$2HgCN^+ + Hg^0 = Hg_2^{2+} + Hg(CN)_2$ ($K = K_2/K_dK_1 = 1.15 \times 10^7$) and the two stoichiometric equations $[HCN]_0 = [HCN] + [HgCN^+] + 2[Hg(CN)_2]$ and $[Hg_2^{2+}]_0 = [Hg_2^{2+}] + [HgCN^+] + [Hg(CN)_2]$.
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Formation of Chloro Complexes of Zinc and Cadmium in Acetic Acid

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Equilibria of zinc and cadmium perchlorates with lithium chloride in 0.1 mol kg^{-1} LiClO$_4$–acetic acid solution have been investigated potentiometrically with an Ag–AgCl electrode. The equilibria of zinc perchlorate with lithium chloride are found to be

$$Zn(ClO_4)_2 + LiCl \xrightleftharpoons{\beta_{11}} ZnCl(ClO_4) + LiClO_4$$

$$2Zn(ClO_4)_2 + 2LiCl \xrightleftharpoons{\beta_{22}} Zn_2Cl_2(ClO_4)_2 + 2LiClO_4$$

$$2Zn(ClO_4)_2 + 3LiCl \xrightleftharpoons{\beta_{23}} Zn_2Cl_3(ClO_4) + 3LiClO_4$$

$$2Zn(ClO_4)_2 + 4LiCl \xrightleftharpoons{\beta_{24}} Zn_2Cl_4 + 4LiClO_4$$

$$2Zn(ClO_4)_2 + 5LiCl \xrightleftharpoons{\beta_{25}} LiZn_2Cl_5 + 4LiClO_4$$

$$2Zn(ClO_4)_2 + 6LiCl \xrightleftharpoons{\beta_{26}} Li_2Zn_2Cl_6 + 4LiClO_4$$

with $\log \beta_{11} = 5.15$, $\log \beta_{22} = 13.58$, $\log \beta_{23} = 18.94$, $\log \beta_{24} = 23.76$, $\log \beta_{25} = 27.21$, and $\log \beta_{26} = 30.09$. The equilibria of cadmium perchlorate with lithium chloride are

$$Cd(ClO_4)_2 + LiCl \xrightleftharpoons{\beta_{11}} CdCl(ClO_4) + LiClO_4$$

$$Cd(ClO_4)_2 + 2LiCl \xrightleftharpoons{\beta_{12}} CdCl_2 + 2LiClO_4$$

$$Cd(ClO_4)_2 + 3LiCl \xrightleftharpoons{\beta_{13}} LiCdCl_3 + 2LiClO_4$$

$$2Cd(ClO_4)_2 + 2LiCl \xrightleftharpoons{\beta_{22}} Cd_2Cl_2(ClO_4)_2 + 2LiClO_4$$

with $\log \beta_{11} = 5.28$, $\log \beta_{12} = 9.60$, $\log \beta_{13} = 13.2$, and $\log \beta_{22} = 13.1$.

Introduction

The formation of halogeno complexes of group 2B elements in solution have been studied by potentiometry, polarography, solvent extraction, etc.[1] Mironov et al.[2] have also studied the ion-pair formation of the halogeno complexes with alkali metals with an amalgam electrode. Morris et al.[3] have investigated systematically the equilibria and structures of the halogeno complexes in solution by various methods. Gutmann et al.[4] have qualitatively studied the formation of halogeno complexes in various solvents. Crystal structures of the complexes have been reported by Brehler et al. and other authors.[5]

In addition to Raman spectra[6-10] and x-ray diffraction,[11-15] densimetry,[16] cryoscopy,[17] and vapor pressure measurements[18] have been used to study the equilibria and the structures of complexes in solution and gas phase. According to these results, it may generally be assumed that the configurations of the complexes in solution are similar to those in crystals. For example zinc ion is octahedrally surrounded by six water molecules in aqueous solution, and the monohalogeno complex is formed by the substitution of one water molecule of the hexaaqua complex by a halogenide ion. The structure of the dihalogeno complex is not unambiguously established as many authors have reported different structures in different solvents. However most of these results point to the tetrahedral dihalogenozinc complex, and the complex of a relatively large cation such as Hg^{2+} seems to have a linear X–M–X structure with the other sites of the octahedron occupied by four solvent molecules. Tri- and tetrahalogeno complexes of the metals are ordinarily of the tetrahedral configuration. Besides the monomeric species, the formation of dimeric complexes has been reported in gas-phase,[19,20] solution,[17] and crystal forms,[21] and polymeric structure, in the molten-salt form.[22,23]

Some qualitative aspects of the formation of the zinc–chloro complex in acetic acid have been reported.[24,25] In the present paper the equilibria of zinc and cadmium perchlorate with lithium chloride in acetic acid are investigated quantitatively by means of potentiometry.

Experimental Section

Zinc and cadmium perchlorates were prepared by dissolving pure metals (99.99%) in hot aqueous perchloric acid solution. After recrystallization from water, the crystals were recrystallized twice from anhydrous acetic acid containing some acetic anhydride. The other reagents were prepared by the same methods as described elsewhere.[26]

Potentiometric measurements were performed as described previously[26] with an Orion Research digital pH/mV meter, Model

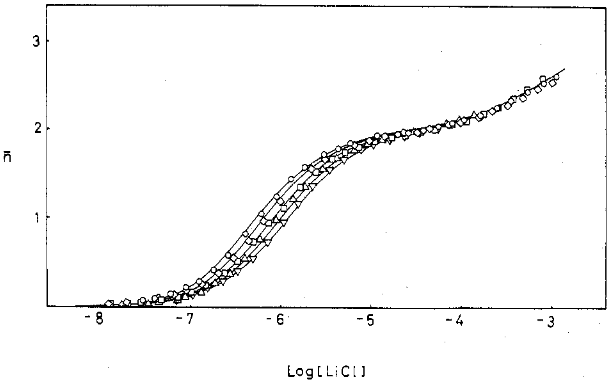


Figure 1. Plot of the formation function of zinc–chloro complexes as a function of log [LiCl]; $C_{LiClO_4} = 0.1$ mol kg^{-1}. C_{Zn} (mol kg^{-1}): ○, 2.000; ◇, 1.000; □, 0.400; △, 0.200; ▽, 0.100 × 10^{-3}. Solid lines are the best fit curves calculated with the constants listed in Table I.

801, at 25.0 °C. The chemical cell used is

$$\underbrace{\mathrm{Hg}|\mathrm{Hg_2Cl_2}|0.27\ \mathrm{mol\ kg^{-1}\ LiCl{-}HOAc\ soln}}_{\text{calomel electrode}}\|-$$

$$\underbrace{0.1\ \mathrm{mol\ kg^{-1}\ LiClO_4{-}HOAc\ soln}}_{\text{salt bridge}}\|-$$

$$\text{sample soln } (0.1\ \mathrm{mol\ kg^{-1}\ LiClO_4{-}HOAc\ soln})|\underbrace{\mathrm{AgCl}|\mathrm{Ag}}_{\substack{\text{Ag–AgCl}\\ \text{electrode}}}$$

where HOAc denotes the acetic acid. The electromotive force of the cell gives rise to the Nernstian response

$$E = E^{\circ\prime} - 59.1 \log [\mathrm{LiCl}] \qquad (1)$$

(The conditional standard potential,[27] $E^{\circ\prime}$, is −89.9 mV.)

Results

Formation of Zinc–Chloro Complexes. Various concentrations of zinc perchlorate solutions containing 0.1 mol kg^{-1} $LiClO_4$ were titrated with lithium chloride, the emf of the cell being measured. The concentration of free lithium chloride not bound to zinc ion, [LiCl], being found from eq 1, we obtain the formation function of zinc–chloro complexes

$$\bar{n} = (C_{LiCl} - [\mathrm{LiCl}])/C_{Zn} \qquad (2)$$

where C denotes the total concentration.

The results are plotted in Figure 1 as a function of log [LiCl]. The plots in the region of $\bar{n} < 2$ do not lie on the same curve. The fact that $\bar{n}$ decreases with increasing concentration of zinc perchlorate indicates the formation of polynuclear complexes. These complexes are considered to be dimers as revealed by the studies in other solvents,[17,19,20] and as we shall see, this accounts well for our experimental results. If the displacement of the curves for a given change of C_{Zn} is larger in the region of $\bar{n} > 1$ than in the region of $\bar{n} < 1$, the monomeric monochloro species should prevail, while in the opposite case most of the monochloro complex should be dimer. In effect, the displacement occurs in the two regions to a similar extent, and thus the presence of both forms of monochloro complexes, i.e., $ZnCl(ClO_4)$ and $Zn_2Cl_2(ClO_4)_2$, is anticipated.

First of all, we shall estimate the formation constant of lower chloro complexes. By assuming the formation of only the monochloro (Zn:Cl = 1:1) complexes in the region of $\bar{n} < 0.5$, we can write the reactions of $Zn(ClO_4)_2$ with LiCl as

$$\mathrm{Zn(ClO_4)_2 + LiCl \overset{\beta_{11}}{\rightleftharpoons} ZnCl(ClO_4) + LiClO_4} \qquad (3)$$

$$\mathrm{2ZnCl(ClO_4) \overset{K_d}{\rightleftharpoons} Zn_2Cl_2(ClO_4)_2} \qquad (4)$$

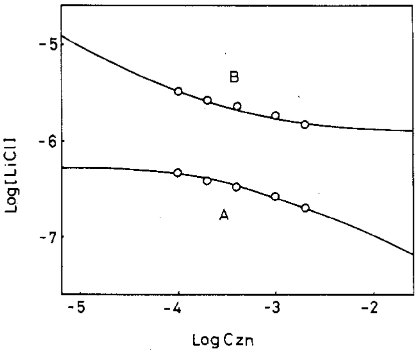


Figure 2. Plot of log [LiCl], read from Figure 1 at constant $\bar{n}$, as a function of log C_{Zn}: A, $\bar{n} = 0.5$; B, $\bar{n} = 1.5$. Solid line A is the normalized curve $X = \log x$, $Y = \log\{-1 + (1 + 4x)^{1/2}\}/2x$; B is the curve $X = -\log x$, $Y = -\log\{-x^{1/2} + (x + 4)^{1/2}\}/2$.

The formation function of the chloro complexes is written as

$$\bar{n} = \{[\mathrm{ZnCl(ClO_4)}] + 2[\mathrm{Zn_2Cl_2(ClO_4)_2}]\}C_{Zn}^{-1} = 1 - [\mathrm{Zn(ClO_4)_2}]C_{Zn}^{-1} \qquad (5)$$

By using the conditional formation constant, β_{11}', and dimerization constant, K_d, which are defined as

$$\beta_{11}' = [\mathrm{ZnCl(ClO_4)}][\mathrm{Zn(ClO_4)_2}]^{-1}[\mathrm{LiCl}]^{-1} = \beta_{11}[\mathrm{LiClO_4}]^{-1} \qquad (6)$$

$$K_d = [\mathrm{Zn_2Cl_2(ClO_4)_2}][\mathrm{ZnCl(ClO_4)}]^{-2} \qquad (7)$$

the total concentration of zinc, C_{Zn}, is given as

$$C_{Zn} = [\mathrm{Zn(ClO_4)_2}] + [\mathrm{ZnCl(ClO_4)}] + 2[\mathrm{Zn_2Cl_2(ClO_4)_2}] = [\mathrm{Zn(ClO_4)_2}] + \beta_{11}'[\mathrm{Zn(ClO_4)_2}][\mathrm{LiCl}] + 2K_d(\beta_{11}')^2[\mathrm{Zn(ClO_4)_2}]^2[\mathrm{LiCl}]^2 \qquad (8)$$

Substitution of eq 5 into eq 8 leads to the relationship

$$2(1 - \bar{n})K_dC_{Zn}(\beta_{11}'[\mathrm{LiCl}])^2 + \beta_{11}'[\mathrm{LiCl}] - \bar{n}(1 - \bar{n})^{-1} = 0 \qquad (9)$$

Solving the quadratic equation, we obtain

$$\beta_{11}'[\mathrm{LiCl}] = {}^1/_4\{-1 + (1 + 8\bar{n}K_dC_{Zn})^{1/2}\}(1 - \bar{n})^{-1} \times K_d^{-1}C_{Zn}^{-1} \qquad (10)$$

From Figure 1 we can read the concentrations of the free lithium chloride for various total concentrations of zinc at a certain $\bar{n}$. The plot of log [LiCl] vs. log C_{Zn} at $\bar{n} = 0.5$ is depicted in Figure 2A. Then eq 10 is rewritten as

$$y = {}^1/_2\{-1 + (1 + 4x)^{1/2}\}x^{-1} \qquad (11)$$

where $x = K_dC_{Zn}$ and $y = \beta_{11}'[\mathrm{LiCl}]$. Fitting the plot of Figure 2A with the normalized curve, $X = \log x$, $Y = \log y$ (solid line), we obtain $\log \beta_{11}' = 6.3$, $\log K_d = 3.4$.

In the region of $\bar{n} > 2$ in Figure 1, the plot lies on the same curve irrespective of the zinc concentration. This implies that all of the chloro complexes higher than the 1:1 complex are dimeric; for example, the 1:2 complex is a dimer (Zn_2Cl_4). If we assume that the equilibria at about $\bar{n} = 1.5$ are written by eq 4 and 12, the formation function, $\bar{n}$, is given by eq 13.

$$\mathrm{Zn_2Cl_2(ClO_4)_2 + 2LiCl \overset{K_{24}^*}{\rightleftharpoons} Zn_2Cl_4 + 2LiClO_4} \qquad (12)$$

$$\bar{n} = \{[\mathrm{ZnCl(ClO_4)}] + 2[\mathrm{Zn_2Cl_2(ClO_4)_2}] + 4[\mathrm{Zn_2Cl_4}]\}C_{Zn}^{-1} = 1 + 2[\mathrm{Zn_2Cl_4}]C_{Zn}^{-1} \qquad (13)$$

By using the dimerization constant, K_d, and conditional formation constant, $K_{24}^{*\prime}$, which is defined as

$$K_{24}^{*\prime} = [\mathrm{Zn_2Cl_4}][\mathrm{Zn_2Cl_2(ClO_4)_2}]^{-1}[\mathrm{LiCl}]^{-2} \qquad (14)$$

Table I. Equilibria of Zinc and Cadmium Perchlorates with Lithium Chloride in Acetic Acid and Their Equilibrium Constants

$Zn(ClO_4)_2 + LiCl \rightleftharpoons ZnCl(ClO_4) + LiClO_4$	$\log \beta_{11} = 5.15 \pm 0.02^a$
$2Zn(ClO_4)_2 + 2LiCl \rightleftharpoons Zn_2Cl_2(ClO_4)_2 + 2LiClO_4$	$\log \beta_{22} = 13.58 \pm 0.05$
$2Zn(ClO_4)_2 + 3LiCl \rightleftharpoons Zn_2Cl_3(ClO_4) + 3LiClO_4$	$\log \beta_{23} = 18.94 \pm 0.04$
$2Zn(ClO_4)_2 + 4LiCl \rightleftharpoons Zn_2Cl_4 + 4LiClO_4$	$\log \beta_{24} = 23.76 \pm 0.01$
$2Zn(ClO_4)_2 + 5LiCl \rightleftharpoons LiZn_2Cl_5 + 4LiClO_4$	$\log \beta_{25} = 27.21 \pm 0.04$
$2Zn(ClO_4)_2 + 6LiCl \rightleftharpoons Li_2Zn_2Cl_6 + 4LiClO_4$	$\log \beta_{26} = 30.09 \pm 0.03$
$Cd(ClO_4)_2 + LiCl \rightleftharpoons CdCl(ClO_4) + LiClO_4$	$\log \beta_{11} = 5.28 \pm 0.03$
$Cd(ClO_4)_2 + 2LiCl \rightleftharpoons CdCl_2 + 2LiClO_4$	$\log \beta_{12} = 9.60 \pm 0.04$
$Cd(ClO_4)_2 + 3LiCl \rightleftharpoons LiCdCl_3 + 2LiClO_4$	$\log \beta_{13} = 13.2^b$
$2Cd(ClO_4)_2 + 4LiCl \rightleftharpoons Cd_2Cl_2(ClO_4)_2 + 2LiClO_4$	$\log \beta_{22} = 13.1 \pm 0.12$

[a] ± values are ±2σ. [b] Tentative value; see text.

the total concentration of zinc, C_{Zn}, is written as

$$C_{Zn} = [ZnCl(ClO_4)] + 2[Zn_2Cl_2(ClO_4)_2] + 2[Zn_2Cl_4] = K_d^{-1/2}(K_{24}{}^{*\prime})^{-1/2}[Zn_2Cl_4]^{1/2}[LiCl]^{-1} + 2(K_{24}{}^{*\prime})^{-1}[Zn_2Cl_4][LiCl]^{-2} + 2[Zn_2Cl_4] \quad (15)$$

Substitution of eq 13 into eq 15 leads to

$$(K_{24}{}^{*\prime})^{-1}[LiCl]^{-2} + \{2(\bar{n} - 1)K_dC_{Zn}\}^{-1/2}(K_{24}{}^{*\prime})^{-1/2} \times [LiCl]^{-1} + (\bar{n} - 2)(\bar{n} - 1)^{-1} = 0 \quad (16)$$

By solving quadratic equation for $(K_{24}{}^{*\prime})^{-1/2}[LiCl]^{-1}$, we obtain

$$(K_{24}{}^{*\prime})^{-1/2}[LiCl]^{-1} = {}^1/_2\{-[2(\bar{n} - 1)K_dC_{Zn}]^{-1/2} + [(2(\bar{n} - 1)K_dC_{Zn})^{-1} - 4(\bar{n} - 2)/(\bar{n} - 1)]^{-1/2}\} \quad (17)$$

When $\bar{n} = 1.5$, eq 17 is rewritten as

$$y = {}^1/_2\{-x^{1/2} + (x + 4)^{1/2}\} \quad (18)$$

where $x = K_d^{-1}C_{Zn}^{-1}$ and $y = (K_{24}{}^{*\prime})^{-1/2}[LiCl]^{-1}$.

Fitting the plot of log [LiCl] vs. log C_{Zn} at $\bar{n} = 1.5$ (Figure 2B) with the normalized curve, $X = -\log x$, $Y = -\log y$ (solid line), we obtain $\log K_{24}{}^{*\prime} = 11.9$ and $\log K_d = 3.1$. The value of K_d obtained here disagrees with the previous one obtained from the plot of log C_{Zn} at $\bar{n} = 0.5$.

The plot for higher [LiCl] in Figure 1 points to the formation of complexes up to Zn:Cl = 1:3. The species formed in this region being dimers, the equilibria are written by

$$Zn_2Cl_4 + LiCl \overset{K_{25}}{\rightleftharpoons} LiZn_2Cl_5 \quad (19)$$

$$LiZn_2Cl_5 + LiCl \overset{K_{26}}{\rightleftharpoons} Li_2Zn_2Cl_6 \quad (20)$$

By using the equilibrium constants of eq 19 and 20, K_{25} and K_{26}, the formation function in the region of $\bar{n} > 2$ is written as

$$\bar{n} = \{4[Zn_2Cl_4] + 5[LiZn_2Cl_5] + 6[Li_2Zn_2Cl_6]\} \times C_{Zn}^{-1} = 2 + {}^1/_2(K_{25}[LiCl] + 2K_{25}K_{26}[LiCl]^2) \times (1 + K_{25}[LiCl] + K_{25}K_{26}[LiCl]^2)^{-1} \quad (21)$$

Fitting the plot of $\bar{n} > 2$ in Figure 1 with the normalized curve, $X = \log x$, $Y = 2 + {}^1/_2(px + 2x^2)(1 + px + x^2)^{-1}$, we obtain $\log K_{25} = 3.5$, $\log K_{26} = 2.9$.

The curves calculated with constants thus obtained are depicted in Figure 3 by solid lines, though to a small extent experimental points deviate systematically from these lines. The deviation is thought to be due to the neglect of the species $Zn_2Cl_3(ClO_4)$ to be formed successively between $Zn_2Cl_2(ClO_4)_2$ and Zn_2Cl_4. Taking into account the formation of species $ZnCl(ClO_4)$, $Zn_2Cl_2(ClO_4)_2$, $Zn_2Cl_3(ClO_4)$, Zn_2Cl_4, $LiZn_2Cl_5$, and $Li_2Zn_2Cl_6$, we calculated the formation constants by the methods of nonlinear least squares with an electronic computer.[26] The formation constants giving a minimum error square sum $U = (\bar{n} - \bar{n}_{calcd})^2$, where $\bar{n}_{calcd}$ is the formation function calculated by the constants, are listed in Table I. The constants are rewritten as $\beta_{22} = K_d\beta_{11}{}^2$, $\beta_{24} = K_d\beta_{11}{}^2K_{24}{}^*$, $\beta_{25} = \beta_{24}K_{25}$, and $\beta_{26} = \beta_{24}K_{25}K_{26}$. The best fit curves calculated by these constants are given by solid lines in Figure 1, from which we see a satisfactory agreement of the experimental points with the calculated.

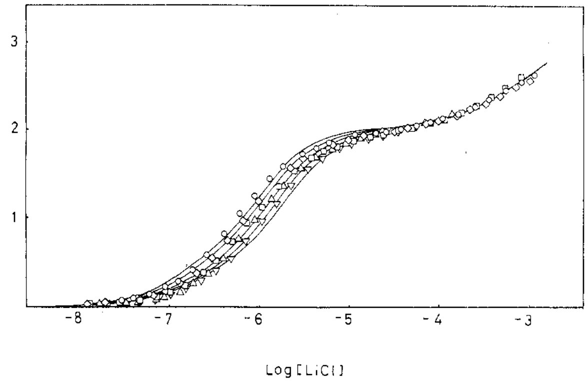


Figure 3. Comparison of the data with the best fit curves (solid lines) calculated by taking into account the formation of the complexes $ZnCl(ClO_4)$, $Zn_2Cl_2(ClO_4)_2$, Zn_2Cl_4, $LiZn_2Cl_5$, and $Li_2Zn_2Cl_6$ (i.e., the species $Zn_2Cl_3(ClO_4)$ is disregarded).

Table II. Error Square Sum for Various Combinations of Zinc-Chloro Complexes (Zn_mCl_n)

No.	"mn" for Zn_mCl_n							U
1	11	22	23	24	25	26		0.073
2	11	22	23	24	25	26	12	0.064
3	11	22	23		25	26	12	0.75
4		22	23	24	25	26		0.32
5	11		23	24	25	26		0.112
6	11	22		24	25	26		0.81
7	11	22	23		25	26		3.70
8	11	22	23	24		26		0.39

The error square sums, U, calculated for various combinations of zinc–chloro complexes ("mn" for Zn_mCl_n) are listed in Table II. Number 1 is the one recommended by the graphical analysis mentioned above. Even if a species "12" is added to no. 1 (no. 2), U does not greatly decrease and the formation constants of the other species change within the probable error. The fraction of the species "12" calculated by the best fit formation constant ($\log \beta_{12} = 9.16 \pm 0.15$) is at most 4%. Consequently, with the occurrence of species "12" being probable, we cannot obtain an unambiguous indication of the formation of the species "12". If we assume the formation of the species "12" instead of the dimeric species "24" (no. 3), U increases considerably. Omission of a species from no. 1 causes a significant increase of U (no. 4–8). Although no. 5 shows relatively small U, U in the region of $\bar{n} < 1.5$ is about twice that of no. 1. Taking into consideration formation of a higher chloro complex, $n/m > 3$, we can never obtain U smaller than that of no. 1. The results thus obtained by the nonlinear least-squares method corroborate the conclusion deduced by the graphical analysis.

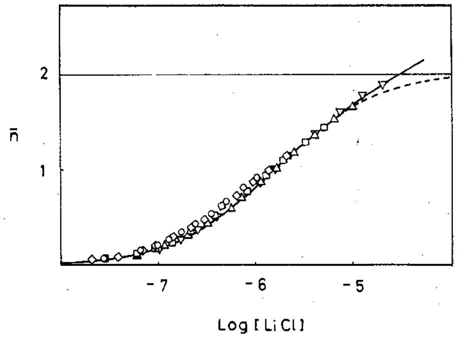


Figure 4. Plot of formation the function of cadmium-chloro complexes as a function of log [LiCl]; C_{LiClO_4} = 0.1 mol kg^{-1}. C_{Cd} (mol kg^{-1}): ○, 1.000; ◇, 0.500; □, 0.200; △, 0.100; ▽, 0.050 × 10^{-3}. The solid line is the best fit curve at very low C_{Cd}. Best fit curves for the other Cd concentrations are omitted for clarity.

Formation of Cadmium–Chloro Complexes. The formation function of chloro complexes of cadmium is plotted as a function of log [LiCl] in Figure 4. Because of the lower solubility of the complex, it was not possible to obtain the data for higher $\bar{n}$.

The change of the total concentration of cadmium does not considerably displace the formation functions, which tend to converge at about $\bar{n} = 1$. This is to say that the dimeric monochloro complex, $Cd_2Cl_2(ClO_4)_2$, is a minor component and that all other species are monomeric. $\bar{n}$ not going up to 2, the equilibria are written as

$$Cd(ClO_4)_2 + LiCl \overset{\beta_{11}}{\rightleftharpoons} CdCl(ClO_4) + LiClO_4 \qquad (22)$$

$$Cd(ClO_4)_2 + 2LiCl \overset{\beta_{22}}{\rightleftharpoons} CdCl_2 + 2LiClO_4 \qquad (23)$$

$$2CdCl(ClO_4) \overset{K_d}{\rightleftharpoons} Cd_2Cl_2(ClO_4)_2 \qquad (24)$$

At lower C_{Cd}, $[Cd_2Cl_2(ClO_4)_2]$ being negligible, the equilibria of cadmium perchlorate with lithium chloride are expressed by eq 22 and 23. By defining conditional formation constants of the monomeric species as

$$\beta_{11}' = [CdCl(ClO_4)][Cd(ClO_4)_2]^{-1}[LiCl]^{-1} = \beta_{11}[LiClO_4]^{-1} \qquad (25)$$

$$\beta_{12}' = [CdCl_2][Cd(ClO_4)_2]^{-1}[LiCl]^{-2} = \beta_{12}[LiClO_4]^{-2} \qquad (26)$$

we obtain the formation function at lower C_{Cd} as

$$\bar{n} = ([CdCl(ClO_4)] + 2[CdCl_2])C_{Cd}^{-1} = (\beta_{11}'[LiCl] + 2\beta_{12}'[LiCl]^2)(1 + \beta_{11}'[LiCl] + \beta_{12}'[LiCl]^2)^{-1} \qquad (27)$$

By the comparison of the plot of $\bar{n}$ vs. log [LiCl] at lower C_{Cd} with the normalized curve, $X = \log x$, $Y = (px + 2x^2)(1 + px + x^2)^{-1}$ (Figure 4, dotted line), we obtain log $\beta_{11}' = 6.28$ and log $\beta_{12}' = 11.60$.

The evaluation of the dimerization constant, K_d, has been carried out in the same manner as in the zinc–chloro complex system. The constant was estimated as log $K_d = 2.6$.

From the deviation of data from the normalized curve at higher [LiCl], we obtain the constant for the equilibrium 28

$$Cd(ClO_4)_2 + 3LiCl \overset{\beta_{13}}{\rightleftharpoons} LiCdCl_3 + 2LiClO_4 \qquad (28)$$

as log $\beta_{13} = 13.2$, which is only a tentative value because of a limited number of experimental points. The formation constants of chloro complexes of cadmium refined by the successive approximation with an electronic computer are summerized in Table I. The best fit curves calculated by the constants are in good agreement with the experimental results. The normalized curve at very low concentration of cadmium is shown in Figure 4 by a solid line as an example.

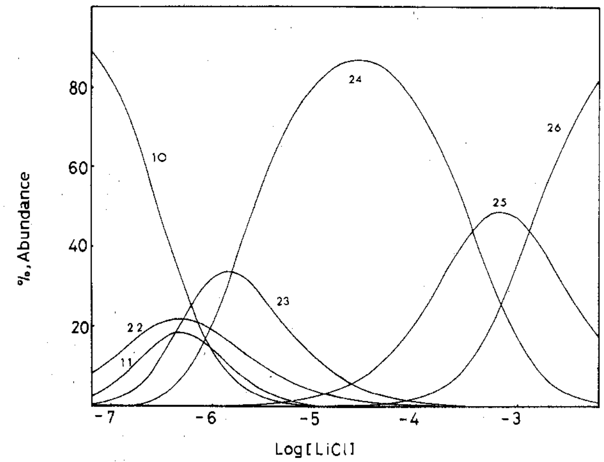


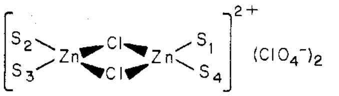
Figure 5. Distribution diagram of chloro complexes of zinc in 0.1 mol kg^{-1} $LiClO_4$-acetic acid solution: 10, $Zn(ClO_4)_2$; 11, $ZnCl(ClO_4)$; 22, $Zn_2Cl_2(ClO_4)_2$; 23, $Zn_2Cl_3(ClO_4)$; 24, Zn_2Cl_4; 25, $LiZn_2Cl_5$; 26, $Li_2Zn_2Cl_6$. $C_{Zn} = 10^{-3}$ mol kg^{-1}.

Discussion

The distribution diagram for chloro complexes of zinc in 0.1 mol kg^{-1} $LiClO_4$–acetic acid solution calculated by the conditional formation constants (β') is depicted in Figure 5. As previous studies in various solvents[4] have been qualitative in nature, minor components and dimeric species seem to have been overlooked.

The cobalt(II) ion is solvated octahedrally by the acetic acid molecule in acetic acid solution.[26] This fact suggests that it is possible for the zinc ion to have the octahedral configuration in acetic acid from the geometrical point of view, since its crystal radius is larger than that of the cobalt(II) ion. Consequently, the solvated ion of zinc in acetic acid is considered to have the same structure as the hydrated ion.[11-13] As ionic dissociation of electrolytes in acetic acid is negligible under these conditions, the ion forms a noncharged ion pair with perchlorate ion, $[Zn(HOAc)_6]^{2+},2(ClO_4^-)$. Monomeric species of the monochloro complex must have the same structure as the hexasolvato ion.

It has been established in various solvents that the dimeric chloro complex is bridged by two chloride ions and that the zinc ion is surrounded tetrahedrally by the chloride ion and the solvent molecule. $Zn_2Cl_2(ClO_4)_2$ is thus considered to have the structure



where S denotes the solvent molecule, acetic acid. The divalent cation forms an ion pair with perchlorate ion, $[Zn_2Cl_2(S)_4]^{2+},2(ClO_4^-)$. The higher chloro complexes are formed by substitution of the solvent molecule by chloride ion and form an ion pair with perchlorate ion or lithium ion, i.e., $[Zn_2Cl_3(S)_3]^+,ClO_4^-$, $[Zn_2Cl_4(S)_2]$, $Li^+,[Zn_2Cl_5(S)]^-$ and $2Li^+,[Zn_2Cl_6]^{2-}$.

The successive formation constants of the species, K_{23}, K_{24}, K_{25}, and K_{26}, are obtained from Table I as log $K_{23} = 5.36$, log $K_{24} = 4.82$, log $K_{25} = 3.45$, and log $K_{26} = 2.88$. The ratio K_{24}/K_{25} (log $(K_{24}/K_{25}) = 1.37$) is much larger than K_{23}/K_{24} (log $(K_{23}/K_{24}) = 0.54$); that is, the coordination of the fifth chloride is less favored than that of the fourth chloride (the first and second chlorides are bridging ligands). The third chloride coordinates to one zinc ion and the fourth to the other; the coordination of the fifth chloride is hindered by the neighboring terminal chloride already attached.

We shall consider the matter from the statistical point of view. We assume that the third chloride substitutes S_1

Then the following three cases are considered for the substitution by the fourth chloride: (1) all remaining solvent molecules, S_2, S_3, and S_4, have the same possibility of substitution; (2) the fourth chloride substitutes only S_2 or S_3 bonded to the zinc ion, Zn_2; (3) only the trans solvent, S_3, is available for substitution. Then, statistical factors of K_{23}/K_{24} for these cases are calculated as 8/3, 4, and 8, respectively.[28] All reactants being noncharged ion pairs, the electrostatic interaction between them is negligible in this system. The observed ratio, therefore, indicates that the second case is most probable. It is considered reasonable that the substitution of S_2 or S_3 by chloride is neither sterically nor electrostatically affected by the third chloride already attached to Zn_1. The statistical factor of $K_{25}/K_{26} = 4$, calculated on the above assumption (2), is in good agreement with the observed value, $\log (K_{25}/K_{26}) = 0.57$ ($K_{25}/K_{26} = 3.7$).

The observed value of $\log (K_{24}/K_{25}) = 1.37$ is much larger than that calculated statistically by using the above assumption, $(K_{24}/K_{25})_{\text{stat}} = 1$. This difference may be attributable to the effect on neighboring terminal chloride already attached. Then we can estimate the equilibrium constant of the following equilibrium to be $10^{1.4}$

$$Zn_2Cl_4(S_2)(S_3) \rightleftharpoons Zn_2Cl_4(S_2)(S_4) \text{ or } Zn_2Cl_4(S_3)(S_4)$$

Monomeric cadmium complexes are considered to have an octahedral configuration, and the difficulties in taking the tetrahedral configuration would prevent the formation of dimeric species.

Although the formation constants of halogeno complexes with group 2B elements increase considerably with increasing atomic number in aqueous solution,[2] the formation constants of monochloro complexes of zinc and cadmium, β_{11}, differ little in acetic acid. The formation enthalpies of the complexes in the gaseous phase are similar for these ions, while the hydration enthalpies of the ions decrease with the atomic number of the central metal ion. Therefore, the difference in the formation constants of halogeno complexes in the aqueous solution is mainly due to the difference in hydration energy. On the other hand, in a solvent of low solvating power such a acetic acid, it seems reasonable that the formation energy of the halogeno complex differs little for zinc and cadmium.

Registry No. $Zn(ClO_4)_2$, 13637-61-1; $Cd(ClO_4)_2$, 13760-37-7; $[ZnCl(S)_5]^+,ClO_4^-$, 59448-52-1; $[Zn_2Cl_2(S)_4]^{2+},2(ClO_4^-)$, 59448-54-3; $[Zn_2Cl_3(S)_3]^+,ClO_4^-$, 59448-56-5; $[ZnCl_4(S)_2]$, 59448-57-6; $Li^+,[Zn_2Cl_5(S)]^-$, 59448-58-7; $2Li^+,[Zn_2Cl_6]^{2-}$, 59448-59-8; $[CdCl(S)_5]^+,ClO_4^-$, 59448-61-2; $CdCl_2$, 10108-64-2; $Li^+,[CdCl_3(S)_3]^-$, 59448-62-3; $[Cd_2Cl_2(S)_4]^{2+},2(ClO_4^-)$, 59448-64-5; $LiClO_4$, 7791-03-9; LiCl, 7447-41-8.

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Notes

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Photochemical Studies of Iridium(III)–Ammine Complexes. Ligand Field Excitation of $Ir(NH_3)_6{}^{3+}$, $Ir(NH_3)_5H_2O^{3+}$, and $Ir(NH_3)_5Cl^{2+}$ in Aqueous Solution

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The photochemistry resulting from ligand field excitation of hexacoordinate d^6 transition metal complexes has been an active area of mechanistic study in recent years.[2–4] Systems investigated include Werner type complexes of Co(III), Rh(III), Ru(II), Fe(II), and Pt(IV), as well as several metal carbonyl systems. Iridium(III) complexes have been shown to be photoactive, and photolytic techniques have been employed for some syntheses.[4] However, the *only* amine complexes for which quantum yields have been reported for the direct excitation of ligand field bands are *trans*-$Ir(en)_2Cl_2{}^+$ and of $Ir(NH_3)_5N_3{}^{2+}$. The former complex undergoes photoaquation of Cl^- with a quantum yield of ~0.1 mol/einstein when irradiated at 350 nm.[5] In contrast, ligand field excitation of the azide complex leads not to substitution reactions but to efficient decomposition of the coordinated azide to give $Ir(NH_3)_5(NH_2Cl)^{3+}$ and N_2 as the products in aqueous HCl.[6] It is unlikely that these products represent a reaction of a ligand field excited state.

Reported here is a quantitative investigation of the photoreactions of $Ir(NH_3)_6{}^{3+}$, $Ir(NH_3)_5H_2O^{3+}$, and Ir-