}$, respectively, the results given in Eq. 10 suggested that much more positive charges might locate at the beryllium atoms within the hydroxo complexes.

The charge distributions within the $\mathrm{Be_2OH^{3+}}$ and $\mathrm{Be_3(OH)_3{}^{3+}}$ complexes may be represented as follows:[27]



$0 < \delta < 1$



$0 < \delta' < 1$

In the models it was simply assumed that solvation of a hydroxo complex of beryllium ions occurred at the beryllium ion, and a hydroxide ion within the complex acted as a joint between beryllium atoms and as to decrease their charges.

The interaction between a beryllium ion and solvent molecules may be essentially electrostatic, so that the bond energy (or the enthalpy of solvation) may be approximately proportional to $z\mu/r^2$, where z, μ, and r stand for the formal charge of beryllium ion in the complex, the dipole moment of the water molecule and the distance between the beryllium ion and the water molecule, respectively. If we assumed that the enthalpy of solvation of a beryllium ion within a hydroxo complex is proportional to the charge of the beryllium ion, the relationship $\delta<\delta'$ may be derived from Eq. 9. Thus, the charge on the hydroxide ions within the Be_2OH^{3+} complex may be larger than that within the $Be_3(OH)_3{}^{3+}$ complex.

Raman spectroscopic measurements of aqua beryllium ions in aqueous solution showed a band at 527 cm^{-1} due to the total symmetric stretching vibration of $Be(OH_2)_4{}^{2+}$.[28] Corresponding frequencies(ν) of the Be–OH_2 stretching vibration within the Be_2OH^{3+} and $Be_3(OH)_3{}^{3+}$ complexes shifted to 497 and 408 cm^{-1}, respectively.[28] The shift of the band of the Be_2OH^{3+} complex is comparatively less than that of the $Be_3(OH)_3{}^{3+}$ complex. If we simply assumed that the interaction between a beryllium ion and water molecules within a complex is purely electrostatic, and thus, ν^2 is approximately proportional to the charge of the beryllium ion, the formal charge of the beryllium ions within the Be_2OH^{3+} and $Be_3(OH)_3{}^{3+}$ complexes were estimated to be +1.78 and +1.20, respectively, or $\delta=0.44$ and $\delta'=0.80$. The results coincided with that derived from a qualitative comparison between Δh_{12}^{t} and Δh_{33}^{t} described above.

Although these considerations were very approximate, the results obtained suggested that the charge distribution within the hydroxo complexes may be strongly related to the enthalpy of solvation, and thus the partial molar enthalpy change of transfer of the complexes from one solvent to another.

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