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Use of a Glass Electrode in the Potentiometric Study of Acid-Base Equilibria of Zinc and Cadmium Acetates in Acetic Acid

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Potentiometric study of acid-base equilibria of zinc and cadmium acetates in acetic acid was undertaken with a glass electrode filled with a $LiCl-HClO_4$ acetic acid solution. Potentiometric titration of 0.1 m $LiClO_4$ acetic acid solution with perchloric acid and lithium acetate reveals that the glass electrode gives rise to the Nernstian response. The equilibrium constant of the reaction, $HClO_4+LiOAc \overset{K_f}{\rightleftharpoons} LiClO_4+HOAc$ is found as $\log K_f=7.86$. The titration of zinc and cadmium acetate with perchloric acid and lithium acetate points to the following equilibria: $M(ClO_4)_2+LiOAc \overset{\beta_1}{\rightleftharpoons} M(OAc)(ClO_4)+LiClO_4$, $M(ClO_4)_2+2LiOAc \overset{\beta_2}{\rightleftharpoons} M(OAc)_2+2LiClO_4$, $M(ClO_4)_2+3LiOAc \overset{\beta_3}{\rightleftharpoons} LiM(OAc)_3+2LiClO_4$. Logarithmic overall formation constants of the acetato complexes, β_1, β_2 and β_3 were determined as 4.04, 7.00 and 9.2 respectively for zinc, and 3.43, 5.46 and 8.0 respectively for cadmium. In addition zinc forms tetraacetate complex with the overall formation constant of $\log \beta_4=12.4$.

Acetic acid has been used as a convenient solvent for the titration of weak bases.[1,2] The huge number of acid-base equilibria in the solvent have been investigated for the analytical purpose, and equilibrium constants of many systems have been obtained by potentiometry, colorimetry, conductometry and other methods.

Various hydrogen ion indicator electrodes have been utilized in potentiometric studies. The hydrogen electrode, being a fundamental electrode, has difficulty in handling and fails sometimes to give a satisfactory reproducibility.[3-6] Glass and chloranil electrodes have been used as indicator electrodes for the acid-base titration,[1] and dissociation constants of acids and bases have been estimated from the relative electromotive forces of the electrodes.[7-11]

In early works, because of a poor precision of instrument, a considerable error was inevitable in potentiometric measurements in acetic acid solution having high electrical resistance.[12] Mukherjee[5] and Bruckenstein and Kolthoff[8] have claimed the reproducibility to less than one millivolt. However the scatter of emf by the variation of electrolyte concentration and the deviation from reversible response point to the reproducibility of the electrodes to about five millivolts. According to studies on the reversibility of the electrode,[4,6,11,13-15] the reproducibility of a potentiometry in acetic acid does not seem to be as good as claimed.

Thus, as stated by Popov,[2] some of the problems can not be resolved without additional careful works on the electrode systems in acetic acid. The poor precision of some earlier works may be due to the absence of medium salt, which lowers the electrical resistance of the solution and keeps the activity coefficient constant, and the presence of impurities such as water.

In the present paper, the response of a glass–calomel electrode cell filled with acetic acid solution is investigated with care. The potentiometric study with this electrode system is undertaken on the acid-base equilibria of zinc and cadmium acetate, *i.e.*, the formation of acetato complexes, for which the formation of higher acetato complex has been pointed out as a result of solubility measurements.[16]

Experimental

Reagents. Acetic acid, perchloric acid and lithium acetate,[17] lithium perchlorate[18] and zinc acetate[19] were prepared by the methods described previously.

Cadmium Acetate: G. R. grade $Cd(OAc)_2\cdot 2H_2O$ was recrystallized twice from acetic acid containing acetic anhydride.

Measurements. *Glass Electrode*: The inner solution of a commercially available glass electrode was replaced by a 0.1 mol/kg LiCl–0.1 mol/kg $HClO_4$ acetic acid solution. An Ag–AgCl electrode was utilized as an inner reference electrode. After standing in 0.1 mol/kg $LiClO_4$ acetic acid solution for 2 days at 100 °C, the glass electode was stored in the same solution. The glass electrode prepared in this manner exhibits smaller drift of potential than the commercially available glass electrode containing aqueous inner solution.

Calomel Electrode: The method of preparation of the calomel electrode composed of 0.27 mol/kg LiCl acetic acid solution has been described elsewhere.[18] The reproducibility of the electrode was found to be less than 0.3 mV. The electrode was connected with the sample solution through a salt bridge. Both salt bridge and sample solution contain 0.1 mol/kg $LiClO_4$ as a medium salt.

Potentiometry. The chemical cell used is written as follows:

$$\underbrace{\text{Ag}|\text{AgCl}|0.1\ \text{mol/kg LiCl, } 0.1\ \text{mol/kg HClO}_4\ \text{AcOH soln.}|\text{glass}}_{\text{glass electrode}}|\text{sample soln. (0.1 mol/kg LiClO}_4\text{HOAc soln.)}\|\underbrace{0.1\ \text{mol/kg LiClO}_4\ \text{HOAc soln.}}_{\text{salt bridge}}\|\underbrace{0.27\ \text{mol/kg LiCl HOAc soln.}|\text{Hg}_2\text{Cl}_2|\text{Hg}}_{\text{calomel electrode}}$$

The potential was measured, in a water-jacketted vessel thermostated at 25.0±0.1 °C, with an Orion research digital pH/mV meter model 801.

The glass electrode shows a variation of about one millivolt of electrode potential in a few days, so the standard potential of the cell should be measured every day.

Results and Discussion

Response of Glass Electrode in Acetic Acid. The following two equilibria are relevant to lithium perchlorate in acetic acid:

$$\mathrm{HClO_4 + LiOAc} \overset{K_f}{\rightleftharpoons} \mathrm{LiClO_4 + HOAc} \tag{1}$$

and

$$\mathrm{Li^+ + ClO_4^-} \overset{K_{\mathrm{LiClO_4}}}{\rightleftharpoons} \mathrm{LiClO_4} \tag{2}$$

Perchloric acid and lithium acetate are weak electrolytes in this medium[1] and we have

$$\mathrm{H^+ + ClO_4^-} \overset{K_{\mathrm{HClO_4}}}{\rightleftharpoons} \mathrm{HClO_4} \tag{3}$$

$$\mathrm{Li^+ + OAc^-} \overset{K_{\mathrm{LiOAc}}}{\rightleftharpoons} \mathrm{LiOAc.} \tag{4}$$

When perchloric acid is added to lithium perchlorate solution, we have the following relationship:

$$[\mathrm{H^+}] + [\mathrm{HClO_4}] - C_{\mathrm{HClO_4}} = [\mathrm{OAc^-}] + [\mathrm{LiOAc}] \tag{5}$$

where $C_{\mathrm{HClO_4}}$ denotes the total concentration of the added perchloric acid. As the ionic dissociation in acetic acid is very weak,[1] Eq. (5) is approximated to Eq. (6).

$$[\mathrm{HClO_4}] - C_{\mathrm{HClO_4}} = [\mathrm{LiOAc}] \tag{6}$$

Substitution of the formation constant of Eq. (1), K_f, into Eq. (6) leads to Eq. (7).

$$[\mathrm{HClO_4}]^2 - C_{\mathrm{HClO_4}}[\mathrm{HClO_4}] - [\mathrm{LiClO_4}]K_f^{-1} = 0. \tag{7}$$

Solving the quadratic equation, we obtain

$$[\mathrm{HClO_4}] = \frac{1}{2}\{C_{\mathrm{HClO_4}} + (C_{\mathrm{HClO_4}}^2 + 4[\mathrm{LiClO_4}]K_f^{-1})^{1/2}\}. \tag{8}$$

From the constant of the equilibrium (3), $K_{\mathrm{HClO_4}}$, the free hydrogen ion concentration is given by:

$$[\mathrm{H^+}] = [\mathrm{HClO_4}]K_{\mathrm{HClO_4}}^{-1}[\mathrm{ClO_4^-}]^{-1}. \tag{9}$$

And from the condition of electroneutrality, we have

$$[\mathrm{H^+}] + [\mathrm{Li^+}] = [\mathrm{OAc^-}] + [\mathrm{ClO_4^-}]. \tag{10}$$

When the concentration of perchloric acid added, $C_{\mathrm{HClO_4}}$, is much smaller than that of lithium perchlorate,

$$[\mathrm{OAc^-}] \text{ and } [\mathrm{H^+}] \ll [\mathrm{Li^+}] \text{ and } [\mathrm{ClO_4^-}]. \tag{11}$$

Consequently Eq. (10) is reduced to

$$[\mathrm{Li^+}] = [\mathrm{ClO_4^-}]. \tag{12}$$

Then the equilibrium constant of Eq. (2) is written as follows:

$$\begin{aligned} K_{\mathrm{LiClO_4}} &= [\mathrm{LiClO_4}][\mathrm{Li^+}]^{-1}[\mathrm{ClO_4^-}]^{-1} \\ &= [\mathrm{LiClO_4}][\mathrm{ClO_4^-}]^{-2}. \end{aligned} \tag{13}$$

The free lithium perchlorate concentration, $[\mathrm{LiClO_4}]$, being approximated as the total concentration, $C_{\mathrm{LiClO_4}}$, Eq. (13) is rewritten as follows:

$$[\mathrm{ClO_4^-}]^2 = C_{\mathrm{LiClO_4}}K_{\mathrm{LiClO_4}}^{-1}. \tag{14}$$

Substitution of Eqs. (8) and (14) into Eq. (9) leads to

$$\begin{aligned} [\mathrm{H^+}] &= \frac{1}{2}\{C_{\mathrm{HClO_4}} + (C_{\mathrm{HClO_4}}^2 + 4C_{\mathrm{LiClO_4}}K_f^{-1})^{1/2}\} \\ &\quad \times K_{\mathrm{LiClO_4}}^{1/2}/(C_{\mathrm{LiClO_4}}^{1/2}K_{\mathrm{HClO_4}}) \end{aligned} \tag{15}$$

As the lithium perchlorate concentration may be regarded as constant,

$$[\mathrm{H^+}] = \frac{1}{2}\{C_{\mathrm{HClO_4}} + (C_{\mathrm{HClO_4}}^2 + 4C_{\mathrm{LiClO_4}}K_f^{-1})^{1/2}\}K \tag{16}$$

where $K = K_{\mathrm{LiClO_4}}^{1/2}/(C_{\mathrm{LiClO_4}}^{1/2}K_{\mathrm{HClO_4}}) = \text{constant}$.

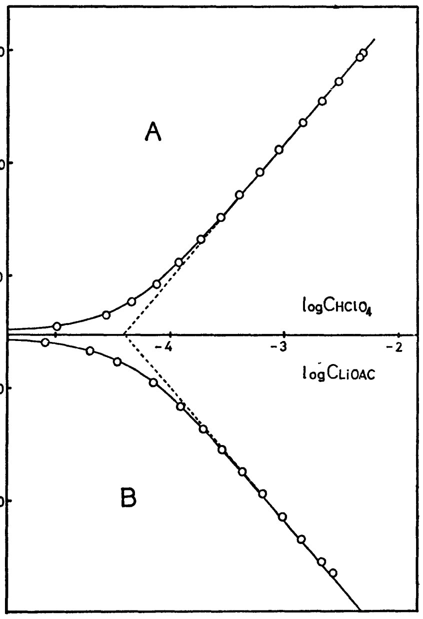

Fig. 1. Electromotive force of 0.1 mol/kg $\mathrm{LiClO_4}$ acetic acid solution as a function of logarithmic concentration of perchloric acid (A) and lithium acetate (B). Solid lines are the normalized curve, $X = \log x$, $Y = 59.1 \log (x + \sqrt{x^2+4})$.

Thus, as the activity coefficient of hydrogen ion is kept constant, the electromotive force of the cell at 25.0 °C is given by:

$$\begin{aligned} E &= E_0 + \frac{RT}{nF}\ln[\mathrm{H^+}] \\ &= E_0' + 59.1 \log \frac{1}{2}\{C_{\mathrm{HClO_4}} + (C_{\mathrm{HClO_4}}^2 \\ &\quad + 4C_{\mathrm{LiClO_4}}K_f^{-1})^{1/2}\}. \end{aligned} \tag{17}$$

$$(E_0' = E_0 + 59.1 \log K)$$

In Fig. 1 (A), electromotive force of 0.1 molal lithium perchlorate acetic acid solution is plotted as a function of logarithmic concentration of added perchloric acid. In order to compare the data with normalized curve, $X = \log x$, $Y = 59.1 \log (x + \sqrt{x^2+4})$, Eq. (17) is rewritten as follows:

$$\begin{aligned} E &= E_0' + 59.1 \log \frac{1}{2} C_{\mathrm{LiClO_4}}^{1/2}K_f^{-1/2} \\ &\quad \times [C_{\mathrm{HClO_4}}C_{\mathrm{LiClO_4}}^{-1/2}K_f^{1/2} \\ &\quad + \{(C_{\mathrm{HClO_4}}C_{\mathrm{LiClO_4}}^{-1/2}K_f^{1/2})^2 + 4\}^{1/2}] \\ &= E' + 59.1 \log [C_{\mathrm{HClO_4}}C_{\mathrm{LiClO_4}}^{-1/2}K_f^{1/2} \\ &\quad + \{(C_{\mathrm{HClO_4}}C_{\mathrm{LiClO_4}}^{-1/2}K_f^{1/2})^2 + 4\}^{1/2}]. \end{aligned} \tag{18}$$

$$\left(E' = E_0' + 59.1 \log \frac{1}{2} C_{\mathrm{LiClO_4}}^{1/2} K_f^{-1/2}\right)$$

By the curve fitting, $\log C_{\mathrm{LiClO_4}}^{-1/2}K_f^{1/2} = 4.44$ was obtained from the reading of abscissa in Fig. 1 (A). As $C_{\mathrm{LiClO_4}} = 0.1$ mol/kg the formation constant of lithium perchlorate was found as $\log K_f = 7.88 \pm 0.05$; and by the extrapolation to $C_{\mathrm{HClO_4}} = 1$ the apparent standard potential, E_0' was estimated as $E_0' = 636$ mV.

The titration of 0.1 mol/kg lithium perchlorate solution with lithium acetate is shown in Fig. 1 (B). In the same way as in the preceding case, the free acetate ion concentration is given as follows:

$$[\mathrm{OAc^-}] = \frac{1}{2}\{C_{\mathrm{LiOAc}} + (C_{\mathrm{LiOAc}}^2 + 4C_{\mathrm{LiClO_4}}K_\mathrm{f}^{-1})^{1/2}\}$$
$$\times K_{\mathrm{LiClO_4}}^{1/2}/(C_{\mathrm{LiClO_4}}^{1/2}K_{\mathrm{LiOAc}}) \qquad (19)$$

where C_{LiOAc} denotes the total concentration of added lithium acetate. By using Eq. (19) and autoprotolysis constant of acetic acid, $K_{\mathrm{HOAc}}=[\mathrm{H^+}][\mathrm{OAc^-}]$, the electromotive force of lithium perchlorate solution ($C_{\mathrm{LiClO_4}}=0.1$ mol/kg and $C_{\mathrm{LiOAc}} \ll C_{\mathrm{LiClO_4}}$) is written as

$$E = E_0 + \frac{RT}{nF}\ln\frac{K_{\mathrm{HOAc}}}{[\mathrm{OAc^-}]}$$
$$= E_0 + 59.1\log K' - 59.1\log\frac{1}{2}\{C_{\mathrm{LiOAc}}$$
$$+ (C_{\mathrm{LiOAc}}^2 + 4C_{\mathrm{LiClO_4}}K_\mathrm{f}^{-1})^{1/2}\}. \qquad (20)$$
$$(K' = K_{\mathrm{LiClO_4}}^{1/2}/(C_{\mathrm{LiClO_4}}^{1/2}K_{\mathrm{LiOAc}}) = \mathrm{constant})$$

In the same manner as in the titration with perchloric acid, comparison of the experimental results with the normalized curve, Eq. (19), gives $\log C_{\mathrm{LiClO_4}}^{-1/2}K_\mathrm{f}^{1/2}=4.42$, *i.e.*, $K_\mathrm{f}=7.84$ and $E_0+59.1\ \log K'=113$ mV.

The experimental values are in excellent agreement with normalized curve (solid lines in Fig. 1), and the formation constant of lithium perchlorate, K_f, obtained by the titration with perchloric acid agrees well with the value obtained by the titration with lithium acetate. Thus the glass electrode described in the experimental section gives rise to a reversible electromotive force.

In addition, from the difference of the apparent standard potentials, $E_0'{}_{(\mathrm{HClO_4})}$ and $E_0'{}_{(\mathrm{LiOAc})}$, K_f is estimated as $\log K_\mathrm{f}=7.86$.

As the concentrations of perchloric acid and lithium acetate are much smaller than that of lithium perchlorate, the fraction of the two aggregated species with lithium perchlorate, $\mathrm{HClO_4 \cdot LiClO_4}$ and $\mathrm{LiOAc \cdot LiClO_4}$, if any, would be constant.

$$\mathrm{HClO_4 + LiClO_4 \rightleftharpoons HClO_4 \cdot LiClO_4} \qquad (21)$$

$$\mathrm{LiOAc + LiClO_4 \rightleftharpoons LiOAc \cdot LiClO_4} \qquad (22)$$

In Fig. 1 (B) the deviation of data from the normalized curve at higher lithium acetate concentration should indicate the dimerization of lithium acetate, *i.e.*,

$$\mathrm{2LiOAc \rightleftharpoons (LiOAc)_2} \qquad (23)$$

Formation of Zinc-Acetato Complex. Reaction of perchloric acid with zinc acetate in solution containing 0.1 mol/kg lithium perchlorate is written as follows:

$$p\mathrm{Zn(OAc)_2} + q\mathrm{HClO_4}$$
$$\rightleftharpoons \mathrm{Zn}_p(\mathrm{OAc})_{2p-q}(\mathrm{ClO_4})_q + q\mathrm{HOAc} \qquad (24)$$

$$p\mathrm{Zn(OAc)_2} + q\mathrm{LiClO_4}$$
$$\rightleftharpoons \mathrm{Zn}_p(\mathrm{OAc})_{2p-q}(\mathrm{ClO_4})_q + q\mathrm{LiOAc}. \qquad (25)$$

It has previously been confirmed that zinc acetate exists as a monomer in acetic acid [19]. When $q>2p$, the species formed should be written as $H_{q-2p}\mathrm{Zn}_p(\mathrm{ClO_4})_q$ or $\mathrm{Li}_{q-2p}\mathrm{Zn}_p(\mathrm{ClO_4})_q$, which can be negligible as will hereinafter be mentioned.

The total concentration of perchlorate, $C_{\mathrm{ClO_4}}$, is given by the following:

$$C_{\mathrm{ClO_4}} = C_{\mathrm{LiClO_4}} + C_{\mathrm{HClO_4}} = [\mathrm{LiClO_4}] + [\mathrm{HClO_4}]$$
$$+ \sum q[\mathrm{Zn}_p(\mathrm{OAc})_{2p-q}(\mathrm{ClO_4})_q], \qquad (26)$$

$$\sum q[\mathrm{Zn}_p(\mathrm{OAc})_{2p-q}(\mathrm{ClO_4})_q]$$
$$= C_{\mathrm{LiClO_4}} + C_{\mathrm{HClO_4}} - [\mathrm{LiClO_4}] - [\mathrm{HClO_4}]. \qquad (27)$$

The total lithium perchlorate concentration, $C_{\mathrm{LiClO_4}}$, is given by Eq. (28).

$$C_{\mathrm{LiClO_4}} = [\mathrm{LiClO_4}] + [\mathrm{LiOAc}]. \qquad (28)$$

Substitution of Eq. (28) to Eq. (27) leads to

$$\sum q[\mathrm{Zn}_p(\mathrm{OAc})_{2p-q}(\mathrm{ClO_4})_q]$$
$$= C_{\mathrm{HClO_4}} - [\mathrm{HClO_4}] + [\mathrm{LiOAc}] \qquad (29)$$

Thus the formation function of perchlorate of zinc, $\bar{n}^*$, is written as follows:

$$\bar{n}^* = (\sum q[\mathrm{Zn}_p(\mathrm{OAc})_{2p-q}(\mathrm{ClO_4})_q])C_{\mathrm{Zn}}^{-1}$$
$$= (C_{\mathrm{HClO_4}} - [\mathrm{HClO_4}] + [\mathrm{LiOAc}])C_{\mathrm{Zn}}^{-1} \qquad (30)$$

As the free concentration of lithium perchlorate, $[\mathrm{LiClO_4}]$, can be approximated by the total concentration, $C_{\mathrm{LiClO_4}}$, Eq. (30) becomes

$$\bar{n}^* = (C_{\mathrm{HClO_4}} - [\mathrm{HClO_4}] + C_{\mathrm{LiClO_4}}[\mathrm{HClO_4}]^{-1}K_\mathrm{f}^{-1})C_{\mathrm{Zn}}^{-1} \qquad (31)$$

In Fig. 2 the results of potentiometric titration of various concentration of zinc acetate solutions containing 0.1 mol/kg lithium perchlorate are plotted as a function of mole ratio $a \equiv C_{\mathrm{HClO_4}}/C_{\mathrm{Zn}}$. By using the following equation:

$$E = E_0' + 59.1\log[\mathrm{HClO_4}] \quad (E_0'=636\ \mathrm{mV}), \qquad (32)$$

free perchloric acid concentration, $[\mathrm{HClO_4}]$, can be calculated from the electromotive force E.

The formation function, $\bar{n}^*$, calculated by Eq. (31) is plotted as a function of log $[\mathrm{HClO_4}]$ in Fig. 3 (open symbols). The plot lies on the same curve irrespective of the zinc acetate concentration. This implies that there is no difference in the degree of polymerization between zinc acetate and the species formed, *i.e.*, all species involved in this reaction are monomer (*i.e.*, $p=1$). Over a range of $\bar{n}^*$ not exceeding 2, the reaction of zinc acetate with perchloric acid is

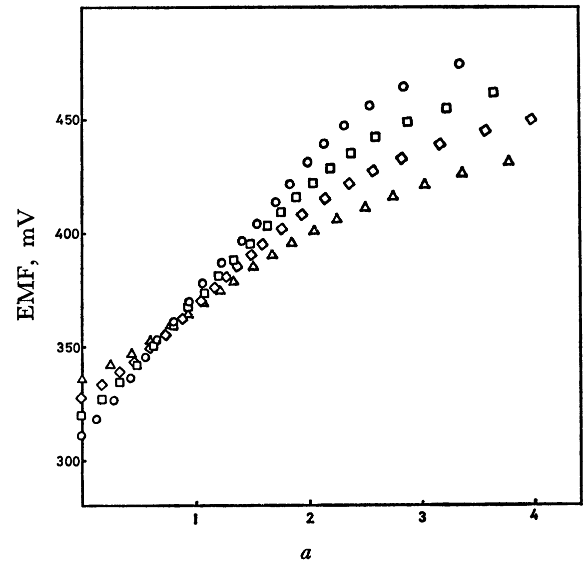

Fig. 2. Electromotive force of various concentrations of zinc acetate as a function of mol ratio $a \equiv C_{\mathrm{HClO_4}}/C_{\mathrm{Zn}}$. C_{Zn}: ○, 1.769; □, 0.885; ◇, 0.442; △, 0.221×10^{-3} mol/kg.

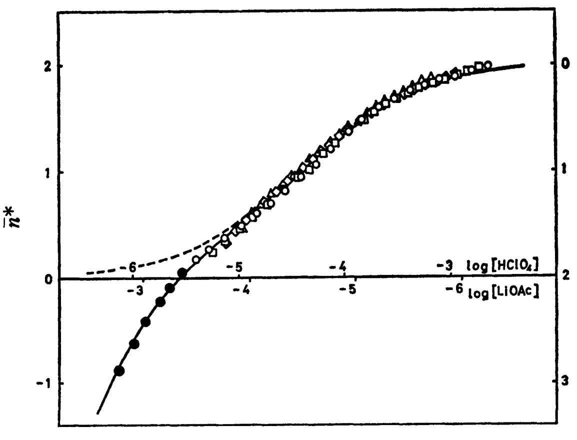

Fig. 3. Plot of formation function of zinc perchlorate, $\bar{n}^*$, and of zinc acetate complex, $\bar{n}$, $(\bar{n}=2-\bar{n}^*)$, as a function of log $[HClO_4]$ and log [LiOAc] (=log $K_f^{-1}C_{LiClO_4}$ − log $[HClO_4]$). Open symbols are the results of titration with perchloric acid. C_{Zn}: ○, 1.769; □, 0.885; ◇, 0.442; △, 0.221×10^{-3} mol/kg. Filled circle is the results with lithium acetate ($C_{Zn}=1.769\times10^{-3}$ mol/kg). Dotted line is the normalized curve, $X=\log x$, $Y=(ax+2x^2)/(1+ax+x^2)$. Solid line is the normalized curve, $X=\log x$, $Y=(ax+2x^2+3bx^3+4cx^4)/(1+ax+x^2+bx^3+cx_4)$.

written as follows:

$$Zn(OAc)_2 + HClO_4 \overset{\beta_1}{\rightleftharpoons} Zn(OAc)(ClO_4) + HOAc \quad (33)$$

$$Zn(OAc)_2 + 2HClO_4 \overset{\beta_2}{\rightleftharpoons} Zn(ClO_4)_2 + 2HOAc. \quad (34)$$

By the use of equilibrium constants of Eqs. (33) and (34),

$$\beta_1^* = [Zn(OAc)(ClO_4)][Zn(OAc)_2]^{-1}[HClO_4]^{-1} \quad (35)$$

$$\beta_2^* = [Zn(ClO_4)_2][Zn(OAc)_2]^{-1}[HClO_4]^{-2}, \quad (36)$$

we obtain

$$\begin{aligned}\bar{n}^* &= ([Zn(OAc)(ClO_4)] + 2[Zn(ClO_4)_2])C_{Zn}^{-1}\\ &= (\beta_1^*[HClO_4] + 2\beta_2^*[HClO_4]^2)\\ &\quad\times(1+\beta_1^*[HClO_4] + \beta_2^*[HClO_4]^2)^{-1}. \quad (37)\end{aligned}$$

Fitting the experimental results with the normalized curve, $X=\log x$, $Y=(ax+2x^2)/(1+ax+x^2)$, we obtained $\log\beta_1^*=4.92$ and $\log\beta_2^*=8.76$ (Fig. 3, dotted line).

Now, zinc acetate solution containing 0.1 mol/kg $LiClO_4$ was titrated with lithium acetate. The formation function calculated by Eq. (38) is plotted in Fig. 3 (filled circles).

$$\bar{n}^* = (-C_{LiOAc}+[HClO_4]-[LiOAc])C_{Zn}^{-1} \quad (38)$$

The plot deviates from the dotted line and goes down to under zero, the fact pointing to the formation of acetato complexes higher than diacetato species, *i.e.*, formation of $Li_{n-2}Zn(OAc)_n$ $(n>2,\ n=2-q)$.

The reaction of zinc acetate with perchloric acid can be rewritten by the reaction of zinc perchlorate with lithium acetate as follows:

$$Zn(ClO_4)_2 + LiOAc \overset{\beta_1}{\rightleftharpoons} Zn(OAc)(ClO_4) + LiClO_4 \quad (39)$$

$$Zn(ClO_4)_2 + 2LiOAc \overset{\beta_2}{\rightleftharpoons} Zn(OAc)_2 + 2LiClO_4 \quad (40)$$

These equilibrium constants, β_1 and β_2, are related with β_1^* and β_2^* as follows:

$$\begin{aligned}\beta_1 &= [Zn(OAc)(ClO_4)][LiClO_4][Zn(ClO_4)_2]^{-1}[LiOAc]^{-1}\\ &= K_f\beta_1^*\beta_2^* \quad (41)\end{aligned}$$

$$\begin{aligned}\beta_2 &= [Zn(OAc)_2][LiClO_4]^2[Zn(ClO_4)_2]^{-1}[LiOAc]^{-2}\\ &= K_f^2\beta_2^* \quad (42)\end{aligned}$$

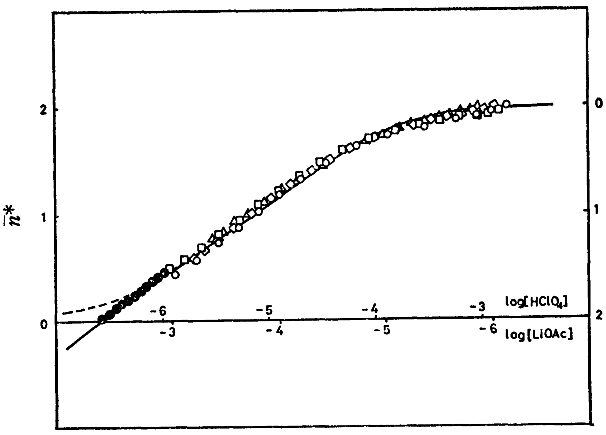

Fig. 4. Plot of formation function of cadmium perchlorate, $\bar{n}^*$, and of cadmium acetato complex, $\bar{n}(\bar{n}=2-\bar{n}^*)$, as a function of log $[HClO_4]$ and log [LiOAc] (=log $K_f^{-1}C_{LiClO_4}$ − log $[HClO_4]$). Open symbols are the results of titration with perchloric acid. C_{Cd}: ○, 4.000; □, 2.000; ◇, 1.000; △, 0.500×10^{-3} mol/kg. Filled circle is the results with lithium acetate ($C_{Cd}=2.000\times10^{-3}$ mol/kg). Dotted line is the normalized curve, $X=\log x$, $Y=(ax+2x^2)/(1+ax+x^2)$. Solid line is the normalized curve, $X=\log x$, $Y=(ax+2x^2+3bx^3)/(1+ax+x^2+bx^3)$.

The free lithium acetate concentration, [LiOAc], and formation function of acetato complex, $\bar{n}$, are written as follows:

$$[LiOAc] = C_{LiClO_4}K_f^{-1}[HClO_4]^{-1} \quad (43)$$

$$\bar{n} = 2 - \bar{n}^*. \quad (44)$$

In Fig. 3 $\bar{n}$ going up to 3 at higher lithium acetate concentration, the formation of triacetato and tetraacetato complexes is anticipated.

$$Zn(ClO_4)_2 + 3LiOAc \overset{\beta_3}{\rightleftharpoons} LiZn(OAc)_3 + 2LiClO_4 \quad (45)$$

$$Zn(ClO_4)_2 + 4LiOAc \overset{\beta_4}{\rightleftharpoons} Li_2Zn(OAc)_4 + 2LiClO_4. \quad (46)$$

Thus the formation function of acetato complex is written as follows:

$$\begin{aligned}\bar{n} &= ([Zn(OAc)(ClO_4)] + 2[Zn(OAc)_2] + 3[LiZn(OAc)_3]\\ &\quad + 4[Li_2Zn(OAc)_4])C_{Zn}^{-1}\\ &= (\beta_1'[LiOAc] + 2\beta_2'[LiOAc]^2 + 3\beta_3'[LiOAc]^3\\ &\quad + 4\beta_4'[LiOAc]^4)(1+\beta_1'[LiOAc] + \beta_2'[LiOAc]^2\\ &\quad + \beta_3'[LiOAc]^3 + \beta_4'[LiOAc]^4)^{-1} \quad (47)\end{aligned}$$

where conditional overall formation constants are defined as $\beta_1'=\beta_1[LiClO_4]^{-1}$, $\beta_2'=\beta_2[LiClO_4]^{-2}$, $\beta_3'=\beta_3[LiClO_4]^{-2}$ and $\beta_4'=\beta_4[LiClO_4]^{-2}$.

By comparison of the plot of $\bar{n}$ *vs.* log [LiOAc] with the normalized curve, $X=\log x$, $Y=(ax+2x^2+3bx^3+4cx^4)(1+ax+x^2+bx^3+cx^4)^{-1}$, β_3' and β_4' are determined from b $(=\beta_3'/\beta_2'^{3/2})$ and c $(=\beta_4'/\beta_2'^2)$, where β_1' and β'_2 have been obtained previously. Thus from the

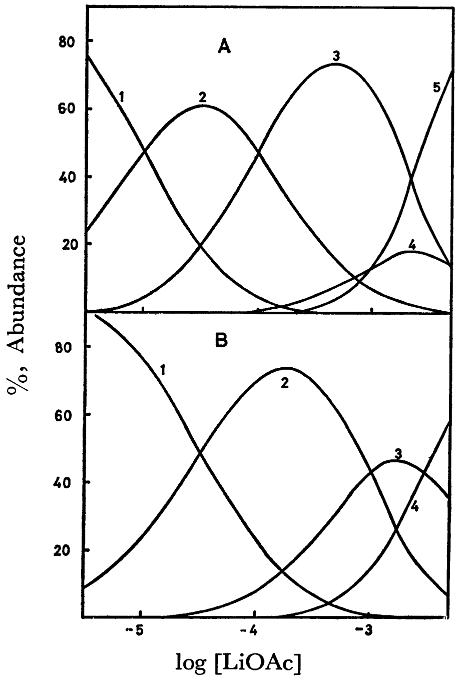

Fig. 5. Distribution diagram of acetato complexes of zinc (A) and cadmium (B) in 0.1 mol/kg $LiClO_4$ acetic acid solution.
1, $M(ClO_4)_2$; 2, $M(OAc)(ClO_4)$; 3, $M(OAc)_2$; 4, $LiM(OAc)_3$; 5, $Li_2M(OAc)_4$.

best fit curve (Fig. 3, solid line), the formation constants of acetato complexes are found as $\log \beta_1 = 4.04 \pm 0.1$, $\log \beta_2 = 7.00 \pm 0.1$, $\log \beta_3 = 9.2 \pm 0.3$ and $\log \beta_4 = 12.4 \pm 0.5$.

Formation of Cadmium-Acetato Complex. Potentiometric titration of cadmium acetate solution containing 0.1 mol/kg $LiClO_4$ with perchloric acid and lithium acetate has been carried out in the same manner as in the titration of zinc acetate. The results are shown in Fig. 4. In the case of cadmium complexes higher than triacetato complex are not observed over the studied range of lithium acetate concentration. The following equilibria are found to be relevant to the cadmium acetate:

$$Cd(ClO_4)_2 + LiOAc \overset{\beta_1}{\rightleftharpoons} Cd(OAc)(ClO_4) + LiClO_4 \quad (48)$$

$$Cd(ClO_4)_2 + 2LiOAc \overset{\beta_2}{\rightleftharpoons} Cd(OAc)_2 + 2LiClO_4 \quad (49)$$

$$Cd(ClO_4)_2 + 3LiOAc \overset{\beta_3}{\rightleftharpoons} LiCd(OAc)_3 + 2LiClO_2 \quad (50)$$

with overall formation constants of $\log \beta_1 = 3.43 \pm 0.1$, $\log \beta_2 = 5.46 \pm 0.1$ and $\log \beta_3 = 8.0 \pm 0.3$.

Fig. 5 depicts the distribution diagrams for acetato complexes of zinc (A) and cadmium (B) in 0.1 mol/kg $LiClO_4$ acetic acid solution calculated from the formation constants obtained in the present paper. Touller and Trémillon have investigated the formation of the acetato complexes of zinc, cadmium and other metals by the use of amalgam electrodes.[20] The formation constants of cadmium–acetato complexes reported by them are in fair accord with ours. The agreement of their constants for zinc with ours is poor presumably because they neglected the higher acetato complexes.

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