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Polarographic Study of Thallium(I) Chelates of 2,2′-Ethylenedioxybis[ethyliminodi(acetic acid)] and Cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic Acid

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D.c. polarographic behavior of thallium(I) ion in 2,2′-ethylenedioxybis[ethyliminodi(acetate)] (GEDTA) and cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetate (CyDTA) solutions was studied systematically. Compositions and stability constants of thallium(I)-GEDTA and CyDTA chelates were determined from the shift of the half-wave potential. In both GEDTA and CyDTA systems, thallium(I) ion gave a single well-defined wave corresponding to the following reversible one-electron reduction.

$$\begin{array}{lcl} \mathrm{TlZ^{3-}} + \mathrm{Hg} + \mathrm{e^-} & = & \mathrm{Tl(Hg)} + \mathrm{Z^{4-}} \\ \Big\updownarrow \mathrm{H^+} & & \qquad\quad \Big\updownarrow n\mathrm{H^+} \\ \mathrm{TlHZ^{2-}} & & \qquad\quad \mathrm{H}_n\mathrm{Z}^{n-4} \end{array}$$

In contrast to the finding of Anderegg and Bottari, thallium(I) ion was found to form not only a normal chelate but also a protonated chelate with CyDTA.

In a previous paper,[1] both the d.c. and a.c. polarographic behaviors of thallium(I) ion in diethylenetriaminepentaacetate (DTPA) solution were studied systematically, and the electrode reaction mechanism determined. From the shift of the half-wave potential or the a.c. peak potential due to complex formation, the composition and stability constant of thallium(I)-DTPA chelate were also estimated.

In this paper, the d.c. polarographic behavior of thallium(I) chelates of 2,2′-ethylenedioxybis-[ethyliminodi(acetic acid)] (GEDTA) and cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) are dealt with, and their compositions and stability constants determined. Thallium(I) ion was found to form not only a normal chelate but also a protonated chelate with these chelating reagents.

Experimental

Reagents. The preparation and standardization of GEDTA and CyDTA solutions were described previously.[2,3] The preparation of thallium(I) perchlorate solution was also described in a previous paper.[1] All other chemicals were of analytical reagent grade and used without further purification. The ionic strength of the sample solution was adjusted to 0.30 by adding an appropriate amount of $NaClO_4$.

Apparatus and Experimental Procedures. All apparatus and experimental procedures were as employed previously.[1,4]

Results and Discussion

D. c. polarographic behavior of thallium(I)-GEDTA chelate was studied with a solution containing an excess of un-complexed GEDTA in the pH range 8.00 to 10.00. Since, in this pH range, a solution containing an excess of un-complexed GEDTA has enough buffer capacity to keep the pH value of the solution constant, no buffer reagent was used. In the CyDTA system, to avoid equilibrium complexity due to the presence of other complex-forming substances, all experiments were conducted with solutions containing an excess of CyDTA in the pH range 10.0 to 11.70.

As shown in Figs. 1 and 2, both thallium(I)-GEDTA and -CyDTA chelates invariably gave single well-defined waves. In both cases, a log-plot gave a linear relation with a slope of -60 mV corresponding to a one-electron reversible reduction. Furthermore, the wave height was exactly proportional to the square-root of the effective pressure on the dropping mercury electorde (DME) and the bulk concentration of thallium(I) ion in both cases. Results are not shown here.

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[1] M. Kodama, T. Noda and M. Murata, This Bulletin, **41**, 354 (1968).

[2] M. Kodama, C. Sasaki and T. Noda, *ibid.*, **41**, 2033 (1968).

[3] M. Kodama and H. Ebine, *ibid.*, **40**, 1857 (1967).

[4] M. Kodama and A. Kimura, *ibid.*, **40**, 1639 (1967).

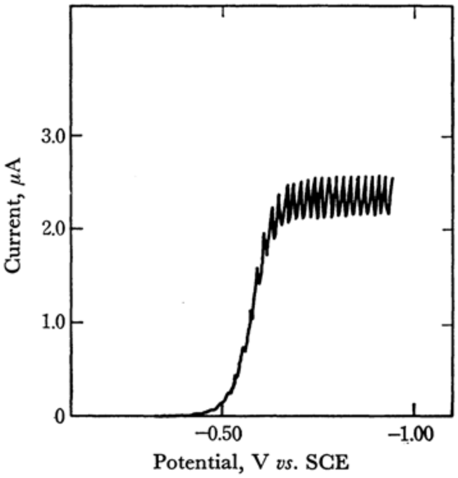

Fig. 1. D. c. polarogram of thallium(I)-GADTA chelate.
pH=8.60, $\mu=0.30$
Concentration of GEDTA=40.0 mM
Concentration of thallium(I)=1.09 mM

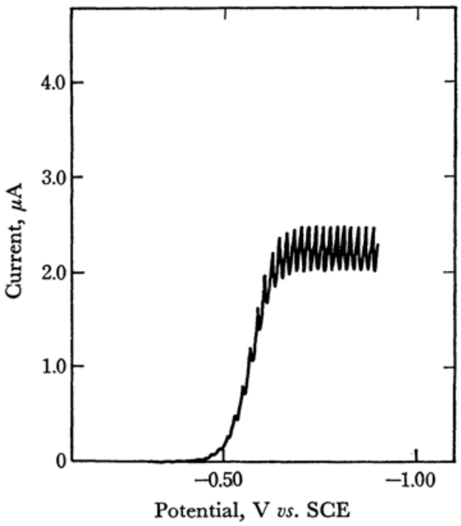

Fig. 2. D. c. polarogram of thallium(I)-CyDTA chelate.
pH=10.68, $\mu=0.30$
Concentration of CyDTA=47.2 mM
Concentration of thallium(I)=1.09 mM

TABLE 1. DEPENDENCE OF $(E_{1/2})_{\mathrm{TlZ}}$ ON THE CONCENTRATION OF CHELATING REAGENT

$\mu=0.30$, Concentration of thallium(I)=1.09 mM

A: GEDTA system pH=8.60

Concentration of GEDTA mM	$(E_{1/2})_{\mathrm{TlZ}}$ V vs. SCE	$\Delta E_{1/2}$, mV	
		Calcd	Obsd
20.0	−0.553	0	0
40.0	−0.583	−33	−30

B: CyDTA system pH=10.68

Concentration of CyDTA mM	$(E_{1/2})_{\mathrm{TlZ}}$ V vs. SCE	$\Delta E_{1/2}$, mV	
		Calcd	Obsd
15.0	−0.550	0	0
27.2	−0.567	−16	−17
47.2	−0.581	−29	−31

As illustrated by data in Table 1, the half-wave potential, $(E_{1/2})_{\mathrm{TlZ}}$, was shifted to more negative potentials with increase in the bulk concentration of un-complexed chelating reagent (GEDTA or CyDTA) according to relation (1), but was independent of thallium(I) concentration.

$$(E_{1/2})_{\mathrm{TlZ}} = \text{constant} - 0.0591 \log [\mathrm{Z}]_f \tag{1}$$

where $[\mathrm{Z}]_f$ is the concentration of the un-complexed chelating reagent.

In GEDTA solution, $(E_{1/2})_{\mathrm{TlZ}}$ was also shifted to more negative potentials with increasing pH of the solution, but no linear relation could be found between $(E_{1/2})_{\mathrm{TlZ}}$ and $\log(\alpha_{\mathrm{H}})_{\mathrm{Z}}$ (Fig. 3). Here, $(\alpha_{\mathrm{H}})_{\mathrm{Z}}$ is expressed as:

$$(\alpha_{\mathrm{H}})_{\mathrm{Z}} = 1 + \frac{[\mathrm{H}^+]}{k_4} + \frac{[\mathrm{H}^+]^2}{k_4 \cdot k_3} + \frac{[\mathrm{H}^+]^3}{k_4 \cdot k_3 \cdot k_2} + \frac{[\mathrm{H}^+]^4}{k_4 \cdot k_3 \cdot k_2 \cdot k_1} \tag{2}$$

where k's are the dissociation constants of GEDTA.

The magnitude of deviation from the linear relation of +60 mV slope expected theoretically for the reversible one-electron reduction of a normal chelate increases with decreasing pH (increasing $(\alpha_{\mathrm{H}})_{\mathrm{Z}}$ value). In the case of the CyDTA system, $(E_{1/2})_{\mathrm{TlZ}}$ was almost independent of the pH value under present experimental conditions ($10.00 < \mathrm{pH} < 11.70$) (Fig. 3). Since CyDTA has the

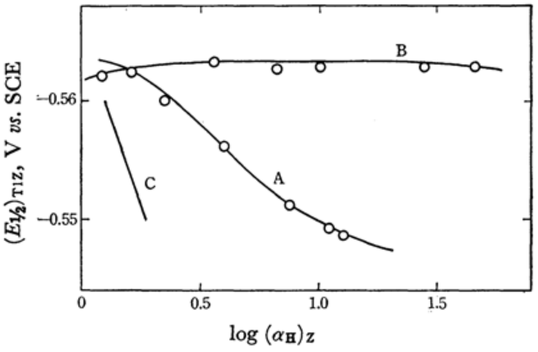

Fig. 3. The relation between $(E_{1/2})_{\mathrm{TlZ}}$ and log $(\alpha_{\mathrm{H}})_{\mathrm{Z}}$.
$\mu=0.30$
Concentration of thallium(I)=1.09 mM
A: GEDTA system, Concentration of GEDTA= 20.0 mM
B: CyDTA system, Concentration of CyDTA= 23.6 mM
C: The line theoretically predicted

$\mathrm{p}K_4$ value of 11.43 ($\mu=0.30$), if only a normal chelate is formed between thallium(I) and CyDTA, the half-wave potential should shift simply to more negative potentials with decreasing pH according to the following relation.

$$(E_{1/2})_{\mathrm{TlZ}} = \text{constant} + 0.0591 \log (\alpha_{\mathrm{H}})_{\mathrm{Z}} \qquad (3)$$

where $(\alpha_{\mathrm{H}})_{\mathrm{Z}}$ is the (α_{H}) value of CyDTA.

Thermodynamically, the formation of a protonated chelate always means an increase in the conditional formation constant, and hence, a negative shift of the half-wave potential. Therefore, the above facts clearly indicate that thallium(I) ion forms not only a normal chelate, TlZ^{3-}, but also a protonated chelate, $\mathrm{TlH}_n\mathrm{Z}^{n-3}$, with both GEDTA and CyDTA. Thus, from the above experimental results and discussion, the following electrode reaction can be assumed,

$$\begin{array}{ccc} \mathrm{TlZ}^{3-} + \mathrm{Hg} + \mathrm{e}^- & = & \mathrm{Tl(Hg)} + \mathrm{Z}^{4-} \\ \Big\updownarrow n\mathrm{H}^+ & & \Big\updownarrow n\mathrm{H}^+ \\ \mathrm{TlH}_n\mathrm{Z}^{n-3} & & \mathrm{H}_n\mathrm{Z}^{n-4} \end{array} \qquad (4)$$

with the half-wave potential expressed as:

$$(E_{1/2})_{\mathrm{TlZ}} = E^0_{\mathrm{Tl}} - 0.0591\Big[\log K_{\mathrm{TlZ}}(1 + K^{\mathrm{H}}[\mathrm{H}^+] + \cdots + K^{n\mathrm{H}}[\mathrm{H}^+]^n) - \log (\alpha_{\mathrm{H}})_{\mathrm{Z}} - \log f_{\mathrm{Tl}^+} + \log [\mathrm{Z}]_f + \log \frac{k_{\mathrm{Tl(Hg)}}}{k_{\mathrm{TlZ}}}\Big] \qquad (5)$$

where K_{TlZ} is the formation constant of a normal thallium(I) chelate, $K^{n\mathrm{H}}=[\mathrm{TlH}_n\mathrm{Z}^{n-3}]/[\mathrm{TlZ}^{3-}]\cdot[\mathrm{H}^+]_n$, n, 1,2,3,$\cdots$, and other symbols have their usual meanings.[1,4)]

As discussed previously on the polarography of thallium(I)-DTPA chelate,[1)] when normal and protonated chelates are formed and the electrode reaction is reversible, the following relation can be expected.

$$K_{\mathrm{TlZ}}(1+K^{\mathrm{H}}[\mathrm{H}^+]+\cdots+K^{n\mathrm{H}}[\mathrm{H}^+]^n) = \text{antilog}\Big[\frac{\Delta E_{1/2}}{0.0591} - \log [\mathrm{Z}]_f + \log \frac{k_{\mathrm{Tl}^+}}{k_{\mathrm{TlZ}}} + \log (\alpha_{\mathrm{H}})_{\mathrm{Z}}\Big] \qquad (6)$$

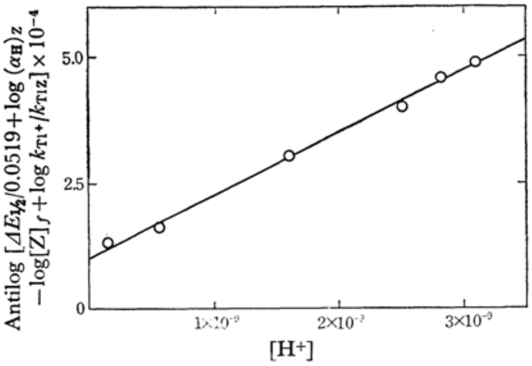

Fig. 4. The relation between antilog $[\Delta E_{1/2}/0.0591 + \log (\alpha_{\mathrm{H}})_{\mathrm{Z}} - \log [\mathrm{Z}]_f + \log (k_{\mathrm{Tl}^+}/k_{\mathrm{TlZ}})]$ and the hydrogen ion concentration.
GEDTA system: $\mu=0.30$,
Concentration of thallium(I) = 1.09 mM

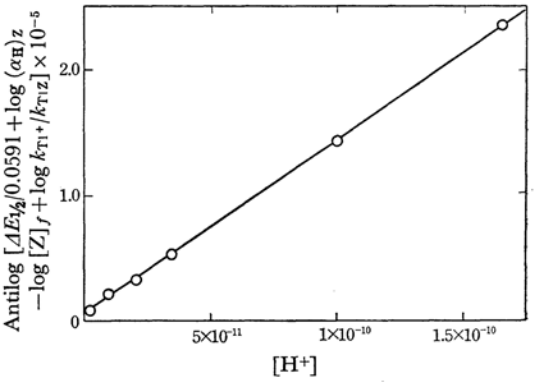

Fig. 5. The relation between antilog $[\Delta E_{1/2}/0.0591 + \log (\alpha_{\mathrm{H}})_{\mathrm{Z}} - \log [\mathrm{Z}]_f + \log (k_{\mathrm{Tl}^+}/k_{\mathrm{TlZ}})]$ and the hydrogen ion concentration.
CyDTA system: $\mu=0.30$,
Concentration of thallium(I) = 1.09 mM

where $\Delta E_{1/2}$ denotes the shift of the half-wave potential due to complex formation.

With the aid of Eq. (6), the composition and stability constants of thallium(I)-GEDTA and -CyDTA chelates were determined using some typical $\Delta E_{1/2}$ values. Results are shown in Figs. 4 and 5. These results clearly show that, in both

TABLE 2. EQUILIBRIUM CONSTANTS* ($\mu=0.30$)

i) Dissociation constants (mixed constants)*1

	pK_1	pK_2	pK_3	pK_4
GEDTA[6)]	1.96	2.57	8.86	9.19
CyDTA[7)]	2.39	3.41	5.93	11.43

ii) Stability constants

	log K_{TlZ}	
Tl(I)-GEDTA chelate	4.0	
Tl(I)-CyDTA chelate	3.8_5	6.7[5)] ($\mu=0.10$)

iii) K^{H} values (mixed constants)

	log K^{H}
Tl(I)-GEDTA system	9.09
Tl(I)-CyDTA system	11.29

*1 These values were calculated from the related constants in solution of ionic strength 0.10 and the activity coefficients of the ions calculated by means of Davies equation.[8)]

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5) G. Anderegg and E. Bottari, *Helv. Chim. Acta*, **50**, 2341 (1967).

6) G. Schwarzenbach, H. Senn and G. Anderegg, *ibid.*, **40**, 1866 (1957).

7) G. Schwarzenbach and H. Ackermann, *ibid.*, **32**, 1682 (1949).

8) J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Inc., Reading, Massachusetts (1964), p. 437.

GEDTA and CyDTA systems, thallium(I) ion forms chelates with the compositions TlZ^{3-} and $TlHZ^{2-}$. From the intercepts and slopes of the linear relation between the right hand side of Eq. (6) and the hydrogen ion concentration, K_{TlZ} and K^{H} values were determined and given in Table 2 together with k values used in the calculation of $(\alpha_{H})_{Z}$.

The finding that thallium(I) ion forms normal and protonated chelates with CyDTA is in contrast to the results of Anderegg and Bottari.5) They have studied the complexation reaction of thallium(I) with CyDTA employing a pH titration method and concluded that thallium(I) ion forms only a normal chelate with a 1-to-1 composition ($\log K_{TlZ}=6.7$, $\mu=0.10$); no detailed experimental results were given, and thus, no satisfactory explanation for this discrepancy can be given.