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A Thermodynamic Study on Hydrolytic Reactions of Lead(II) Ion in an Aqueous Solution and Dioxane-Water Mixtures. I. A Potentiometric Study

Takayoshi Kawai, Shin-ichi Ishiguro, and Hitoshi Ohtaki*

Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

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The hydrolytic reactions of lead(II) ions were studied at 25 °C by means of potentiometric titrations by using a glass electrode in water and dioxane–water mixture (dioxane contents: 0.1 and 0.2 mol fractions) containing 3 mol dm^{-3} $\mathrm{LiClO_4}$ as a constant ionic medium. Four complexes, $\mathrm{Pb_3(OH)_3^{3+}}$, $\mathrm{Pb_4(OH)_4^{4+}}$, $\mathrm{Pb_3(OH)_4^{2+}}$, and $\mathrm{Pb_6(OH)_8^{4+}}$ were found in the solvent systems examined at $\mathrm{pH} \lesssim 8$, and the formation constant $^*\beta_{pq}$ for the reaction, $q\mathrm{Pb^{2+}} + p\mathrm{H_2O} = \mathrm{Pb}_q(\mathrm{OH})_p^{(2q-p)+} + p\mathrm{H^+}$, was determined. The autoprotolysis constants K_1 in the same solvent systems were also obtained by use of a hydrogen electrode. The formation constant $\beta_{pq}(={}^*\beta_{pq}/K_1{}^p)$ for the reaction, $q\mathrm{Pb^{2+}} + p\mathrm{OH^-} = \mathrm{Pb}_q(\mathrm{OH})_p^{(2q-p)+}$ was evaluated by combining the formation constants $^*\beta_{pq}$ and the autoprotolysis constants obtained. The free energy change of transfer from water to a dioxane–water mixture for the reaction could be estimates as $\Delta G^{\mathrm{t}}_{pq} = -RT\ln\{\beta_{pq}(\mathrm{mix})/\beta_{pq}(\mathrm{aq})\}$. The values $(1/p)\Delta G^{\mathrm{t}}_{pq}$ of hydroxo complexes of various metal ions such as lead(II), copper(II), nickel(II), beryllium(II), and cadmium(II) ions were approximately independent of the complexes at a given concentration of dioxane. This result suggested that the formal charge per metal ion of the complex, z' $(=z-p/q$; z: charge of a metal ion), rather than the total charge of the complex, $zq-p$, is essential for the interactions between the hydroxo complexes and solvent molecules.

The hydrolytic reactions of lead(II) ion have so far been studied in aqueous solution containing various ionic media.[1-3] Recently, Olin has reported formation of four hydrolytic species, *i.e.*, the $\mathrm{PbOH^+}$ and $\mathrm{Pb_4(OH)_4^{4+}}$ complexes in the relatively low pH region $(5<\mathrm{pH}<7)$ and the $\mathrm{Pb_3(OH)_4^{2+}}$ and $\mathrm{Pb_6(OH)_8^{4+}}$ complexes at a higher pH $(6<\mathrm{pH}<8)$.[4] The $\mathrm{Pb_4(OH)_4^{4+}}$ and $\mathrm{Pb_6(OH)_8^{4+}}$ complexes are predominant species and most of lead(II) ions exist as the hydroxo complexes at $\mathrm{pH}>6$. The structures of the $\mathrm{Pb_4(OH)_4^{4+}}$ and $\mathrm{Pb_6(OH)_8^{4+}}$ complexes have been studied by means of X-ray diffraction.[5,6] Raman spectroscopic studies on the complexes have also been reported.[7]

We have previously reported the medium effect on the hydrolytic reactions of various divalent metal ions such as beryllium,[8] copper,[9] nickel,[10] and cadmium[11] in dioxane–water mixtures. It has been found that the composition of the hydrolytic species and the formation constant $^*\beta_{pq}$ for the reaction, $q\mathrm{M}^{z+} + p\mathrm{H_2O} = \mathrm{M}_q(\mathrm{OH})_p^{(zq-p)+} + p\mathrm{H^+}$ are generally little affected by the solvent composition up to 0.5 mole fraction (*ca.* 88 w/w %) of dioxane in the medium.

In the present study, the hydrolytic reactions of lead(II) ions were studied in water and dioxane–water mixtures. The autoprotolysis reaction of solvent was also investigated in the same solvent systems. On the basis of the formation constants of the hydroxo complexes of lead(II) ions, together with those of other metal ions previously obtained, the medium effect for the hydrolytic reactions of divalent metal ions is discussed.

Experimental

All measurements were carried out at (25.00±0.02) °C in a liquid paraffin bath set in a room thermostated at (25±0.5) °C. Lithium perchlorate was used as an ionic medium to keep the concentration of perchlorate ions at 3 mol dm^{-3}. Total concentrations of lead(II) ions examined were changed from 0.001 to 0.08 mol dm^{-3}. The total concentration of lead(II) ions was kept constant throughout a series of potentiometric titrations. The cell used for the emf measurements of the autoprotolysis reaction of the solvent was as follows:

$$\mathrm{Ref}\,|\,\text{Test Solution}\,|\,\mathrm{H_2(Pt)} \tag{A}$$

$$\mathrm{Ref} = \left|\begin{array}{l}3\ \mathrm{mol\ dm^{-3}}\\ \mathrm{LiClO_4}\\ \text{in Mixture}\end{array}\right|\begin{array}{l}3\ \mathrm{mol\ dm^{-3}}\\ \mathrm{LiClO_4}\\ \text{in aqueous}\\ \text{solution}\end{array}\left|\begin{array}{l}0.01\ \mathrm{mol\ dm^{-3}}\\ \mathrm{AgClO_4}\\ 2.99\ \mathrm{mol\ dm^{-3}}\\ \mathrm{LiClO_4}\\ \text{aqueous}\\ \text{solution}\end{array}\right|\mathrm{AgCl{-}Ag} \tag{B}$$

The emf differences between the two hydrogen electrodes immersed in the same test solution were within 0.1 mV. The emf reached a constant value within 15—20 min after the addition of $\mathrm{HClO_4}$ solution and remained unchanged within ±0.05 mV for at least 5—6 h. The cells used for emf measurements of free-hydrogen and free-lead(II) ions were, respectively, as follows:

$$\mathrm{Ref}\,|\,\text{Test Solution}\,|\,\mathrm{GE} \tag{C}$$

$$\mathrm{Ref}\,|\,\text{Test Solution}\,|\,\mathrm{Pb(Hg)}. \tag{D}$$

The emfs of both glass electrode (GE) and lead amalgam electrode reached a constant values within a minute and remained unchanged within ±0.1 mV for at least 5—6 h.

Reagents and Analysis. Lead(II) Perchlorate. A stock solution of lead(II) perchlorate was prepared as follows: First, reagent grade lead(II) nitrate was recrystallized twice from water. The lead nitrate crystals thus prepared were dissolved in perchloric acid of super special grade diluted with water. Lead perchlorate was crystallized from the solution by evaporating under vacuum and crystals thus obtained were recrystallized from perchloric acid solution by repeating the above procedure. Finally, lead perchlorate thus obtained was recrystallized twice from water. The concentration of lead(II) ions in the stock solution was gravimetrically determined in the form of lead sulfate.

Lithium Perchlorate and Lithium Hydroxide were prepared by the procedures as described in the previous paper.[12]

Dioxane was purified by an ordinary method.[12]

Apparatus. Beckman (No. 40495 and 40498) glass electrodes were used in combination with an Orion Digital pH Meter Model 801. Hydrogen electrodes used were prepared according to Feltham and Spiro.[13] The hydrogen electrodes were stored in a 0.1 mol dm^{-3} H_2SO_4 solution and were electrolyzed about 30 min in the solution before measurements. Lead amalgam electrodes were prepared as described in Ref. 14 and the electrode cell design used was described in a previous paper.[15] The Ag–AgCl electrodes used as references were prepared according to Brown.[16] The emfs of hydrogen and lead amalgam electrodes were measured by using Takeda Riken Digital Voltmeter (TR-6515). For studying hydrolytic reactions of lead(II) ions, glass electrodes were used, while lead amalgam electrodes were used for measurements of potential changes with varying concentrations of dioxane in an acidic solution containing a constant total concentration of lead(II) ions where no hydrolysis occurs.

Results

The Autoprotolysis Constant of Solvent. An H_0 mol dm^{-3} $HClO_4$ ($H_0 \simeq 0.07$) solution containing $(3-H_0)$ mol dm^{-3} $LiClO_4$ was titrated with an LiOH solution containing 3 mol dm^{-3} $LiClO_4$, the concentration of LiOH in the titrant is about 0.03 mol dm^{-3}. The emf E at equilibrium is written by the following equation:

$$\begin{aligned} E &= E_{0,\mathrm{H}} + 59.154 \log\,[\mathrm{H}^+] + 59.154 \log y_{\mathrm{H}} \\ &\quad + E_{\mathrm{j}} - \Delta E_{\mathrm{p}} \\ &= E^*_{0,\mathrm{H}} + 59.154 \log\,[\mathrm{H}^+] + E_{\mathrm{j}} - \Delta E_{\mathrm{p}} \end{aligned} \tag{1}$$

where

$$\Delta E_{\mathrm{p}} = 29.577 \log\,(P_{\mathrm{H}}/P_{0,\mathrm{H}}) \tag{2}$$

and $E_{0,\mathrm{H}}$ is a constant and P_{H} and $P_{0,\mathrm{H}}$ stand for partial pressures of hydrogen gas at each point and initial point of the emf measurements, respectively. The value log $(P_{\mathrm{H}}/P_{0,\mathrm{H}})$ was so small in a course of one series of titrations that it was neglected. E_{j} is the liquid junction potential between the reference electrode and the test solution. y_{H} denotes the activity coefficient of hydrogen ion in the solution. Equation 1 is rewritten by using the autoprotolysis constant $K_{\mathrm{i}}(=[\mathrm{H}^+][\mathrm{OH}^-])$ as follows:

$$\begin{aligned} E &= E^*_{0,\mathrm{H}} + 59.154 \log\,(K_{\mathrm{i}}/[\mathrm{OH}^-]) \\ &= E^*_{0,\mathrm{A}} - 59.154 \log\,[\mathrm{OH}^-]. \end{aligned} \tag{3}$$

Since $E^*_{0,\mathrm{H}}$ and $E^*_{0,\mathrm{A}}$ are constant in a constant ionic medium with a constant composition of solvent, the autoprotolysis constant was estimated by using the $E^*_{0,\mathrm{H}}$ and $E^*_{0,\mathrm{A}}$ values obtained by Gran's plots in relatively low acidic and basic regions of the solution, where the liquid junction potentials were negligible.

$$\log K_{\mathrm{i}} = \frac{E^*_{0,\mathrm{A}} - E^*_{0,\mathrm{H}}}{59.154} \tag{4}$$

The autoprotolysis constants obtained in various solutions by using hydrogen electrodes are summarized in Table 1.

Formation Constants of Hydroxo Complexes of Lead(II) Ions. The hydrolytic reactions of metal ions may be written as follows:

$$q\mathrm{M}^{z+} + p\mathrm{H}_2\mathrm{O} = \mathrm{M}_q(\mathrm{OH})_p{}^{(zp-q)+} + p\mathrm{H}^+. \tag{5}$$

The average number of hydrogen ion set free per metal ion, Z, is an experimentally determinable quantity as given by the following equation:

$$Z = \frac{[\mathrm{H}^+]-\boldsymbol{H}}{B} = \sum_p\sum_q p\,{}^*\beta_{pq}[\mathrm{M}^{z+}]^q[\mathrm{H}^+]^{-p}/B \tag{6}$$

where ${}^*\beta_{pq}$ is the formation constant of the $\mathrm{M}_q(\mathrm{OH})_p{}^{(zq-p)+}$ complex given by Eq. 7;

$${}^*\beta_{pq} = [\mathrm{M}_q(\mathrm{OH})_p{}^{(zq-p)+}][\mathrm{H}^+]^p/[\mathrm{M}^{z+}]^q \tag{7}$$

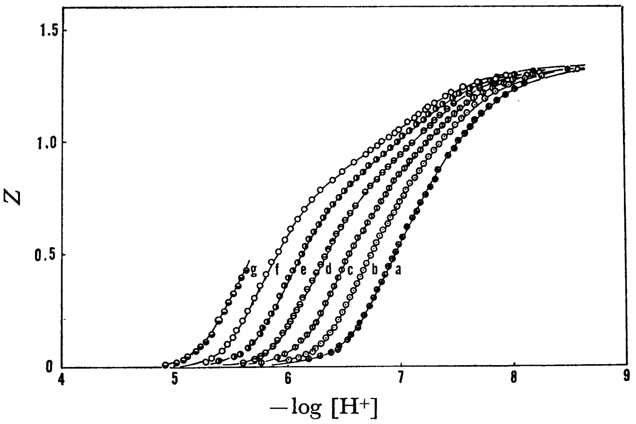

Fig. 1. Formation curves of the hydroxo complexes of lead (II) ions plotted as Z *vs.* −log [H$^+$] in aqueous solution.
Solid lines show calculated curves of Z with the formation constants listed in Table 3. The total concentrations of lead(II) ions in the solutions are (in mol dm^{-3}); a: 0.001251, b: 0.002521, c: 0.005055, d: 0.01001, e: 0.02000, f: 0.04001, g: 0.08008.

TABLE 1. DETERMINATION OF pK_{i} IN VARIOUS AQUEOUS ORGANIC MIXTURES CONTAINING 3 mol dm^{-3} $LiClO_4$[a)]

	Aqueous solution		0.1 mole fraction (35.2 w/w %) Dioxane–water		0.2 mole fraction (55.0 w/w %) Dioxane–water		0.2 mole fraction (30.8 w/w %) Methanol–water		0.2 mole fraction (39.0 w/w %) Ethanol–water	
	$E^*_{0,\mathrm{H}}$	$E^*_{0,\mathrm{A}}$	$E^*_{0,\mathrm{H}}$	$E^*_{0,\mathrm{A}}$	$E^*_{0,\mathrm{H}}$	$E^*_{0,\mathrm{A}}$	$E^*_{0,\mathrm{H}}$	$E^*_{0,\mathrm{A}}$	$E^*_{0,\mathrm{H}}$	$E^*_{0,\mathrm{A}}$
1	616.19	−203.43	645.15	−219.19	664.69	−245.77	627.31	−208.29	625.75	−225.02
2	616.35	−203.54	644.72	−219.33	664.10	−246.11	627.39	−208.22	625.98	−225.11
3	617.06	−203.56	644.85	−219.47	663.31	−246.24	627.38	−208.27	626.46	−225.14
4	616.73	−203.63	644.86	−219.42	663.57	−246.30	627.33	−208.32	626.40	−225.37
5	616.73	−203.45	644.90	−219.16	663.40	−245.95	627.37	−208.30	626.42	−225.33
6	616.75	−203.53							626.39	−225.31
Mean	616.73	−203.51	644.90	−219.31	663.42	−246.07	627.36	−208.29	626.42	−225.13
Dev.	±0.37	±0.13	±0.25	±0.16	±0.15	±0.24	±0.06	±0.03	±0.30	±0.25
pK_{i}	13.87±0.01		14.61±0.01		15.38±0.01		14.13±0.01		14.40±0.01	

a) The values of emf are given by mV units.

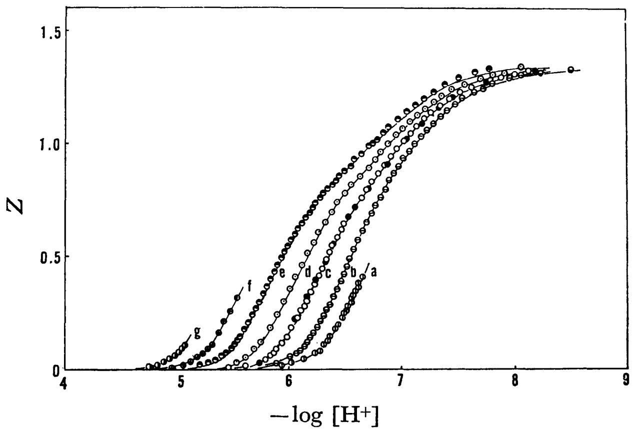

Fig. 2. Formation curves of the hydroxo complexes of lead(II) ions plotted as Z *vs.* $-\log [H^+]$ in 0.1 mole fraction dioxane-water mixture.
Solid lines show calculated curves of Z with the formation constants listed in Table 3. The total concentrations of lead(II) ions in the solutions are (in mol dm^{-3}); a: 0.01253, b: 0.002501, c: 0.005001, solid circles denote measured points by back titrations, d: 0.01001, e: 0.02002, f: 0.04001, g: 0.08000.

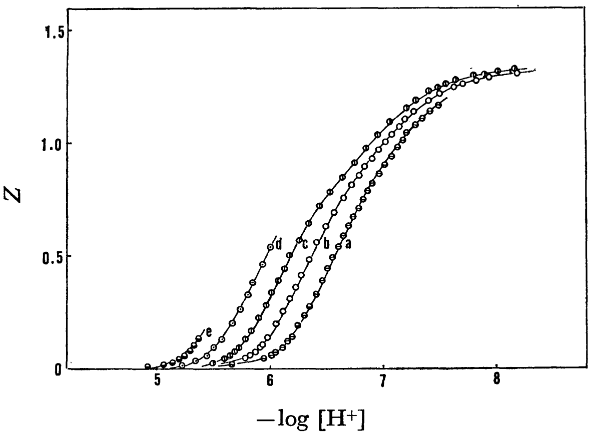

Fig. 3. Formation curves of the hydroxo complexes of lead(II) ions plotted as Z *vs.* $-\log [H^+]$ in 0.2 mole fraction dioxane-water mixture.
Solid lines show calculated curves of Z with the formation constants listed in Table 3. The total concentrations of lead(II) ions in the solutions are (in mol dm^{-3}); a: 0.002414, b: 0.005055, c: 0.01009, d: 0.02017, e: 0.03988.

and $\boldsymbol{H}$ denotes an analytical excess of hydrogen ions, B the total concentration of metal ion, $[M^{z+}]$ and $[H^+]$ the concentrations of free M^{z+} and H^+ ions, respectively. The results obtained are summarized in Figs. 1—3 as Z *vs.* $-\log [H^+]$ plots. The formation curves were analyzed by means of a graphical method at the first step of calculation, as has been used in previous papers.[8–11] However, we met with difficulties to

Table 2. Determination of the formation constants $^*\beta_{pq}$ for the hydroxo complexes of lead(II) ion by the least-squares method

	Aqueous solution			0.1 mole fraction Dioxane–water			0.2 mole fraction Dioxane–water		
	Initial	Final	Fixed	Initial	Final	Fixed	Initial	Final	Fixed
PbOH	−8.80	(−8.314)	−7.65	−7.20	—	−7.41	−7.27	—	−7.21
$Pb_2(OH)_2$	−11.89	—		−11.52	(−11.581)		−11.52	(−11.310)	
$Pb_3(OH)_3$	−15.62	−15.286		−15.29	−14.982		−15.29	−14.813	
$Pb_4(OH)_4$	−19.25	−19.423	−19.14	−18.61	−18.598	−18.44	−18.57	−19.171	−18.63
$Pb_5(OH)_5$	−22.93	(−24.877)							
$Pb_6(OH)_6$	−26.61	—							
$Pb_7(OH)_7$	−30.29	—							
$Pb_8(OH)_8$	−33.97	—							
$Pb_9(OH)_9$	−37.65	—							
$Pb_3(OH)_4$	−22.75	−22.782	−22.75	−21.79	−21.788	−21.79	−21.75	−21.738	−22.73
$Pb_6(OH)_8$	−42.32	−42.329	−42.32	−40.92	−40.751	−40.75	−41.17	−41.122	−41.18
$Pb_9(OH)_{12}$	−61.89	—							
Pb_2OH	−6.48	—							
$Pb(OH)_2$	−15.00	(−16.372)		−4.96	—		−4.96	—	
$Pb_3(OH)_2$	−10.16	—							
$Pb_2(OH)_3$	−19.02	—							
$Pb_4(OH)_3$	−13.84	—							
$Pb_5(OH)_4$	−17.52	—					−25.61	—	
$Pb_4(OH)_5$				−25.61	—				
$Pb_6(OH)_5$	−20.90	—							
$Pb_5(OH)_6$				−29.37	—		−29.37	—	
$Pb_6(OH)_7$	−36.40	(−36.186)		−33.14	—		−33.14	—	
U	11.46	0.0219	0.0307	0.533	0.0537	0.0562	0.369	0.0208	0.0280

Initial: Formation constants initially assumed. Final: Formation constants finally obtained. Fixed: The set of the complexes is fixed at that proposed by Olin, but the formation constants of the complexes are floated.
( ): Minor species and uncertain. —: Unreasonable species which is rejected in the course of the calculation.

estimate the composition of complexes formed in a relatively low pH region if there exists either $Pb_4(OH)_4^{4+}$ or $Pb_3(OH)_3^{3+}$, or both. Therefore, the composition of the complexes formed and their formation constants were determined by the least-squares method using an electronic computer (HITAC 8700). As a first guess, a number of possible species were assumed to be present in the systems, and then unreasonable species were rejected in the course of the least-squares optimization. The method used was essentially based on the principle of the LETAGROP program developed by Sillén.[17] The minimum value of the error square sum $U=\sum(Z_{\mathrm{obsd}}-Z_{\mathrm{calcd}})^2$ for a given system was searched by choosing the best set of the composition (p and q) and the formation constants of the complexes in the system. As is shown in Table 2, the only four complexes, $Pb_3(OH)_3^{3+}$, $Pb_4(OH)_4^{4+}$, $Pb_3(OH)_4^{2+}$, and $Pb_6(OH)_8^{4+}$ were finally obtained as possible species in all the solvent systems examined. Formation of the $PbOH^+$ complex proposed by Olin[4] was rather uncertain in our measurements (see Table 2). An examination of the least-squares calculation by assuming a set of complexes, $PbOH^+$, $Pb_4(OH)_4^{4+}$, $Pb_3(OH)_4^{2+}$, and $Pb_6(OH)_8^{4+}$, which had been proposed by Olin, gave a larger error square sum than that for a set of the complexes, $Pb_3(OH)_3^{3+}$, $Pb_4(OH)_4^{4+}$, $Pb_3(OH)_4^{2+}$, and $Pb_6(OH)_8^{4+}$, and the $PbOH^+$ complex was excluded in the course of the refinement. In Table 2, columns "Initial" and "Final" show the initially assumed and finally obtained composition and stability constants of the complexes, respectively. Lack of number in the column "Final" means that the relevant complex is rejected as an unreasonable one during the course of the refinement. "Fixed" denotes that the set of the complexes is fixed at the proposed one by Olin, and the formation constants of the complexes are allowed to change to reach the minimum error square sum. Since the Z values never exceed 1.5, possible combinations of $p/q<1.5$ are assumed as the inital sets of complexes. Values in parentheses are uncertain ones. The final results obtained for the formation constants of the hydroxo complexes of lead(II) ions are summarized in Table 3, together with the autoprotolysis constants of the solvents.

TABLE 3. AUTOPROTOLYSIS CONSTANT $K_1(=[H^+][OH^-])$ AND FORMATION CONSTANTS OF HYDROXO COMPLEXES OF LEAD(II) ION IN AQUEOUS AND DIOXANE–WATER MIXTURES CONTAINING 3 mol dm^{-3} $LiClO_4$

$q Pb^{2+}+pH_2O=Pb_q(OH)_p^{(2q-p)}+pH^+$

$^*\beta_{pq}=[Pb_q(OH)_p^{(2q-p+)}][H^+]^p/[Pb^{2+}]^q$

	Mole fraction of dioxane		
	0.0	0.1	0.2
pK_1	13.87 (0.01)	14.61 (0.01)	15.38 (0.01)
$-\log{}^*\beta_{33}$	−15.29 (0.03)	−14.98 (0.03)	−14.81 (0.03)
$-\log{}^*\beta_{44}$	−19.42 (0.02)	−18.60 (0.02)	−19.17 (0.02)
$-\log{}^*\beta_{43}$	−22.78 (0.05)	−21.79 (0.05)	−21.74 (0.05)
$-\log{}^*\beta_{86}$	−42.33 (0.02)	−40.75 (0.02)	−41.12 (0.02)

Uncertainties of the formation constants were estimated as 3σ where σ denotes the standard deviation.

Discussion

As seen in Table 3, the formation constants of all of the lead(II) hydroxo complexes, $\log{}^*\beta_{pq}$, were only slightly changed by the addition of dioxane in an aqueous solution, the fact having been found for other divalent metal ions so far examined.[8–11] Combination of the formation constant $^*\beta_{pq}$ with the autoprotolysis constant of solvent K_1 leads to the formation constant β_{pq} for the hydrolytic reaction as follows:

$$qM^{z+}+pOH^-=M_q(OH)_p^{(zq-p)+} \quad (8)$$

$$\beta_{pq}=[M_q(OH)_p^{(zq-p)+}]/[M^{z+}]^q[OH^-]^p$$
$$={}^*\beta_{pq}/K_1^p. \quad (9)$$

Thus, the free energy change of transfer for Reaction 8 from the aqueous solution to a dioxane–water mixture is obtained as follows:

$$\Delta G_{pq}^t=\Delta G_{pq}^\circ(\mathrm{mix})-\Delta G_{pq}^\circ(\mathrm{aq})$$
$$=-RT\ln\{\beta_{pq}(\mathrm{mix})/\beta_{pq}(\mathrm{aq})\}. \quad (10)$$

The free energy changes of transfer ΔG_{pq}^t against the mole fraction of dioxane in the mixtures are represented in Fig. 4. The values ΔG_{pq}^t were negative for all of the hydrolytic species, as well as metal and hydrogen ions, and became more negative with an increase in the concentration of dioxane. However, no clear correlation was found between ΔG_{pq}^t and the composition or the total charge of the hydroxo complexes. ΔG_{pq}^t may be expressed in terms of the partial molar free energy change of transfer of a species i, Δg_i^t, as follows:

$$\Delta G_{pq}^t=\Delta g_{pq}^t-q\Delta g_M^t-p\Delta g_{OH}^t. \quad (11)$$

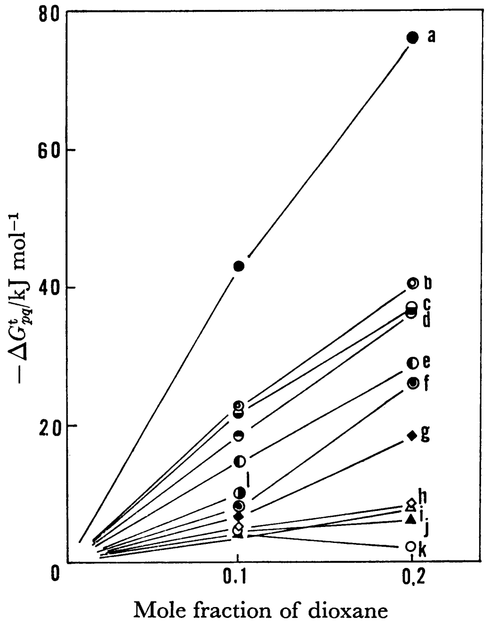

Fig. 4. Free energy changes of transfer of hydroxo complexes of divalent metal ions against the mole fraction of dioxane in mixed solvents.
a: $Pb_6(OH)_8^{4+}$, b: $Pb_3(OH)_4^{2+}$, c: $Pb_4(OH)_4^{4+}$, d: $Ni_4(OH)_4^{4+}$, e: $Pb_3(OH)_3^{3+}$, f: $Be_3(OH)_3^{3+}$, g: $Cu_2(OH)_2^{2+}$, h: $CuOH^+$, i: Cd_2OH^{3+}, j: Be_2OH^{3+}, k: Cu_2OH^{3+}, l: $Cu_3(OH)_2^{4+}$.

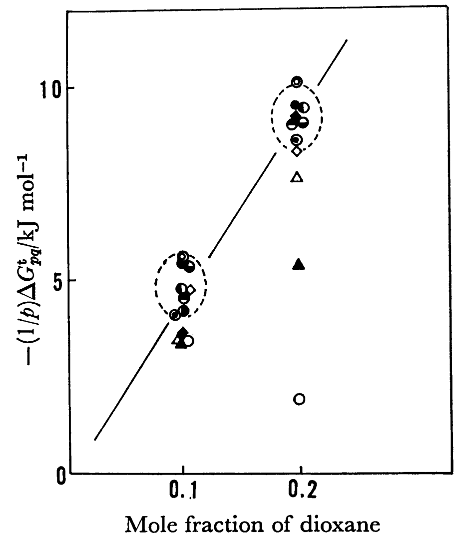

Fig. 5. Free energy changes of transfer per hydroxide ion of hydroxo complexes of divalent metal ions against the mole fraction of dioxane in mixed solvents.
Symbols are the same as those in Fig. 4.

Since the number of OH^- ion involved in a hydroxo complex depends on its composition, the values, $(1/p)\Delta G^t_{pq}$, were subsequently compared in Fig. 5 instead of ΔG^t_{pq} in Fig. 4. The values $(1/p)\Delta G^t_{pq}$ were approximately independent of the complexes examined at a given solvent composition, except for some complexes such as Cd_2OH^{3+}, Cu_2OH^{3+}, and Be_2OH^{3+}, which are all minor species in their systems. For the partial molar free energy change of transfer Δg^t_i from an aqueous solution to a dioxane–water mixture, it has been reported that Δg^t_i of a cation is usually negative and the value becomes more negative for ions with small ionic radius and that the reverse is the case for anions.[18)]

In order to estimate the value of Δg^t_{pq}, the changes of the activity coefficients of lead(II) and hydrogen ions were measured at a constant total concentration of a relevant ion with varying solvent compositions by measuring emfs of cells (C) and (D). Emfs of the cells may be written as follows: for cell (C)

$$E_H = E_{0,H} + 59.154\log[H^+] + 59.154\log y_H + E_j \quad (12)$$

and for cell (D)

$$E_{Pb} = E_{0,Pb} + 29.577\log[Pb^{2+}] + 29.577\log y_{Pb} + E_j. \quad (13)$$

Since we used glass electrodes, ΔE_p equals zero. y_i denotes the activity coefficient of a species i in the solution. An activity coefficient of a species i in a given solvent may be described as follows:

$$y_i = y_i(aq)\cdot y_i(solvent) = y_i(mix) \quad (14)$$

where $y_i(aq)$ represents the activity coefficient of species i in an aqueous medium in which y_i approaches unity at infinite dilution. y_i may be reasonably assumed to be constant in a constant ionic medium of a given solvent. $y_i(solvent)$ is a function of solvent composition in a given ionic medium and is unity in an aqueous solution.

Since $E_{0,H}$ is a constant independent of solvent composition, changes in E_H with changing solvent compositions at a constant $[H^+]$ is given as

$$\begin{aligned}\Delta E_H &= E_H(mix) - E_H(aq)\\ &= 59.154\log\{y_H(mix)/y_H(aq)\} + \{E_j(mix) - E_j(aq)\}\\ &= 59.154\log y_H(solvent) + \{E_j(mix) - E_j(aq)\}. \quad (15)\end{aligned}$$

Thus, ΔE_H may be independent of $[H^+]$, but depends on the solvent composition of 3 mol dm^{-3} $LiClO_4$ solution, as far as the term $\{E_j(mix) - E_j(aq)\}$ is negligibly small. Similar measurements were carried out for ΔE_{pq} by using lead amalgam lelectrodes.

The emf changes of cells (C) and (D), ΔE_H and ΔE_{Pb}, respectively, were measured at constant $[H^+]$ and $[Pb^{2+}]$. Since the measurements were carried out in an acidic solution where no hydrolysis of metal ion occurs, $[H^+]$ is equal to the total concentration of the acid in the solution, and $[Pb^{2+}]$ is equal to the total concentration of the metal ion, B.

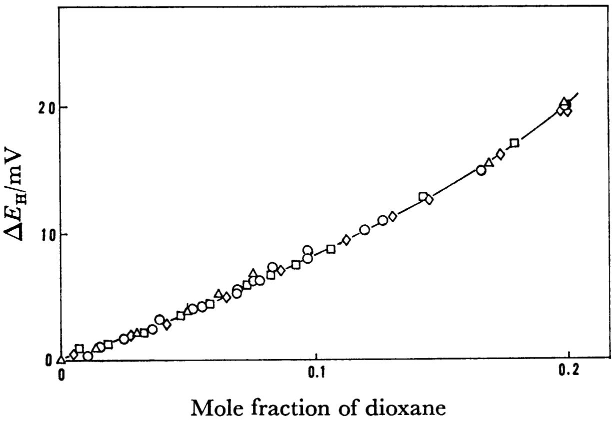

Fig. 6. Emf changes of cell (C) with varying solvent compositions.
The concentrations of hydrogen ions (in mol dm^{-3}); are; △: 0.00 (extrapolated by Gran's plot), (Ref$_1$), ○: 0.010 (Ref$_1$), □: 0.020 (Ref$_1$), ◇: 0.020 (Ref$_2$). Ref$_1$ and Ref$_2$ indicate the reference cells (E) and (F), respectively, used in the measurements.

The emf for cell (C) was measured by using two different reference electrodes in order to check the effect of the different liquid junction on potentials.

Ref$_1$ =	3 mol dm^{-3} $LiClO_4$ in aqueous solution	0.01 mol dm^{-3} $AgClO_4$ 2.99 mol dm^{-3} $LiClO_4$ in aqueous solution	AgCl-Ag	(E)
Ref$_2$ =	3 mol dm^{-3} $LiClO_4$ in 0.2 mole fraction dioxane–water mixture	0.01 mol dm^{-3} $AgClO_4$ 2.99 mol dm^{-3} $LiClO_4$ in aqueous solution	AgCl-Ag	(F)

As is seen from Fig. 6, ΔE_H obtained fell on one curve. Therefore, the liquid junction potentials of the cells were found to be negligible.

In these measurements, the changes of the activity coefficients or the partial molar free energy changes of transfer, Δg^t, of hydrogen and lead(II) ion in a 3 mol dm^{-3} $LiClO_4$ can be described with a good approximation as follows:

$$\Delta g^{t}_{H} = -RT\ln\{y_{H}(\text{mix})/y_{H}(\text{aq})\} = -F\Delta E_{H} \qquad (16)$$

$$\Delta g^{t}_{Pb} = -RT\ln\{y_{Pb}(\text{mix})/y_{Pb}(\text{aq})\} = -2F\Delta E_{Pb} \qquad (17)$$

where F stands for Faraday constant. The Δg^{t}_{H} and Δg^{t}_{Pb} values with varying mole fractions of dioxane are shown in Fig. 7.

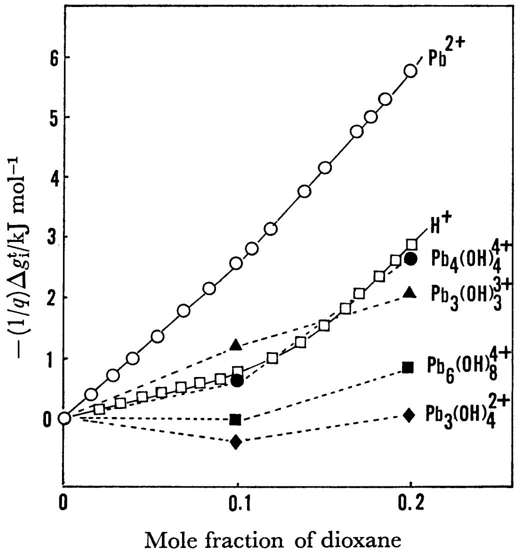

Fig. 7. Partial molar free energy changes of transfer of H^+, Pb^{2+}, and $Pb_q(OH)_p^{(2q-p)+}$ with varying solvent compositions.

The thermodynamic formation constant of the $M_q(OH)_p{}^{(zq-p)+}$ complex is given in terms of activities as follows:

$$\begin{aligned} {}^{*}\beta^{\circ}_{pq} &= (a_{pq}\cdot a_{H}{}^{p})/(a_{M}{}^{q}\cdot a_{H_2O}{}^{p}) \\ &= \frac{[M_q(OH)_p{}^{(zq-p)+}][H^+]^p}{[M^{z+}]^q}\cdot\frac{1}{[H_2O]^p}\cdot\frac{y_{pq}y_{H}{}^{p}}{y_{M}{}^{q}f_{H_2O}{}^{p}}. \end{aligned} \qquad (18)$$

f_{H_2O} represents the activity coefficient of water in a mixed solvent expressed by the mole fraction scale of the solvent component. If the standard state of any reacting species is so chosen that the activity coefficient of the species appraoches unity when the composition of the solution approaches 3 mol dm^{-3} LiClO$_4$ aqueous solution, ${}^{*}\beta_{pq}$ obtained in the aqueous solution is given as the formation constant at the standard state ($={}^{*}\beta^{\circ}_{pq}$), and is independent of the solvent composition at a given temperature. The activity coefficient y is defined in terms of molarity and is independent of the concentration of the relevant species in a given constant ionic medium, but is dependent on the solvent composition, as is shown in Eq. 14.

Since the value $[M_q(OH)_p{}^{(zq-p)+}]\,[H^+]^p/[M^{z+}]^q = {}^{*}\beta_{pq}$ is experimentally determinable for the complex $M_q(OH)_p{}^{(zq-p)+}$ in a given solvent and ${}^{*}\beta^{\circ}_{pq}$ is defined as the formation constant of the complex in the aqueous solution, the difference between the formation constants obtained in a mixed solvent and an aqueous solution is given as follows:

$$\begin{aligned} \Delta\ln{}^{*}\beta_{pq} &= \ln{}^{*}\beta_{pq}(\text{mix}) - \ln{}^{*}\beta_{pq}(\text{aq}) \\ &= p\ln[H_2O] + \ln(y_{M}{}^{q}/y_{H}{}^{p}) \\ &\quad - \ln(y_{pq}/f_{H_2O}{}^{p}). \end{aligned} \qquad (19)$$

The first two terms of the right hand side of Eq. 19 are experimentally determined, and thus, the value $\ln(y_{pq}/f_{H_2O}{}^{p})$ is estimated. If we assume that $f_{H_2O}=1$ as a first approach over the range of the solvent composition examined here, the values may represent the variations of the activity coefficient of the $M_q(OH)_p{}^{(zq-p+)}$ complex in the dioxane–water mixtures containing 3 mol dm^{-3} LiClO$_4$ at 25 °C. The partial molar free energy change of transfer of the $M_q(OH)_p{}^{(zq-p)+}$ complex may thus be calculated as follows:

$$\begin{aligned} \Delta g^{t}_{pq} &= -RT\ln[H_2O]^p + q\Delta g^{t}_{M} - p\Delta g^{t}_{H} \\ &\quad + RT\Delta\ln{}^{*}\beta_{pq}. \end{aligned} \qquad (20)$$

$(1/q)\Delta g^{t}_{pq}$ with varying mole fractions of dioxane are shown in Fig. 7.

As is seen from Fig. 7, Δg^{t}_{H} and Δg^{t}_{Pb} are both negative and become more negative with an increase in the mole fraction of dioxane. $(1/q)\Delta g^{t}_{pq}$ seems to vary with a similar trend to Δg^{t}_{H} and Δg^{t}_{pq}. At a given mole fraction of dioxane, the $(1/q)\Delta g^{t}_{pq}$ values are smaller than Δg^{t}_{pq}, and the smaller the formal charge, $(zq-p)/q$, of a hydroxo complex is, the smaller $(1/q)\Delta g^{t}_{pq}$ may become. The same results have previously been obtained for the hydroxo complex of cadmium.[11)]

Equation 4 is rewritten as follows:

$$\frac{1}{p}\Delta G^{t}_{pq} = \frac{q}{p}\left(\frac{1}{q}\Delta g^{t}_{pq} - \Delta g^{t}_{M}\right) - \Delta g^{t}_{OH}. \qquad (21)$$

The values $(1/p)\Delta G^{t}_{pq}$ of formation of hydroxo complexes of divalent metal ions examined are approximately independent of the complexes at a given solvent composition. Since the contribution of Δg^{t}_{OH} to $(1/p)\Delta G^{t}_{pq}$ is the same for all the hydroxo complexes and $(1/q)\Delta g^{t}_{pq}$ may vary with the formal charge of the complexes, the term $(q/p)\{(1/q)\Delta g^{t}_{pq} - \Delta g^{t}_{M})\}$ may be independent of the complexes but dependent on the composition of solvents. Thus, at a given solvent composition,

$$\frac{q}{p}\left(\frac{1}{q}\Delta g^{t}_{pq} - \Delta g^{t}_{M}\right) \approx k(\text{constant}). \qquad (22)$$

The formal charge z' per metal ion of the complex is defined as follows:

$$z' = \frac{1}{q}(zq-p) = z - p/q. \qquad (23)$$

Thus, replacing $z-z'$ to p/q in Eq. 22, we rewrite the equation for free energy change of transfer of an $M_q(OH)_p{}^{(zq-p)+}$ complex in terms of the formal charge of the complex as follows:

$$\frac{1}{q}\Delta g^{t}_{pq} \approx \Delta g^{t}_{M} + k(z-z'). \qquad (24)$$

Since $(1/q)\Delta g^{t}_{pq}$ may be less negative than Δg^{t}_{M} (see Fig. 7), the value k may be positive at a given solvent composition. Thus, Eq. 24 indicates that the value $(1/q)\Delta g^{t}_{pq}$ of a hydroxo complex approaches the value of Δg^{t}_{M} when the formal charge z' of the complex approaches z, the charge of the free metal ion.

Medium effects on the thermodynamic parameters of the hydrolytic reactions of metal ions may be mainly due to changes in solvation structures of the species involved.[18–20)] Ion-solvent interactions of the hydroxo complexes of beryllium ions in dioxane–water mixtures were discussed in a previous paper.[20] The enthalpy changes of transfer per hydroxide ion $(1/p)\Delta H^{t}_{pq}$ [$=(q/p)\{(1/q)\Delta h^{t}_{pq}-\Delta h^{t}_{M}\}-\Delta h^{t}_{OH}$, where Δh^{t}_{i} denotes the partial molar enthalpy change of transfer of species i] strongly depended on metals.[20,21] Consequently, the value $(1/q)\Delta h^{t}_{pq}$ depends on both p/q and Δh^{t}_{M} at a given solvent composition.

The different features of the solvent effects between ΔG^{t}_{pq} and ΔH^{t}_{pq} of hydroxo complexes of divalent metal ions may be explained as follows: For a strongly solvated metal ion (*i.e.*, $(1/p)\Delta H^{t}_{pq}$ may be largely negative for such an ion), the ion may have a large ordering effect for the solvent molecules even in the secondary solvation shell of the ion, and thus, $(1/p)\Delta S^{t}_{pq}$ may become less positive. Therefore, the effect due to $(1/p)\Delta H^{t}_{pq}$ on $(1/p)\Delta G^{t}_{pq}$ may be compensated by the effect due to $(1/p)\Delta S^{t}_{pq}$, and thus, the $(1/p)\Delta G^{t}_{pq}$ value becomes practically independent of metal ion.

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