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D. C. and A. C. Polarographic Behavior of Thallium(I) Ions in Diethylenetriaminepentaacetate Solutions

Mutsuo KODAMA, Tomohiko NODA and Mitsuko MURATA

Department of Chemistry, Ibaraki University, Mito, Ibaraki

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The reduction reaction of Tl(I) ions in DTPA solutions was studied d.c.- and a.c.-polarographically, and the composition and the stability constants of normal and hydrogen chelates of Tl(I) ions with DTPA, TlZ^{4-}, and TlHZ^{3-} were determined. The reduction of Tl(I)-DTPA chelates at the DME proceeds reversibly in the polarographic sense according to this scheme:

$$\begin{array}{ccccccccc} \mathrm{TlZ}^{4-} & + & e^- & + & \mathrm{Hg} & \rightleftharpoons & \mathrm{Tl(Hg)} & + & \mathrm{Z}^{5-} \\ {\scriptstyle \mathrm{H}^+}\downharpoonleft\upharpoonright & & & & & & & & {\scriptstyle n\mathrm{H}^+}\downharpoonleft\upharpoonright \\ \mathrm{TlHZ}^{3-} & & & & & & & & \mathrm{H}_n\mathrm{Z}^{n-5} \end{array}$$

The stability constants of TlZ^{4-} and TlHZ^{3-} were found to be $10^{5.45}$ and $10^{4.24}$($\mu=0.40$). The determination of the a.c. summit-potentials, E_p, and the introduction of E_p into the Kolthoff and Lingane equation of polarographic waves of metal complexes were also discussed.

Trace quantities of surface-active substances can often exert a strong effect on the electrode process. In most cases, it has been shown that even minute amounts of surface-active substances present in the background solutions of analytical-grade-reagents are sufficient to change the measured rate of the electrode processes by a factor of 50 and to decrease the height of a. c. polarographic waves quite markedly.[1,2]

For this reason, an electrode reaction which proceeds reversibly in the d. c. polarographic sense cannot always be expected to be reversible under the influence of an alternating voltage.

Gupta and Chatterjee[3] have introduced a. c. polarographic summit-potentials in place of d. c. polarographic half-wave potentials into the Kolthoff-Lingane equation[4] for the reduction of a metal complex ion and have tried to determine the ligand number and the stability constants of the cadmium ammonia complex. However, the introduction they attempted can be safely undertaken only when the electrode reaction is reversible in both d. c. and a. c. polarography.

The theory of the a. c. polarography predicts that the plot of the d. c. potential, E, against log-$[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ will give a straight line with a $\pm 0.118/n$ V slope for reversible electrode processes. Consequently, the reversibility of the electrode process can be tested by this log-plot, and the summit-potential can be determined to be the potential where the two linear portions intersect; *i. e.*, the $\log[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ is equal to zero.

The a. c. polarographic behavior of a thallium(I) ion and its complexes has been known to be apparently reversible, and exceptionally unaffected by the addition of such surface-active substances as gelatin.[5] In view of the fact that the rate constant of the reduction reaction of thallium(I) is markedly decreased by the addition of a surface-active substance, this may indicate that, even in the presence of surface-active substances, the rate constant of the reduction process remains so large that the process behaves reversibly. At the dropping mercury electrode, thallium(I)-DTPA chelate ions also give a single well-defined reversible wave both d. c. and a. c. polarographically. In this study, the electrode reaction of thallium(I)-DTPA chelates was investigated by d. c. and a. c. polarographic methods, and the stability constant of thallium(I)-DTPA chelate and the protolytic stability constant of its hydrogen chelate, TlHZ^{3-}, were determined.

Experimental

Reagents. The standard solution of thallium(I) perchlorate was prepared by dissolving a known amount of pure thallium metal in a reagent-grade perchloric acid.

Commercial reagent-grade diethylenetriaminepentaacetic acid (DTPA) was recrystallized from an aqueous

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[1] B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience, New York (1963), p. 268.

[2] N. Tanaka, R. Tamamushi and M. Kodama, *Anal. Chim. Acta*, **20**, 573 (1959).

[3] S. L. Gupta and M. K. Chatterjee, *J. Electroanal. Chem.*, **8**, 245 (1964).

[4] I. M. Kolthoff and J. J. Lingane, "Polargoraphy," Vol. 1, Interscience, New York (1952).

[5] J. E. B. Randles, *Discussions Faraday Soc.*, **1**, 11 (1947).

solution by adding hydrochloric acid, and then dissolved into a sodium hydroxide solution. The concentration of a DTPA solution was standardized against pure metallic zinc.

Apparatus. All d.c. current-voltage curves were measured by using a manual polarograph similar to that of Kolthoff and Lingane[4] and were corrected for the residual current and the *i-R* drop. The a.c. polarograms were recorded with a Yanagimoto PA-102 pen-recording polarograph operated manually. The d.c. potentials applied were accurately determined by using a Shimadzu K-2 potentiometer.

The rate of the flow of mercury, m, and the drop time, t_d, of the dropping mercury electrode (DME) were 1.24_8 mg/sec and 6.30 sec respectively, as measured in an air-free 0.1 M acetate buffer solution of pH 4.80 with an open circuit and at 60 cm of a mercury column at 25°C. A saturate calomel electrode (SCE) with a large area was used as the reference electrode; it was connected to the cell solution through a Hume and Harris-type salt bridge.[6] In the a.c. polarographic measurements, a 200 μF condenser was used to minimize the effect of the cell resistance.[7] The pH value of the solution was measured with a glass electrode pH meter (Hitachi-Horiba Model M4).

The dissolved oxygen in the solution was removed by bubbling pure nitrogen gas through the solution, and all the measurements were conducted on solutions with a constant ionic strength of 0.4 ($NaClO_4$).

Results and Discussion

Reversibility of the Electrode Reaction of Thallium(I) - Diethylenetriaminepentaacetate at the DME. The electrode reaction of thallium(I) ions in solutions containing an excess of DTPA was studied over the pH range from 7.30 to 10.20. In the present study, no other buffer reagent was used because in the pH range studied the system containing an excess of DTPA is considered to have enough buffer capacity to maintain the pH value of the solution constant.

A Tl(I)-DTPA chelate gives a single well-defined d. c. polarogram (Fig. 1); its limiting current was found to be proportional to the square root of the effective pressure of mercury applied to the DME (Table 1) and to the concentration of thallium(I) ions (Fig. 2). The relation between $\log[i/(i_l-i)]$ and E, where i, i_l and E have their usual meanings, gave exclusively a straight line with a slope of 60 mV, corresponding to a one-electron reduction (Fig. 3).

In a. c. polarography, also, typical polarograms were obtained; their summit potentials coincided with the half-wave potential of the d. c. polarogram (Fig. 1). This may mean that the electrode reaction of a Tl(I)-DTPA chelate proceeds reversibly in the a. c. polarographic sense. This conclusion can also be confirmed by the facts that the peak

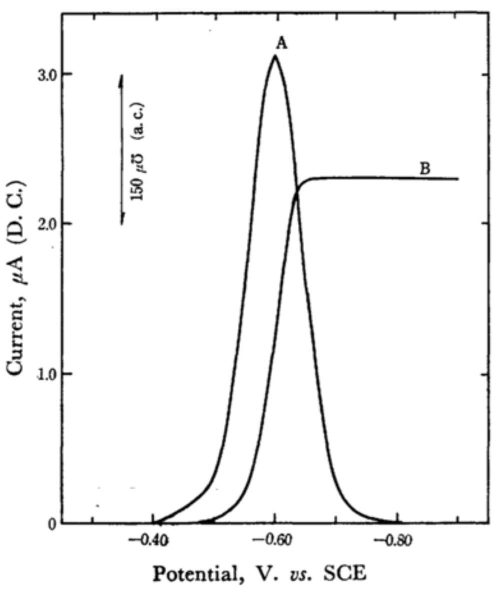

Fig. 1. Polarograms of Tl(I)-DTPA chelate.
pH=8.8, μ=0.40, C_{Tl^+}=1.09 mM
C_{DTPA}=25.0 mM
A: D. c. polarogram, B: A. c. polarogram,
senstivity=6.0 μ℧/mm

TABLE 1. THE RELATION BETWEEN THE LIMITING CURRENT, i_l, AND THE EFFECTIVE PRESSURE, h_c, ON THE DME
pH=9.88, C_{DTPA}=40 mM, C_{Tl^+}=1.09 mM

h_0, cm	$h_c^{1/2}$	i_l, μA	$i_l/h_c^{1/2}$
50	6.97	2.04_0	0.293
60	7.66	2.24_1	0.293
70	8.28	2.45_0	0.296
80	8.86	2.65_5	0.299

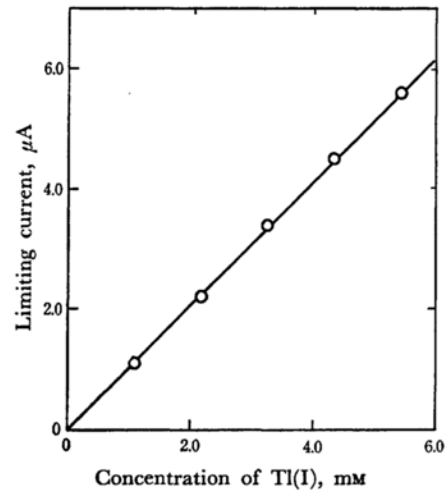

Fig. 2. The relation between the concentration of thallium ion and the limiting current.
pH=9.90, μ=0.40, C_{DTPA}=40.0 mM

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[6] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Analyt. Ed.*, **15**, 465 (1943).

[7] B. Breyer, F. Gutamann and S. Hacobian, *Australian J. Sci. Res., Ser. A*, **4**, 595 (1951).

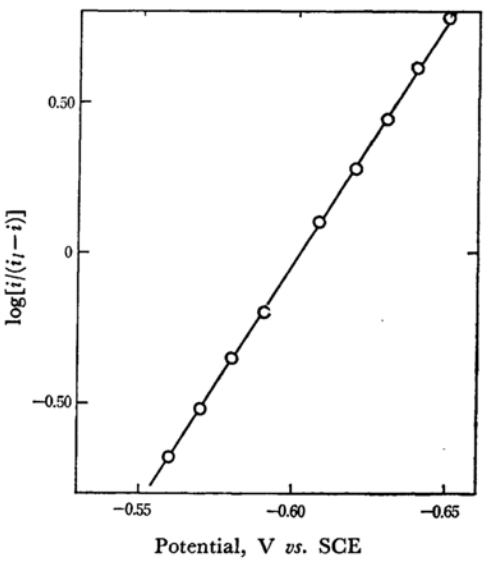

Fig. 3. The d. c. log-plot analysis of the cathodic wave of Tl(I)-DTPA chelate.
pH=8.80, $\mu=0.40$, $C_{\mathrm{Tl}^+}=1.09$ mM
$C_{\mathrm{DTPA}}=25.0$ mM

height of the a. c. polarogram is exactly proportional to the concentration of the Tl(I)-DTPA chelate that the ratio of the peak height of a Tl(I)-DTPA chelate to that of a Tl(I) ion is nearly equal to the ratio of their limiting currents.

To be more exact, the reversibility of the electrode reaction at the electrode, which is polarized under the influence of an a. c. voltage of a small amplitude, should be tested by the a. c. log-plot method, *i. e.*, the plot of $\log[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ against E, where I_p and I are the peak height and the height of a. c. polarogram at a given value of E, respectively.

The well-known relation (2) of the a. c. polarographic current derived for the following electrode reaction[8,9];

$$\mathrm{O} + ne^- = \mathrm{R} \tag{1}$$

holds only when the reaction (1) proceeds reversibly in the polarographic sense:

$$I = (n^2\boldsymbol{F}^2\cdot A/4\boldsymbol{RT})\cdot D_0{}^{1/2}\cdot\omega^{1/2}\cdot C_0\cdot\Delta E \times \mathrm{sech}^2[(n\boldsymbol{F}/2\boldsymbol{RT})(E - E_{1/2})]\cdot\sin(\omega t + \pi/4) \tag{2}$$

The notation definitions are as follows:

n=number of electrons involved in the electrode reaction
$\boldsymbol{F}$=Faraday's constant, A=electrode area
$\boldsymbol{R}$=ideal gas constant,
T=absolute temperature
D_0=diffusion coefficient of the species 0
C_0=bulk concentration of the species 0,
ω=frequency,
ΔE=amplitude of the applied alternating potential,
$E_{1/2}$=reversible polarographic half-wave potential for the electrode reaction (1)

Similarly, in the reduction of a metal complex,

$$\mathrm{MX}_m{}^{n-mb} + ne^- + \mathrm{Hg} = \mathrm{M(Hg)} + m\mathrm{X}^{b-} \tag{3}$$

when the boundary condition (4), which shows conclusively that the electrode reaction (3) is reversible, is satisfied by the system under the a. c. polarographic conditions, the relation (5) can be obtained by the mathematical treatment employed by Matsuda,[8] Delmastro and Smith,[9] and Underkofler and Shain[10] to derive the relation (2):

$$(C_{\mathrm{MX}_m}/C_{\mathrm{M(Hg)}})_{x=0} = \Theta\cdot\exp[-\nu\sin\omega t] \tag{4}$$

where $\theta = \exp[n\boldsymbol{F}/\boldsymbol{R}T(E-(E_{1/2})_c)]$,

$\nu = n\boldsymbol{F}\cdot\Delta E/\boldsymbol{R}T,$

$$(E_{1/2})_c = E^\circ{}_{\mathrm{M(Hg)}} + \boldsymbol{R}T/n\boldsymbol{F}[\ln k_{\mathrm{M(Hg)}}\cdot f_c/k_c - \ln K_c - m\cdot\ln C_x\cdot f_x]^{4)},$$

E=d. c. potential applied,
$E^\circ{}_{\mathrm{M(Hg)}}$=standard potential,
k's=diffusion current constants,
f's=activity constants,
C_x=the concentration of X^{b-} at the electrode surface, and
$K_c=[\mathrm{MX}_m{}^{n-mb}]/[\mathrm{M}^{n+}]\cdot[\mathrm{X}^{b-}]^m$.

$$I = (n^2\boldsymbol{F}^2\cdot A/4\boldsymbol{RT})\cdot D^{1/2}{}_{\mathrm{MX}_m}\cdot\omega^{1/2}\cdot C_{\mathrm{MX}_m}\cdot\Delta E \times \mathrm{sech}^2[(n\boldsymbol{F}/2\boldsymbol{R}T)(E-(E_{1/2})_c)]\cdot\sin(wt+\pi/4) \tag{5}$$

By casting the relation (5) into logarithmic form and by rearranging the resulting equation, one can obtain the following equation at 25°C;

$$E = (E_{1/2})_c + 2\times 0.0591/n\log[(I_p/I)^{1/2}-(I_p-I/I)^{1/2}] \tag{6}$$

Here I_p represents the peak height of the a. c. polarogram of MX_m^{n-mb}.

This relation, (6), clearly indicates that the summit potential in a. c. polarography can be safely equated with the half-wave potential in d. c. polarography when the electrode reaction is reversible, even under a. c. polarographic conditions, that the plot of E against $\log[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ gives a straight line with a slop of ±0.118/nV, and that the summit potential can be determined as the potential where the $\log[(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ is zero.

A typical example of an a. c. log-plot is shown in Fig. 4. The slopes found were +134 mV and −132 mV respectively, and the summit potential determined by the method described above agreed well with the half-wave potential (Table 2). Considering the effects of spherical diffusion,[10] of

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[8] H. Matsuda, *Z. Elektrochem.*, **61**, 489 (1957).

[9] J. R. Delmastro and D. E. Smith, *Anal. Chem.*, **38**, 169 (1966).

[10] W. L. Underkofler and I. Shain, *Anal. Chem.*, **37**, 218 (1965).

TABLE 2. THE EFFECT OF pH ON THE HALF-WAVE POTENTIAL AND ON THE SUMMIT POTENTIAL

$C_{DTPA}=25.0$ mM, $C_{Tl^+}=1.09$ mM

pH	$E_{1/2}$ V *vs.* SCE	E_p V *vs.* SCE
7.30	-0.521_0	-0.523_1
7.60	-0.536_0	-0.539_0
8.27	-0.576_5	-0.577_0
8.80	-0.602_0	-0.598_0
9.18	-0.616_1	-0.613_0
9.80	-0.617_2	-0.619_0

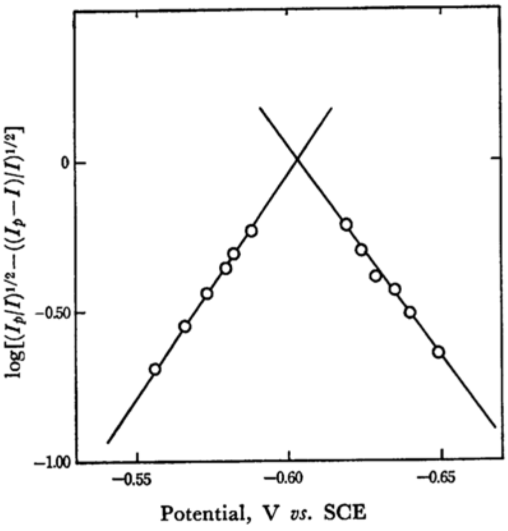

Fig. 4. The a. c. log-plot analysis of the cathodic wave of Tl(I)-DTPA chelate.
pH=8.80, $\mu=0.40$, $C_{Tl^+}=1.09$ mM
$C_{DTPA}=25.0$ mM

TABLE 3.

a) The relation between the concentration of Tl(I) ion and the half-wave potential or the summit potential (E_p).

$C_{DTPA}=40$ mM, pH=10.00

C_{Tl^+} mM	$E_{1/2}$ V *vs.* SCE	E_p V *vs.* SCE
1.09	-0.635_0	-0.638_0
2.18	-0.634_0	-0.640_0

b) The effect of the concentration of DTPA on $E_{1/2}$ or E_p.

$C_{Tl^+}=1.09$ mM, pH=9.20

C_{DTPA} mM	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$ mV	E_p V *vs.* SCE	ΔE_p mV	$\Delta E_{calcd.}$ mV
15	-0.598	0	-0.593	0	0
25	-0.617	16	-0.613	20	15
40	-0.633	35	-0.624	31	33

the charging current[10] and of the incomplete compensation for the ohmic resistance of the cell circuit,[11] the above facts may be taken as conclusively indicating the reversible process.

The Mechanism of the Electrode Reduction of Tl(I)-DTPA Chelate at the DME. In view of the experimental facts that the half-wave potential or the summit potential is independent of the concentration of Tl(I) ions added (Tables 3a, 3b), but shifts with a change in the concentration of DTPA, C_{DTPA}, according to the relation;

$$\Delta E_{1/2}/\Delta \log C_{DTPA}$$
$$\text{or}\quad \Delta E_s/\Delta \log C_{DTPA} = -0.0591\text{ V}$$

the following mechanism can be assumed for the reduction of the Tl(I)-DTPA chelate when the presence of a hydrogen chelate of Tl(I)-DTPA is taken into consideration, as in the case of other metal chelates of DTPA:[12]

$$\begin{array}{lcl} \mathrm{TlZ^{4-}} & + \mathrm{e^-} + \mathrm{Hg} = \mathrm{Tl(Hg)} + & \mathrm{Z^{5-}} \\ \downarrow\uparrow \mathrm{H^+} & & n\mathrm{H^+}\downarrow\uparrow \\ \mathrm{TlHZ^{3-}} & & \mathrm{H}_n\cdot\mathrm{Z}^{n-5} \end{array} \qquad (7)$$

where Z^{5-} refers to the completely-dissociated DTPA.

Assuming that $a_{Hg}=1$ and $f_{Tl(Hg)}=1$, the relation (8) can be derived for the mechanism (7):

$$(E_{1/2})_{TlZ} = E^\circ_{Tl(Hg)} + 0.0591\left[\log\frac{f_{Tl^+}\cdot k_{Tl(Hg)}}{k_{TlZ}} - \log C_{DTPA} + \log\frac{\alpha_H}{K_{TlZ}\cdot(1+K^H_{TlHZ}[H^+])}\right] \quad (8)$$

where $K_{TlZ} = [TlZ^{4-}]/[Tl^+]\cdot[Z^{5-}]$,

$K^H_{TlZ} = [TlHZ^{3-}]/[TlZ^{4-}]\cdot[H^+]$,

and $\alpha_H = [H^+]/k_5 + [H^+]^2/k_4\cdot k_5 + \cdots + [H^+]^5/k_1\cdot k_2\cdot k_3\cdot k_4\cdot k_5$.

Remembering the relation theoretically predicted for the half-wave potential of the reduction of a Tl(I) ion at the DME,[4,13] the shift of the half-wave potential of a Tl(I) ion, $\Delta E_{1/2}$, by the chelate formation with DTPA can be derived as:

$$\Delta E_{1/2} = 0.0591\left[\log\frac{k_{TlZ}}{k_{Tl^+}} + \log C_{DTPA} + \log\frac{K_{TlZ}(1+K^H_{TlHZ}[H^+])}{\alpha_H}\right] \quad (9)$$

From the above theoretical consideration, it can be concluded that, for the reaction mechanism (7), the plot of antilog$[\Delta E_{1/2}/0.0591+\log\alpha_H+\log k_{Tl^+}/k_{TlZ}-\log C_{DTPA}]$ against $[H^+]$ can give a linear relation with a slope of $K^H_{TlHZ}\cdot K_{TlZ}$, and that the antilog value at $[H^+]=0$ corresponds to K_{TlZ}. Here, the shift of the summit-potential, ΔE_p,

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[11] E. R. Brown, T. G. McCord, D. E. Smith and D. D. Deford, *Anal. Chem.*, **38**, 1119 (1966).

[12] M. Kodama and A. Kimura, This Bulletin **40**, 1639 (1967).

[13] M. Kodama, S. Naito and M. Ebine, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 576 (1963).

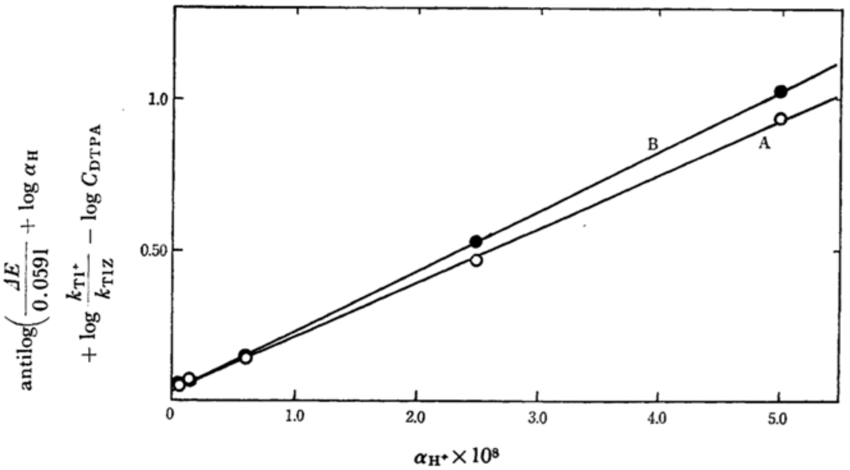

Fig. 5. The plot of antilog $[\Delta E/0.0591 + \log \alpha_H + \log k_{Tl^+}/k_{TlZ} - \log C_{DTPA}]$ against $[H^+]$.
$\mu = 0.40$, $C_{Tl^+} = 1.09$ mM, $C_{DTPA} = 25.0$ mM
A: d. c., B: a. c.

by the chelate formation can be used in place of $\Delta E_{1/2}$.

The theoretical conclusion thus obtained was tested by using some of the typical data. The results are shown in Fig. 5. From the tangents of the linear relations and the antilog value at $[H^+] = 0$ in Fig. 5, the K_{TlZ} and K^H_{TlHZ} values were determined; they are listed in Table 4, together with dissociation constants and diffusion current constants used in the calculations. The dissociation constants listed were calculated by using the value reported by Vandegaer *et al.*[14]; calculation was done in a manner similar to that described previously.[12]

It is very interesting that the K^H_{TlHZ} value found is much greater than the K_{TlZ} value, making a marked contrast with that of the DTPA chelates of divalent or tervalent metal ions.

The complex formation reaction has been known to provide many useful polarographic methods for the analysis of metal ions. For instance, in a mixture of lead(II) and thallium(I) ions not containing a complex-forming reagent, it is very difficult to determine simultaneously those metal ions by the polarographic method, because the two metal ions are reduced at potentials so close togehter. However, in the solution containing a chelating reagent such as EDTA, the reduction wave of the lead(II) ion shifts to the negative potential, and so the resolutive determination of lead(II) and thallium(I) can be effected successfully. The resolution of the polarographic waves has generally been treated in an experimental manner, and few theoretical and quantitative discussions on it have appeared. In a. c. polarography, it has been reported[15] that, when the difference in the summit potential, ΔE_p, of a. c. polarograms is greater than 40 mV, the peak height of each polarogram can be determined accurately. However, this conclusion is somewhat experimental. From the foregoing discussion, it is very clear that the magnitude of the resolution of a. c. polarograms can be estimated quantitatively with the aid of Eq. (6). In the most favorable cases, a ΔE_p value greater than 117/n mV is theoretically required to determine the a. c. peak height within a 3.0% limit of error.

TABLE 4

i) Dissociation constant of DTPA[13] (mixed constants, $\mu = 0.40$)
$pK_1 = 1.75$, $pK_2 = 2.43$, $pK_3 = 4.20$, $pK_4 = 8.45$, $pK_5 = 10.02$

ii) Formation constants of chelates* ($\mu = 0.40$)

	D. C.	A. C.
K_{TlZ}	$10^{5.45}$	$10^{5.53}$
$K\mathrm{K}^{H}_{TlHZ}$** $\left(= \frac{[TlHZ^{3-}]}{[TlZ^{4-}][H^+]}\right)$	$10^{8.81}$	$10^{8.78}$

iii) Diffusion current constants, k's
$k_{Tl^+} = 4.44$ (μA/mM)
$k_{TlZ} = 2.12$ (μA/mM) at pH 9.90

iv) The ratio of peak height between Tl(I) ion and Tl(I)-DTPA chelate.

$$\text{Ratio} = \frac{(I_p)_{Tl^+}}{(I_p)_{TlZ}} = 2.39$$

* Obtained by the present authors
** Mixed constant

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[14] J. Vandegaer, S. Chaberek and A. E. Frost, *J. Inorg. Nucl. Chem.*, **11**, 210 (1959).

[15] T. Fujinaga and M. Maruyama, "Polarography," Vol. 1, Nankodo, Tokyo (1962), p. 97.