# Polarographic and Anodic Stripping Polarographic Studies of Aliphatic Polyamine Complexes of Several Metal Ions

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(Received September 3, 1973)

The polarography of several aliphatic polyamine complexes of Pb(II), Zn(II), and Ni(II), and the anodic stripping polarography of polyamine complexes of Zn(II), Cd(II), Pb(II), and Cu(II) were studied. The aliphatic polyamines used were ethylenediamine(en), 1,3-propanediamine(1,3-pn), 1,2-propanediamine(1,2-pn), diethylenetriamine(den), and triethylenetetramine(trien). These lead(II) complexes gave a one-step reversible wave which was diffusion-controlled. The relation between the logarithm of the concentration of polyamine and the half-wave potential of the Pb(II) complex was straight, so that one species of complex ion was found to be predominant in the bulk of solution. The ionic species in the bulk of solution were found to be $Pb(en)_2^{2+}$, $Pb(1,3\text{-}pn)_2^{2+}$, $Pb(1,2\text{-}pn)_2^{2+}$, $Pb(den)_2^{2+}$, and $Pb(trien)^{2+}$. The stability constants of these complexes were calculated and were found to increase in the order of $Pb(1,3\text{-}pn)_2^{2+} < Pb(en)_2^{2+} < Pb(1,2\text{-}pn)_2^{2+} < Pb(den)_2^{2+} < Pb(trien)^{2+}$. The polarographic waves of Zn(II)-polyamine and Ni(II)-polyamine complexes were irreversible and diffusion-controlled, so the electrode reactions of these complexes were assumed using Matsuda-Ayabe's theory. All these polyamine complexes of Zn(II), Cd(II), Pb(II), and Cu(II) gave well-defined anodic stripping polarograms. 1,3-pn was the best complexing reagent among these polyamines, because it gave the best separation of the peaks of the anodic stripping polarograms of the four metal ions. Calibration curves were obtained from 0.01 to 0.10 ppm for Zn(II), Pb(II), and Cu(II), and from 0.001 to 0.010 ppm for Cd(II) in 0.4 M 1,3-pn and 0.2 M KCl media. The effects of acid and base on the anodic stripping polarograms were also studied.

It has been well known that aliphatic polyamines react with metal ions to give stable complexes in a fairly strongly alkaline medium.[1] The copper(II) and cadmium(II)-ethylenediamine(en), 1,2-propanediamine(1,2-pn), 1,3-propanediamine(1,3-pn), diethylenetriamine(den), and triethylenetetramine(trien) complexes were studied by means of a dropping mercury electrode.[2-4] Also, zinc(II) and nickel(II)-en complexes,[5] the lead(II)-trien complex[6] and the nickel(II)-1,2-pn complex[7] were studied by means of a dropping mercury electrode.

Anodic stripping polarography has been known to be a sensitive method for the analysis of the metal ions and various supporting electrolyte solutions have been used.[8] Moreover, the anodic stripping polarography of nickel(II), cobalt(II), manganese(II) has been studied in an aqueous solution of polyamine.[9] In a fairly strongly acidic solution (<pH 2), the hydrogen wave interferes with the determination of the zinc (II) ion, so it is interesting that anodic stripping polarography is carried out in an alkaline medium.

The present paper will report about the electrode reaction of lead(II), zinc(II), and nickel(II) in an aqueous solution of polyamine and about an application of these polyamine complexes to trace analysis by anodic stripping polarography.

## Experimental

*Materials.* All the solutions of the amines, obtained from the Tokyo Kasei Co., Ltd, were standardized by 0.1 M HCl using a B.P.B. indicator. The lead(II) nitrate, zinc(II) nitrate and nickel(II) nitrate were standardized with 0.01 M EDTA. The potassium nitrate was once recrystallized and was used as a supporting electrolyte for polarography. Gelatine was used as a maximum suppressor for the zinc(II) and nickel(II) complexes. The potassium chloride was purified by extracting heavy metal ions with dithizone–chloroform system, after then having been recrystallized twice and heated at 300 °C in an electric furnace for 3 hr and it was used as the supporting electrolyte for anodic stripping polarography. The standard solution of the metal ions for anodic stripping polarography was prepared from metal chlorides. Water was deionized on a mixed-bed ion-exchange resin and was then distilled from an alkaline permanganate.

*Apparatus.* The polarograms were recorded with a Shimadzu polarograph, model RP-50. The initial potentials were measured with a Shimadzu potentiometer, model K-2. The span voltage was 1.0 V for lead(II), and 2.0 V for zinc-(II) and nickel(II). An H-type cell with a saturated calomel electrode was then used. The dropping mercury electrode (DME) used for lead(II) and zinc(II) had an $m$ value of 2.47 mg/s and a drop time of 3.47 s at the mercury column height of 70 cm in a distilled water with an open circuit. The other DME used for nickel(II) had an $m$ value of 1.75 mg/s and a drop time of 2.85 s at the mercury column height of 40 cm at the applied potential of −1.40 V *vs.* SCE. All the DC polarograms were recorded in a thermostat at 25.0± 0.1 °C.

The block diagram of anodic stripping polarograph is shown in Fig. 1. The potential-current curves were recorded with a X–Y recorder (D5–SN, Rikendenshi Co., Ltd.). The potential was driven by a sweep generator (Sanyo Denki Co., Ltd.). The scanning rate was 0.1 V/s. The initial voltage

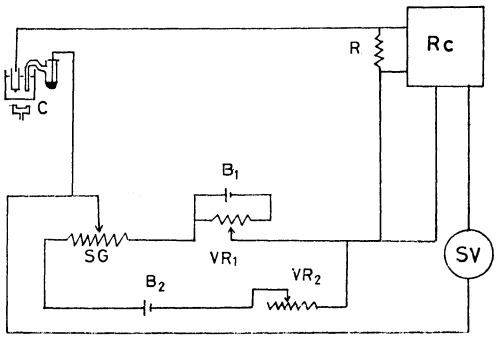


Fig. 1. Block diagram of anodic stripping polarograph. Rc, X-Y recorder; SV, standard voltage generator; C, electrolytic cell; $B_1$, $B_2$, battery; R, load resistor; SG, sweep generator; $VR_1$, $VR_2$, variable resistor

of the X–Y recorder was adjusted by a standard voltage generator (SV-12, Rikendenshi Co., Ltd.). The applied potential was controlled by $B_1$ and $B_2$. A balanced-head, stationary hanging mercury drop electrode(HMDE)[10] was used. The surface area of HMDE used was 0.028 $cm^2$. A saturated calomel electrode was used as the reference electrode. The cell assembly has been reported elsewhere.[11]

*Procedure.* The polarographic electrolyte solutions were prepared by placing a stock solution of metal(II) nitrate, potassium nitrate, polyamine and, lastly, a fresh solution of gelatine in a 25 ml flask. The anodic stripping polarographic electrolyte solutions were prepared by placing a stock solution of metal(II)-chloride, potassium chloride and polyamine in a 50 ml flask. Oxygen was removed from the electrolyte solutions by passing nitrogen gas through them for about 10—15 min, prior to the measurements of the DC polarogram and pre-electrolysis in anodic stripping polarography. The procedure of anodic stripping polarography was as follows. The electrolyte solution was stirred at 360 rpm during the pre-electrolysis with a magnetic stirrer by means of synchronous rotating motor. Following the pre-electrolysis for a certain time, the stirring was stopped for 30 s, then the potential was scanned into a positive direction in order to strip the deposited metal anodically from the mercury electrode. All the anodic stripping polarographic measurements were carried out at room temperature.

## Results and Discussion

*Polarography of Lead(II) Complexes.* Typical DC polarogram of the lead(II)-polyamine complex is given in Fig. 2(a). The limiting current varied with the

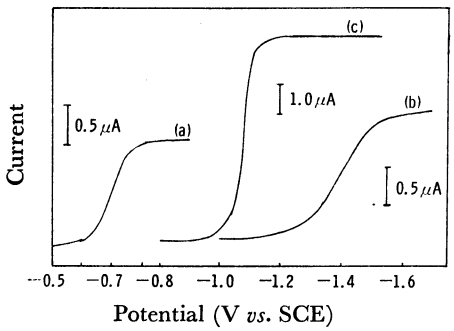


Fig. 2. Typical DC polarograms of Pb(II), Zn(II), and Ni(II) in the aqueous solution of aliphatic polyamine.
(a) 0.44 mM Pb(II) in 0.19 M ethylenediamine and 0.2 M $KNO_3$
(b) 0.44 mM Zn(II) in 0.10 M 1,2-propanediamine, 0.2 M $KNO_3$ and 0.01% gelatine
(c) 0.98 mM Ni(II) in 0.10 M 1,3-propanediamine, 0.2 M $KNO_3$ and 0.015% gelatine

mercury column height, while the $i_l/\sqrt{H_{corr}}$ value, where $H_{corr}$ is the value corrected for the back pressure, was constant, this indicates that the electrode reactions were diffusion-controlled. The waves were analyzed by the log plot method from the current $i$ at the potential of $E$ of the dropping mercury electrode and the limiting current, $i_l$. The reciprocal slopes of the log plot of the lead(II) waves are given in Table 1 and these electrode reactions were reversible, two-electron reactions. The limiting current was gradually lowered with an increase in the concentration of the polyamine, because of the enhancement of the viscosity of the electrolyte solution.[5] In Fig. 3, the half-wave potentials are plotted against the logarithm of the various concentrations of the ligand. The resultant curves are straight, so only one ionic species is predominant in this concentration range.[12] The slope of $E_{1/2}$ *vs.* log $C$ for en was 0.056 V, for 1,2-pn 0.057 V, for 1,3-pn 0.055 V and for den 0.056 V, indicating that two molecules of en, 1,2-pn, 1,3-pn or den were attached to lead(II) ion,[12] while for trien

Table 1. Polarography of lead(II)-polyamine complexes

| Concen (M) | $-E_{1/2}$ (V *vs.* SCE) | $i_d$ (μA) | Reciprocal slope of log plot (mV) | $-\log k_d$ |
|---|---|---|---|---|
| | | en | | |
| 0.194 | 0.600 | 3.45 | 29 | 8.47 |
| 0.388 | 0.617 | 3.38 | 30 | 8.44 |
| 0.575 | 0.627 | 3.32 | 29 | 8.41 |
| 0.766 | 0.632 | 3.17 | 29 | 8.31 |
| 0.957 | 0.645 | 3.06 | 29 | 8.56 |
| | | | average | 8.44 |
| | | 1,2-pn | | |
| 0.053 | 0.576 | 3.37 | 30 | 8.78 |
| 0.071 | 0.584 | 3.27 | 29 | 8.78 |
| 0.089 | 0.590 | 3.25 | 28 | 8.78 |
| 0.178 | 0.599 | 3.18 | 28 | 8.49 |
| 0.356 | 0.617 | 3.33 | 28 | 8.48 |
| 0.534 | 0.629 | 3.10 | 29 | 8.54 |
| 0.713 | 0.638 | 2.98 | 29 | 8.58 |
| 0.891 | 0.641 | 2.98 | 29 | 8.51 |
| | | | average | 8.62 |
| | | 1,3-pn[a] | | |
| 0.100 | 0.577 | 2.00 | 30 | 8.21 |
| 0.200 | 0.596 | 1.84 | 29 | 8.21 |
| 0.400 | 0.614 | 1.77 | 28 | 8.21 |
| 0.600 | 0.623 | 1.73 | 29 | 8.17 |
| 1.00 | 0.631 | 1.57 | 29 | 8.00 |
| | | | average | 8.16 |
| | | den | | |
| 0.053 | 0.627 | 3.25 | 31 | 10.50 |
| 0.088 | 0.640 | 3.25 | 31 | 10.47 |
| 0.176 | 0.657 | 3.03 | 29 | 10.47 |
| 0.355 | 0.672 | 3.01 | 29 | 10.30 |
| 0.533 | 0.679 | 2.75 | 29 | 10.27 |
| 0.710 | 0.688 | 2.80 | 29 | 10.30 |
| 0.888 | 0.697 | 2.80 | 29 | 10.40 |
| | | | average | 10.39 |
| | | trien | | |
| 0.043 | 0.654 | 3.03 | 29 | 10.21 |
| 0.089 | 0.666 | 3.11 | 29 | 10.32 |
| 0.107 | 0.671 | 2.93 | 29 | 10.37 |
| 0.215 | 0.679 | 2.88 | 29 | 10.37 |
| 0.431 | 0.693 | 2.55 | 29 | 10.50 |
| 0.646 | 0.702 | 2.23 | 29 | 10.63 |
| 0.863 | 0.705 | 2.05 | 29 | 10.64 |
| | | | average | 10.43 |

a) [Pb(II)]: 0.22 mM

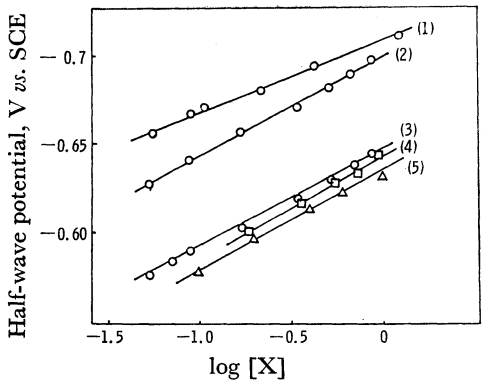


Fig. 3. Relation between $E_{1/2}$ of lead (II) complexes and log [X].
(1) trien; (2) den; (3) 1,2-pn; (4) en; (5) 1,3-pn

the slope was 0.034 V, indicating that one molecule of trien was attached. Because white precipitates were observed when 0.44 mM of Pb(II) was used in the case of the Pb(II)-1,3-pn system, 0.22 mM of Pb(II) was used. The limiting current of the Pb(II)-1,3-pn complex was linearly proportional to the concentration from 0 to 0.33 mM Pb(II) ion. The den complex is of interest because its maximum coordination number is three. The 1:2 complex for the den complex was observed in the case of copper-(II),[2] cadmium(II),[3] mercury(II),[13] and zinc(II)[14] complexes. The dissociation constants ($k_d$), which were calculated from Lingane's equation,[12] are given in Table 1. The stability constant of the trien complex was in good agreement with that obtained potentiometrically by Reiley and Schmid,[15] but slightly higher than that obtained by Lai and Chen,[6] probably because of the hydrolysis of the lead(II) ion. The stability constants increased in the order of: 1,3-pn complex<en complex<1,2-pn complex<den complex<trien complex; this tendency was identical with that of the copper(II)[2] and cadmium(II)[3] complexes. The stability constant of the complexes with a tri- or tetradentate ligand was larger than that of those with a bidentate ligand. Among these diamine complexes, the stability constant of the 1,2-pn complex was largest, probably because of its five-membered ring and one methyl group.

*Polarography of Zinc(II) Complexes.* The polarography of zinc(II)-1,2-pn, 1,3-pn, den, and trien complexes was studied in this work. A typical DC polarogram of Zn(II)-polyamine complex is given in Fig. 2(b). All the zinc(II)-polyamine complexes gave one-step waves. The currents varied with the mercury column height and the $i_l/\sqrt{H_{corr}}$ value was constant, indicating that the electrode reactions were entirely diffusion-controlled. The reciprocal slope of the log plot was 0.044 V for 1,2-pn, 0.049 V for 1,3-pn, 0.045 V for den and 0.050 V in trien concentration range from 0.006 to 0.030 M and 0.045 V in trien concentration range from 0.059 to 0.295 M for trien complex. These values demonstrated that these electrode reactions were irreversible reduction processes. When only the $MX_N^{m+}$ complex, which is predominant in the bulk of the solution, dissociates very rapidly into the $MX_p^{m+}$ complex in the vicinity of the electrode surface, when the $MX_p^{m+}$ complex is reduced irreversibly at DME, and when its electrode reaction is diffusion-controlled, then Matsuda-Ayabe's equation for the irreversible half-wave potential of the complex ion[16] is expressed as:

$$(E_{1/2})_{irr} = 2.3\frac{RT}{\alpha nF}\left\{\log\frac{(k_f^\circ)_B}{\sqrt{D_N}} - (N-p)\log[X] + \frac{1}{2}\log\tau - 0.053\right\} \quad (1)$$

where [X] is the concentration of the polyamine, $\alpha$ is the transfer coefficient, $\tau$ is the dropping time of DME, $(k_f^\circ)_B$ is the forward (reduction) rate constant of the electron transfer process at the potential of the normal hydrogen electrode, and $D_N$ is the diffusion coefficient of the complex ion $MX_N^{m+}$ (all activities are assumed to be unity in above equation). The $(N-p)$ value can be obtained from the slope of the $(E_{1/2})_{irr}$ *vs.* log [X.] plot and the value of the reciprocal slope of log plot. The relation between $(E_{1/2})_{irr}$ and log [X] is given in Fig. 4. The slope obtained for 1,2-pn was 0.045 V, for 1,3-pn 0.054 V, for den 0.045 and for trien 0.050 V and 0.005 V. The calculated $(N-p)$ values for the zinc-(II)-polyamine complexes are given in Table 2(i). If

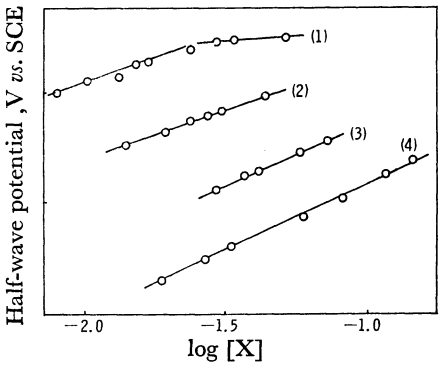


Fig. 4. Relation between $E_{1/2}$ of zinc(II) complexes and log[X].
(1) trien; (2) den; (3) 1,2-pn; (3) 1,2-pn; (4) 1,3-pn

TABLE 2. THE CALCULATED VALUE OF $(N-p)$ OF Zn(II) AND Ni(II)-POLYAMINE COMPLEXES

| i) Zn(II)-polyamine complexes | 1, 2-pn | 1, 3-pn | den | trien | |
|---|---|---|---|---|---|
| $(N-p)$ | 1.1 | 1.2 | 1.0 | 1.0[a] | 0.01[b] |

| ii) Ni(II)-polyamine complexes | 1, 3-pn | den | | trien | |
|---|---|---|---|---|---|
| $(N-p)$ | 1.8 | 1.0[c] | 0.0[d] | 0.96[e] | 0.0[f] |

a) 0.006 M≦trien≦0.030 M. b) 0.059 M≦trien≦0.295 M. c) 0.003 M≦den≦0.035 M. d) 0.071 M≦den≦0.284 M. e) 0.003 M≦trien≦0.028 M. f) 0.042 M≦trien≦0.056 M.

the value of $N$ is known, $p$ may be assumed. The zinc(II)-polyamine complexes have been studied potentiometrically and the ionic species in the bulk of solution were known except for the zinc(II)-1,3-pn system.[17] $Zn(1,2\text{-pn})_3^{2+}$, $Zn(den)_2^{2+}$, and $Zn(trien)^{2+}$ were predominant in the aqueous solution of each polyamine. From the values of $(N-p)$ and the complexes in the bulk

of the solution, the following rapid dissociation-association reactions were assumed for the electrode reactions of the zinc(II)-polyamine complexes:
for the 1,2-pn complex:

$$Zn(1,2\text{-pn})_3^{2+} \rightleftarrows Zn(1,2\text{-pn})_2^{2+} + 1,2\text{-pn}$$

for the 1,3-pn complex:

$$Zn(1,3\text{-pn})_N^{2+} \rightleftarrows Zn(1,3\text{-pn})_{N-1}^{2+} + 1,3\text{-pn}$$

for the den complex:

$$Zn(den)_2^{2+} \rightleftarrows Zn(den)^{2+} + den$$

for the trien complex:

$$Zn(trien)^{2+} \rightleftarrows Zn^{2+} + trien \quad (0.006M \leqq trien \leqq 0.030M).$$

Above 0.059 M trien, $Zn(trien)^{2+}$ would participate in the electrode reaction.

*Polarography of Nickel(II) Complexes.* The polarography of nickel(II)-1,3-pn, den, and trien complexes were investigated in this work. The polarography of the nickel(II)-1,2-pn complex had been reported elsewhere.[8] A typical DC polarogram of the nickel(II)-polyamine complex is given in Fig. 2(c). All the nickel(II)-polyamine complexes investigated in this work gave a one-step wave. The $i_l/\sqrt{H_{corr}}$ value was also constant, indicating that the electrode reaction was entirely diffusion-controlled. Polarograms were recorded in the ranges of concentration of 1,3-pn from 0.018 to 1.03 M, of den from 0.003 to 0.284 M and of trien from 0.003 to 0.056 M. The half-wave potentials were shifted to more negative value with an increase in the concentration of polyamine as is shown in Fig. 5. However, the half-wave potentials of the den or

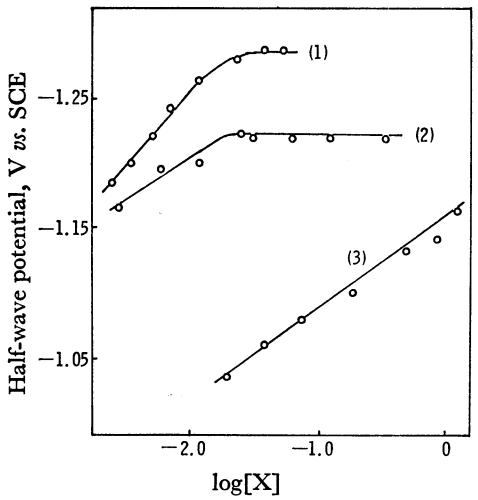


Fig. 5. Relation between $E_{1/2}$ of nickel(II) complexes and log[X].
(1) trien; (2) den; (3) 1,3-pn

trien complex were constant from 0.071 to 0.284 M den or from 0.042 to 0.056 M trien respectively. The reciprocal slope of the log plot was 0.038 V for the 1,3-pn complex, 0.056 V for the den complex in the concentration from 0.003 to 0.284 M den and 0.120 V for the trien complex in the concentration range of 0.003 to 0.056 M trien. These values demonstrated that these electrode reactions were irreversible electrode process and that Eq. (1) can be used to interpret the waves. The slope of $(E_{1/2})_{irr}$ *vs.* log [X] plot was 0.075 V for the 1,3-pn complex, 0.055 V in the ranae of 0.003—0.035 M of den and 0.00 V in the range of 0.071—0.288 M of den and 0.115 V in the range of 0.003—0.028 M trien, and 0.00 V in the range of 0.042—0.056 M trien. The ionic species of Ni(II)-polyamine complexes in the bulk of solution had been studied potentiometrically,[17] and $Ni(1,3\text{-pn})_3^{2+}$, $Ni(den)_3^{2+}$ and $Ni(trien)_2^{2+}$ were observed. The calculated $(N-p)$ values of Ni(II)-polyamine complexes are given in Table 2(ii). Thus, the following dissociation-association reactions were assum ed for the electrode reaction of Ni(II)-polyamine complexes:
for the 1,3-pn complex:

$$Ni(1,3\text{-pn})_3^{2+} \rightleftarrows Ni(1,3\text{-pn})^{2+} + 2(1,3\text{-pn})$$

for the den complex:

$$Ni(den)_2^{2+} \rightleftarrows Ni(den)^{2+} + den \quad (0.003M \leqq den \leqq 0.035M)$$

for the trien complex:

$$Ni(trien)_2^{2+} \rightleftarrows Ni(trien)^{2+} + trien \quad (0.003M \leqq trien \leqq 0.028M).$$

It is shown that the ionic states of these complexes which participate in the electrode reaction must form a 1:1 complex at lower concentrations of these polyamines. Above 0.071 M den and 0.042 M trien, $Ni(den)_2^{2+}$ and $Ni(trien)_2^{2+}$ must directly participate in the electrode reaction.

*Anodic Stripping Polarography.* The present work and past works demonstrated that Cu(II), Pb(II), Cd(II), and Zn(II) formed stable complexes with en, 1,2-pn, 1,3-pn, den, and trien. As an application of these polyamine complexes to trace analysis, anodic stripping polarographic studies of these four metal ions were carried out in aqueous solutions of these polyamines. The peak potentials were measured in an aqueous solution of 0.05 M of each polyamine, they are shown in Fig. 6. 1,3-pn was found to be the best reagent among these polyamines, because it gave the best separation of the peaks of these metal ions. Typical anodic stripping polarograms of Zn(II), Cd(II), Pb-

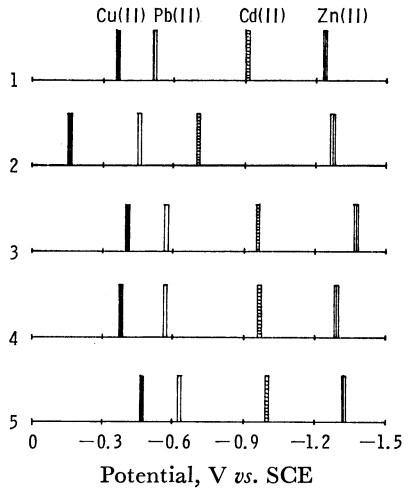


Fig. 6. Peak potentials of 0.1 ppm of Zn(II), Cd(II), Pb(II) and Cu(II) in 0.05 M polyamine and 0.2 M KCl.
(1) en; (2) 1,3-pn; (3) 1,2-pn; (4) den; (5) trien

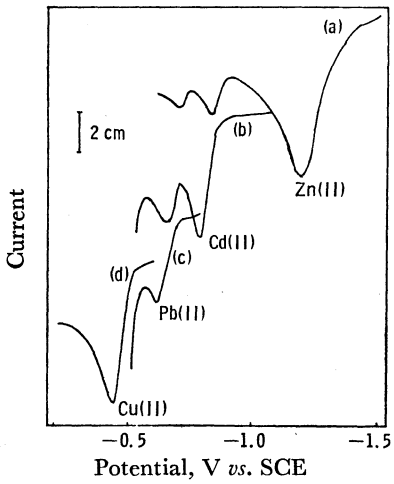


Fig. 7. Anodic stripping polarograms of 0.1 ppm of Zn(II), Cd(II), Pb(II), and Cu(II) in 0.4 M 1,3-pn and 0.2 M KCl.
Pre-electrolysis potential (V *vs.* SCE): (a), −1.50 V; (b), −1.10 V; (c), −0.80 V; (d), −0.60 V
Pre-electrolysis time (min): (a), 1; (b), 1; (c), 2; (d), 1
Record. sens., 0.04 μA/cm

(II), and Cu(II) in 0.4 M 1,3-pn are given in Fig. 7. The pre-electrolysis potential was −1.50 V *vs.* SCE for Zn(II), −1.10 V *vs.* SCE for Cd(II), −0.80 V *vs.* SCE for Pb(II) and −0.60 V *vs.* SCE for Cu(II). With choices of these pre-electrolysis potentials, interference by more cathodic waves could be omitted. Because the electrode reaction of Cu(II)-polyamine complex is a two-electron transfer process, its anodic stripping peak current could be sharper than that of Cu(II) in thiocyanate, $NH_3$, chloride or pyridine, in which a two-step wave of Cu(II) appears.[12] The calibration curves are given in Figs. 8 and 9. The wave height of these ions were linearly proportional to the concentration of the metal ions. The effects of acid and base on these anodic stripping polarograms

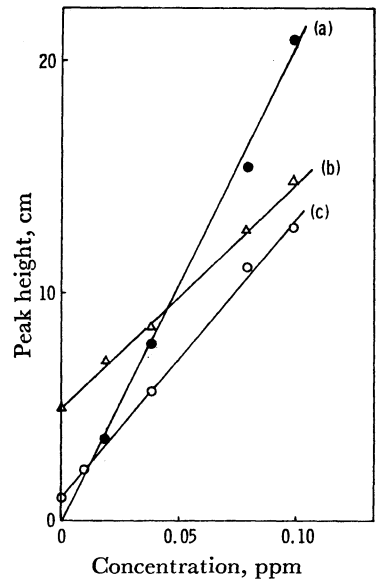


Fig. 8. Calibration curves of Cu(II), Pb(II), and Zn(II).
Pre-electrolysis time for (a) Zn(II) and (b) Cu(II): 2 min; and for (c) Pb(II): 5 min.
Other conditions: the same as those in Fig. 7.

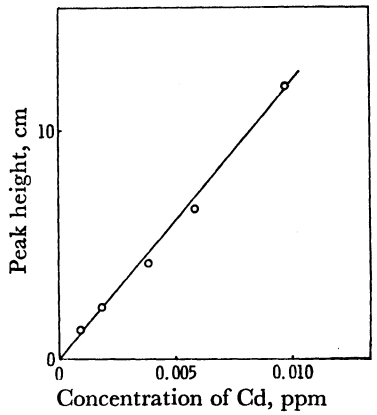


Fig. 9. Calibration curve of Cd(II)
Pre-electrolysis time: 5 min; Record. sens., 0.016 μA/cm
Other conditions: the same as those in Fig. 7.

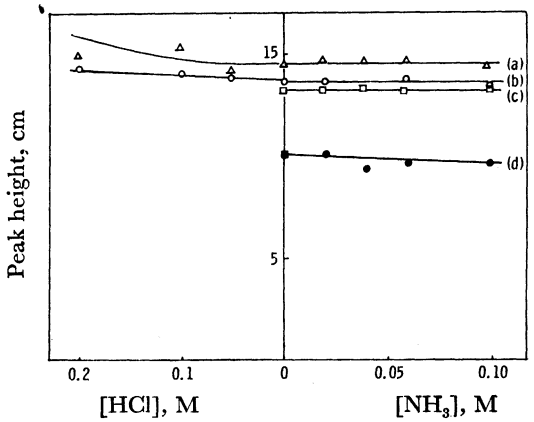


Fig. 10. Effects of hydrochloric acid and $NH_3$ on the peak heights of Zn(II), Cd(II), Pb(II), and Cu(II).
(a) [Zn(II)]: 0.150 ppm; (b) [Cd(II)]: 0.10 ppm; (c) [Pb(II)]: 0.080 ppm; (d) [Cu(II)]: 0.070 ppm
Pre-electrolysis time for Zn(II), Cu(II) and for Pb(II): the same as those in Fig. 8; and for Cd(II): 2 min.
Other conditions: the same as those in Fig. 7.

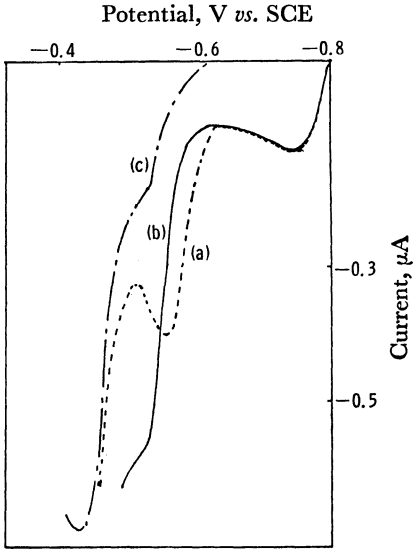


Fig. 11. Effect of hydrochloric acid on the anodic stripping polarograms of Cd(II), Pb(II), and Cu(II)
HCl: (a), 0.1 M; (b), 0.2 M; (c), 0.2 M
Pre-electrolysis potential: (a) and (b), −0.80 V *vs.* SCE, and (c), −0.60 V *vs.* SCE
Other conditions: the same as those in Fig. 10.

were also studied. 0.01—0.10 M $NH_3$ or 0.1—0.2 M hydrochloric acid was added to a mixture of Zn(II), Cd(II), Pb(II), and Cu(II), 0.4 M 1,3-pn and 0.2 M KCl, and then anodic stripping polarograms were recorded. The results are shown in Figs. 10 and 11. The wave heights of Cu(II), Pb(II), Cd(II), and Zn(II) were almost constant when $NH_3$ was added, but a slight increase in the wave heights of Zn(II) and Cd-(II) was observed with an increase of the concentration of hydrochloric acid. And also, by the addition of hydrochloric acid the peak potentials of Cu(II) and Pb(II) were shifted to so positive a potential that the peak height of Pb(II) and Cu(II) could not be exactly measured (Fig. 11). Accordingly, it is necessary to neutralize the acidic test solution by $NH_3$ prior to the determination.

The author is grateful to Professor S. Misumi of Kyushu University for his kind discussions and also to Dr. H. Kakiyama of the National Industrial Research Institute, Kyushu, for his continual encouragement.

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