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Ionic Equilibria in Mixed Solvents. XII. Hydrolysis of Cadmium(II) Ion in Dioxane-Water and Methanol-Water Mixtures

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The hydrolytic reactions of cadmium(II) ions were studied at 25 °C in dioxane–water and methanol–water mixtures with varying compositions of the organic solvents, each mixture containing 3 mol dm^{-3} (Li)ClO_4 as an ionic medium. Emf measurements were carried out over the range of the total cadmium(II) concentrations of 0.2 to 0.8 mol dm^{-3} in all the systems. Two complexes Cd_2OH^{3+} and $CdOH^+$ were found in the dioxane–water mixtures, but the latter complex was not detected in the methanol–water system. The formation constant of the Cd_2OH^{3+} complex was slightly larger in the methanol–water mixtures than in the dioxane–water mixtures at the same mole-fraction concentration of the organic solvents.

The formation of the mononuclear complex $CdOH^+$ was reported by many authors[1–6] in the hydrolytic reactions of cadmium(II) ion in aqueous solutions. The formation of the dinuclear Cd_2OH^{3+} complex, which has been first reported by Biedermann and Ciavatta,[7] was confirmed by us in a previous work.[8] However, the existence of the tetranuclear $Cd_4(OH)_4{}^{4+}$ complex was doubtful as an equilibrium species of hydrolyzed cadmium ions.[8]

The solvent effects on the hydrolytic reactions of various metal ions such as beryllium,[9–11] copper,[12,13] nickel,[14] and aluminium[15] have so far been studied in various aqueous–organic mixtures and the results can be summarized as follows: 1) The formation constants of the complexes, most of which were large polynuclear complexes, were little affected by the solvent composition even though the dioxane concentration changed widely, *e.g.*, 0—83% w/w, in contrast with the dissociation constants of carboxylic acids[16] and phenols,[17] which markedly changed with the solvent composition. 2) Similar results were found in other solvent systems, water–methanol, water–ethanol, and water–acetone mixtures. 3) The solvent effects on the hydrolytic reactions of metal ions were qualitatively explained by Kawai[18] in terms of the changes in the activity coefficients of the ions in solutions.

However, Wada and his coworkers[19,20] have shown that the formation constant $^*\beta_{1,1}$ of the mononuclear hydroxo complex of Fe^{3+} monotonously increased with the increase of the concentration of methanol in which 0.5 mol dm^{-3} (Na,H)ClO_4 was contained as an ionic medium, as well as the formation constant of the $FeCl^{2+}$ complex in the same ionic medium, containing methanol up to 0.52 mole fraction (about 66% w/w).

In order to find if the formation constant of a mononuclear hydroxo complex would be affected by the solvent composition of aqueous mixed solvents in a different manner from that of a polynuclear complex, we have examined the hydrolysis of cadmium(II) ions in dioxane–water and methanol–water mixtures, because both mononuclear and polynuclear complexes are formed in this system and their formation constants can be determined with reasonable accuracies in various mixed media.

Experimental

Reagents. *Cadmium(II) Perchlorate*: Cadmium oxide (99.99%, Mitsuwa Pure Chemicals Co., Osaka) was dissolved in 1: 1 $HClO_4$ (Super special grade, Wako Pure Chemical Ind., Osaka) and cadmium perchlorate thus prepared was recrystallized three times from water. The purity of the cadmium oxide had been checked by emission spectroscopy.

Lithium perchlorate and *lithium hydroxide* were prepared by the same procedures as described in the previous paper.[8] *Dioxane* purified by the ordinary method[13] was stored in a refrigerator and melted just before preparation of a test solution. *Methanol* of reagent grade was distilled twice.

Apparatus. Beckman (No. 40498) glass electrodes were used in combination with an Orion Digital pH Meter Model 801. A cadmium-ion selective electrode Model 94-48A (Orion Research Inc., Mass., USA) was used, and the potentials were measured by use of Takeda Riken Digital Multimeter 6854. The potentials were reproducible within ±0.1 mV in the mixed solvents used. A Metrohm E211 type Coulometer was employed as a current source for generation of hydrogen ions in a solution during the course of titrations. Silver–silver chloride electrodes set in the Kawai type[11] of the half-cell were prepared according to Brown.[21]

Preparation of the Test Solutions. A slightly acid cadmium(II) perchlorate solution in a mixed solvent was placed in a glass vessel and bubbled with nitrogen gas to remove carbon dioxide, and then a small amount of CdO powder was added to the solution. White precipitates appeared in the solution while agitating for several hours. The agitation was continued for a day passing nitrogen gas through the mixture and then the glass vessel was tightly sealed. The mixture was still continuously agitated for about 20 days in a thermostated room at 25±1.5 °C. Then the solution was filtered through G-3 and G-4 glass filters and the filtrate was left to stand for one day at 25 °C in a liquid paraffin thermostat. This solution was filtered again through a G-4 glass filter to a measuring vessel. The volume of the test solution was determined from the weight and density of the test solution in the vessel. The total concentration of cadmium ion in the test solution was determined gravimetrically as $Cd_2P_2O_7$.

The method of emf measurements was essentially the same as that used in the previous works of this series.

All the measurements were carried out at 25.00±0.02 °C in a liquid paraffin bath set in a room thermostated at 25.0±1.5 °C.

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Results and Discussion

When cadmium(II) ions hydrolyze in a solution, the reaction equilibrium may be written as follows:

$$q\mathrm{Cd}^{2+} + p\mathrm{H_2O} = \mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+. \qquad (1)$$

The average number of hydrogen ion set free per metal ion Z is given as follows:

$$Z = \sum_q \sum_p p\,{}^*\beta_{p,q} b^q h^{-p}/B, \qquad (2)$$

where ${}^*\beta_{p,q}$ is the formation constant of a species defined by Eq. 3

$${}^*\beta_{p,q} = [\mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+}]h^p/b^q, \qquad (3)$$

and B stands for the total concentration of cadmium ion, $b=[\mathrm{Cd}^{2+}]$ and $h=[\mathrm{H}^+]$ at equilibrium.

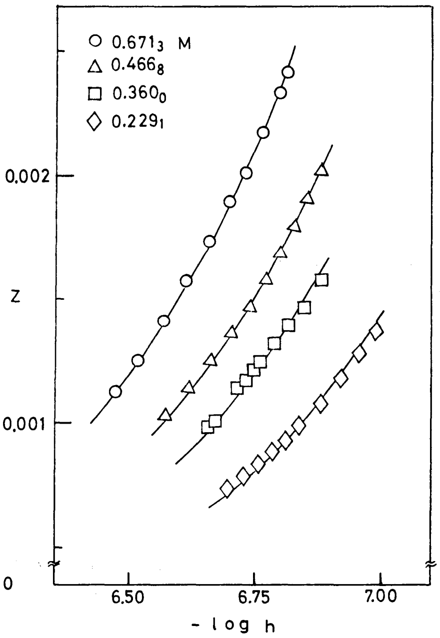

Fig. 1. Values of Z *vs.* $-\log h$ in the 0.10 mole fraction dioxane–water mixture. Solid lines show calculated curves of Z with the formation constants listed in Table 1.

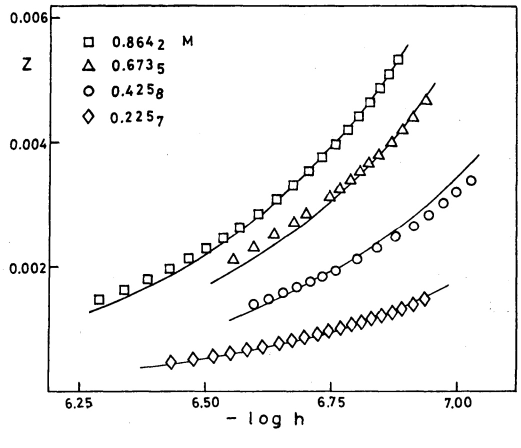

Fig. 2. Values of Z *vs.* $-\log h$ in the 0.10 mole fraction methanol–water mixture. Solid lines show calculated curves of Z with the formation constant listed in Table 1.

Typical results represented by Z plotted against $-\log h$ are graphically shown in Figs. 1 and 2 for the 0.1 mole fraction dioxane–water and methanol–water systems, respectively. According to the same procedure described in the previous paper,[8] we obtained a set of horizontal lines of Zh *vs.* h^{-1} and the intercepts which were dependent on B in each solvent. Thus we concluded that homoligandic complexes, $p=1$, were formed and the equilibrium species were $\mathrm{Cd_2OH^{3+}}$ and $\mathrm{CdOH^+}$.

Table 1. Formation constants ($\log {}^*\beta_{p,q}$) of the $\mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+}$ complex in dioxane–water and methanol–water mixtures at 25 °C

Solvent	Dioxane–Water		Methanol–Water
	$\mathrm{Cd_2OH^{3+}}$	$\mathrm{CdOH^+}$	$\mathrm{Cd_2OH^{3+}}$
Aqueous	−9.13±0.01	−10.3±0.1	−9.13±0.01
0.05 mole fraction	−9.23±0.02	−9.9±0.1	−9.07±0.02
0.10 mole fraction	−9.28±0.02	−10.7±0.1	−9.08±0.02
0.15 mole fraction	−9.37±0.02	−11.0±0.1	—
0.20 mole fraction	−9.3±0.2	−10.7±0.5	−9.3 ±0.2

Table 1 lists the values of $\log {}^*\beta_{p,q}$ determined by the least squares method[18] with a help of an electronic computer HITAC 8700 situated at the Tokyo Institute of Technology. The solid lines in Figs. 1 and 2 show calculated Z values with the constants which are inserted into Eq. 4.

$$Z = ({}^*\beta_{1,1} bh^{-1} + {}^*\beta_{1,2} b^2 h^{-1})/B \qquad (4)$$

In the methanol–water mixtures, the values of ${}^*\beta_{1,1}$ were so small in all the solvents that the values were not evaluated with reasonable accuracies.

The solvent effect of the organic solvents on the formation constants of cadmium(II) hydroxo complexes is rather small as is expected from the results obtained previously of this series.

The formation constant of the $\mathrm{Cd_2OH^{3+}}$ complex monotonously decreases with the increase of the dioxane concentration. In the methanol–water mixtures ${}^*\beta_{1,2}$ is slightly larger than that in aqueous solution, but the change in ${}^*\beta_{1,2}$ is not systematic. The formation constant of the $\mathrm{CdOH^+}$ complex in the dioxane–water mixtures first increases with increasing concentration of dioxane up to 0.05 mole fraction and then decreases. The similar change in the formation constants, *i.e.*, ${}^*\beta_{p,q}$ increases with the dioxane concentration and then decreases after passing through a broad maximum at around 0.1 mole fraction dioxane, has been observed in ${}^*\beta_{3,3}$ of beryllium,[10] ${}^*\beta_{1,1}$ of copper,[13] ${}^*\beta_{4,4}$ of nickel,[14] and ${}^*\beta_{4,4}$ and ${}^*\beta_{8,6}$ of lead hydroxo complexes.[18] The values of ${}^*\beta_{1,1}$ of the mononuclear $\mathrm{CdOH^+}$ complex changed in a different manner from that of ${}^*\beta_{1,1}$ of $\mathrm{Fe^{3+}}$ observed by Wada and his coworkers.[19,20]

Since the changes in ${}^*\beta_{p,q}$ in a constant ionic medium with the solvent composition are caused by the changes of the ratios of activity coefficients of relevant ions in Eq. 1 and the concentration of water, the changes of the activity coefficients of the metal and hydrogen ions were measured with varying solvent compositions by means of emf measurements of the cells,

$$\text{Cd(selective electrode)}|\text{test solution}|\text{Ref} \tag{5}$$

and

$$\text{GE}|\text{test solution}|\text{Ref.} \tag{6}$$

The potentials of the cells may be written as follows: for cell (5)

$$E_{\mathrm{Cd}} = E^{\circ}_{\mathrm{Cd}} + 29.58 \log b + 29.58 \log y_{\mathrm{Cd}} + E_{\mathrm{j}} \tag{7}$$

and for cell (6)

$$E_{\mathrm{H}} = E^{\circ}_{\mathrm{H}} + 59.15 \log h + 59.15 \log y_{\mathrm{H}} + E_{\mathrm{j}} \tag{8}$$

where y denotes the activity coefficient of a species in the solution. In an acid solution where no hydrolysis of cadmium ion occurs, $B=b$. At low and constant b and h, the potential changes of cells 5 and 6 with the solvent composition are proportional to the values of log $\{y_{\mathrm{Cd(mix)}}/y_{\mathrm{Cd(aq)}}\}$ and log $\{y_{\mathrm{H(mix)}}/y_{\mathrm{H(aq)}}\}$, respectively, and the change of the liquid junction potentials is negligible in a high ionic medium.[22] Thus, the changes of the activity coefficients of cadmium and hydrogen ions in a 3 mol dm^{-3} LiClO$_4$ can be described with a good approximation as follows:

$$\log \{y_{\mathrm{Cd(mix)}}/y_{\mathrm{Cd(aq)}}\} = \Delta E_{\mathrm{Cd}}/29.58, \tag{9}$$

and

$$\log \{y_{\mathrm{H(mix)}}/y_{\mathrm{H(aq)}}\} = \Delta E_{\mathrm{H}}/59.15, \tag{10}$$

where ΔE_{Cd} and ΔE_{H} represent the potential changes of cells (5) and (6), respectively, with the solvent composition.

If the standard state of any reacting species is so chosen that the activity coefficient of the species approaches unity when the solution approaches 3 mol dm^{-3} LiClO$_4$ aqueous solution, the activity coefficient of the reacting species y in the aqueous medium is regarded as unity. Therefore, Eqs. 9 and 10 may be simplified as Eqs. 11 and 12, respectively.

$$\log y_{\mathrm{Cd}} = \Delta E_{\mathrm{Cd}}/29.58 \tag{11}$$

and

$$\log y_{\mathrm{H}} = \Delta E_{\mathrm{H}}/59.15 \tag{12}$$

The values of log y_{Cd} and log y_{H} thus evaluated in dioxane–water and methanol–water mixtures are plotted against the concentration of the organic solvents in Figs. 3 and 4, respectively.

The formation constant of the $\mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+}$ complex is given in terms of activities as follows:

$$\begin{aligned} {}^*\beta^{\circ}_{p,q} &= \frac{a_{\mathrm{Cd}_q(\mathrm{OH})_p} \cdot a^p_{\mathrm{H}}}{a^q_{\mathrm{Cd}} \cdot a^p_{\mathrm{H_2O}}} \\ &= \frac{[\mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+}] \cdot h^p}{b^q} \cdot \frac{1}{[\mathrm{H_2O}]^p} \cdot \frac{y_{\mathrm{Cd}_q(\mathrm{OH})_p} \cdot y^p_{\mathrm{H}}}{y^q_{\mathrm{Cd}} \cdot f^p_{\mathrm{H_2O}}}. \end{aligned} \tag{13}$$

${}^*\beta^{\circ}{}_{p,q}$ is the formation constant thermodynamically defined, which 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 constant ionic medium, but is dependent on the solvent composition. $f_{\mathrm{H_2O}}$ is the activity coefficient of water in a mixed solvent expressed by the mole fraction scale of the solvent component. Since the value $[\mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+}]h^p/b^q = {}^*\beta_{p,q}$ is experimentally determinable for the complex $\mathrm{Cd}_q(\mathrm{OH})_p{}^{(2q-p)+}$ in a given solvent and ${}^*\beta^{\circ}{}_{p,q}$ is the formation constant of the complex in the aqueous medium according to definition stated above, the difference between the formation constants obtained in a mixed solvent and in the aqueous solution may be given as follows:

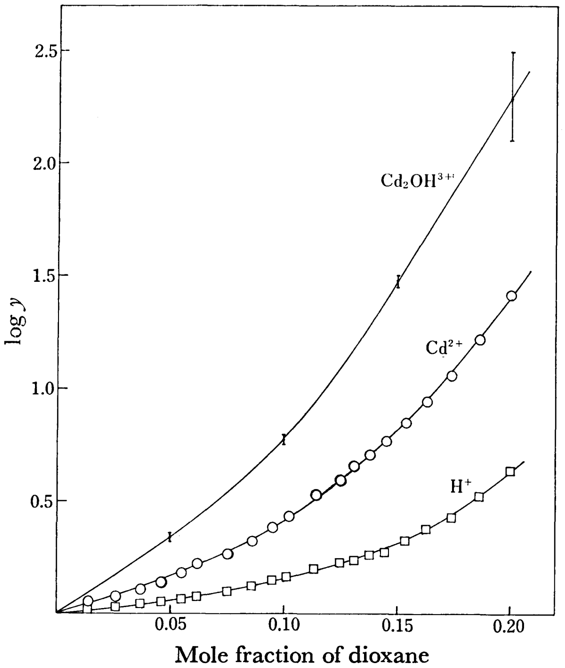

Fig. 3. Variations of log y for H$^+$, Cd^{2+}, and Cd$_2$OH^{3+} ions with the concentration of dioxane-water mixtures. The error bar shown for the Cd$_2$OH^{3+} curve represents an estimated error in log $y_{\mathrm{Cd_2OH}}$ from the uncertainty of the log ${}^*\beta_{1,2}$ value.

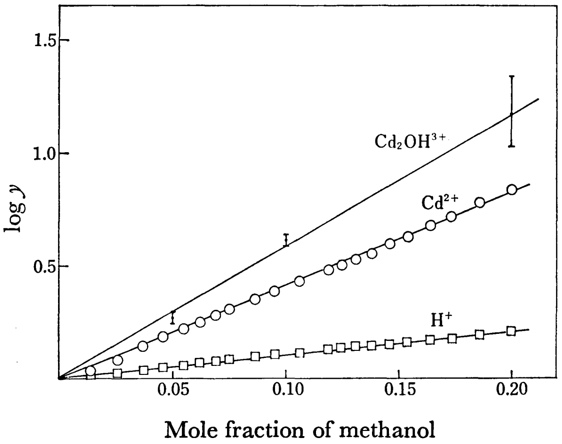

Fig. 4. Variations of log y for H$^+$, Cd^{2+}, and Cd$_2$OH^{3+} ions with the concentration of methanol in methanol–water mixtures. The error bar shown for the Cd$_2$OH^{3+} curve represents an estimated error in log $y_{\mathrm{Cd_2OH}}$ from the uncertainty of the log ${}^*\beta_{1,2}$ value.

$$\begin{aligned} \Delta \log {}^*\beta_{p,q} &= \log {}^*\beta_{p,q}(\mathrm{mix}) - \log {}^*\beta_{p,q}(\mathrm{aq}) \\ &= \log [\mathrm{H_2O}]^p + \log \{y^q_{\mathrm{Cd}}/y^p_{\mathrm{H}}\} \\ &\quad - \log \{y_{\mathrm{Cd}_q(\mathrm{OH})_p}/f^p_{\mathrm{H_2O}}\}. \end{aligned} \tag{14}$$

The first two terms of the right hand side of Eq. 14 can be determined experimentally and log $\{y_{\mathrm{Cd}_q(\mathrm{OH})_p}/f_{\mathrm{H_2O}}{}^p\}$ is thus determined. The values of log $\{y_{\mathrm{Cd}_q(\mathrm{OH})_p}/f_{\mathrm{H_2O}}{}^p\}$ are plotted for the Cd$_2$OH^{3+} complex against the mole fractions of dioxane and methanol at $[H_2O]=0.95$, 0.90, 0.85, and 0.80 in Figs. 3 and 4, respectively. If we can assume that $f_{H_2O}=1$ as a first approach over the range of the solvent composition examined here, the curves thus drawn may represent the variations of the activity coefficients of the Cd_2OH^{3+} complex in the dioxane–water and methanol–water mixtures containing 3 mol dm^{-3} $LiClO_4$ at 25 °C. It seems reasonable that the activity coefficient of the Cd_2OH^{3+} ion, as well as those of Cd^{2+} and H^+ ions, was more sensitive to the solvent composition in the dioxane–water mixtures than that in the methanol–water mixtures, because it is expected that the dielectric constants of the former solvent may be lower than that of the latter at the same mole-fraction composition. The change in the activity coefficient of the Cd_2OH^{3+} ion was much larger than those of Cd^{2+} and H^+ ions in the both solvents as is expected from the larger charge of the complex ion.

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