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Polarographic Behavior of Diethylenetriaminepentaacetic Acid at the Dropping Mercury Electrode

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Anodic waves of DTPA at DME in the presence and in the absence of calcium(II) and magnesium(II) ions were studied systematically, and the stability constants of mercury(II)-DTPA chelates were determined. The electrode reaction for the anodic waves of DTPA proceeds reversibly in a polarographic sense. In the presence of magnesium(II) ions, however, DTPA gives an irreversible wave. This may be ascribed to the slow reaction of the magnesium(II)-DTPA chelate. The use of DTPA as a titrant in the amperometric titration of metal ions which do not yield a polarographic wave under the usual polarographic conditions was also discussed briefly.

Many works on the chelate formation reaction of diethylenetriaminepentaacetic acid (DTPA) with mercury(II) ions have been published.[1-3] In an acid medium, DTPA forms 1-to-1 normal and hydrogen chelates with mercury(II) which are considerably more stable than the corresponding mercury(II)-EDTA chelates. This can be attributed to the increased number of donor atoms present and to the more basic character of DTPA.[2]

As in the case of EDTA,[4] DTPA gives rise a single well-defined anodic wave at the dropping mercury electrode (DME). The present work was undertaken in an attempt to obtain insight concerning the electrode reaction mechanism of DTPA anodic waves in the presence and in the absence of calcium(II) and magnesium(II) ions, and to study the complexation reaction of DTPA with mercury(II) by the polarographic method.

The use of DTPA as a titrant in the amperometric determination of calcium(II) and lanthanum(III), which do not yield a reduction wave under the usual polarographic conditions, was also examined.

Experimental

All polarographic studies were carried out in an acetate buffer with an ionic strength of 0.30 at 25°C. The ionic strength of the solution was adjusted by adding appropriate amounts of sodium perchlorate. The oxygen dissolved in the sample solution was removed by bubbling pure nitrogen gas through the solution.

The d.c. current-voltage curves were measured by a manual polarograph similar to that of Kolthoff and Lingane.[5] The a.c. and d.c. polarograms were recorded automatically by a Yanagimoto Galvarecorder GA-103. The d.c. polarographic data given in this paper were corrected for the residual current and the ohmic drop of the cell circuit.

For all the measurements we used a dropping mercury electrode with an m value of 1.24_0 mg/sec and a drop time t_d of 4.80 sec at a mercury height of 60 cm in an air-free 0.10 M acetate buffer solution ($\mu=0.30$) of pH 4.80 at -0.60 V *vs.* SCE. A saturated calomel electrode with a large surface area was used as the reference electrode. When the a.c. polarograms were recorded, a platinum wire electrode with a large surface area was inserted into the electrolytic solution as a third electrode. It was terminated at SCE through a 200 μF capacitor in order to minimize the impedance of the cell.[6]

DTPA of analytical reagent grade was recrystallized from an aqueous solution by adding an excess amount of hydrochloric acid, and dissolved into the redistilled water by neutralizing it with a suitable amount of sodium hydroxide. The concentration of the DTPA solution was checked by Mg titration, using Eriochrom Black T as an indicator. Calcium(II) and magnesium(II) perchlorate solutions were prepared by dissolving pure calcium and magnesium carbonates into a perchloric acid solution. Their concentrations were standardized against the standard EDTA solution.[7]

All the other chemicals were of analytical reagent grade and were used without further purification.

Results and Discussion

Polarographic Behavior of DTPA in the Absence of Metal Ions. As is shown in Fig. 1, DTPA in an acetate buffer solution gives a single well-defined anodic wave at DME. The limiting current was found to be proportional to the bulk concentra-

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[1] G. Anderegg, P. Nageli, F. Muller and G. Schwarzenbach, *Helv. Chim. Acta*, **42**, 827 (1959).

[2] J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).

[3] T. Moeller and L. C. Thomson, *J. Inorg. Nucl. Chem.*, **24**, 499 (1962).

[4] C. N. Reilley, W. G. Scribner and C. Temple, *Anal. Chem.*, **28**, 450 (1956).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience, New York (1952), p. 297.

[6] B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research. Ser. A*, **4**, 595 (1951).

[7] W. Biedermann and G. Schwarzenbach, *Chimia*, **2**, 56 (1948).

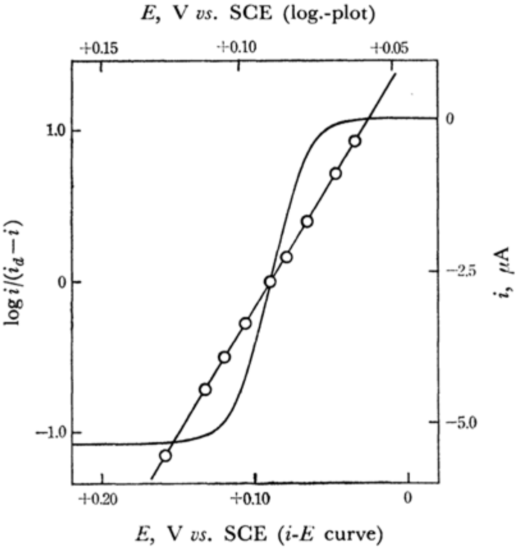

Fig. 1. D.C. polarogram of DTPA.
pH=4.80, $\mu=0.30$, $[\mathrm{Ac}]_t=0.10$ M
Concentration of DTPA=1.00 mM

Table 1. The relation between limiting current and the concentration of DTPA
pH=4.80, $\mu=0.30$, $[\mathrm{Ac}]_t=0.10$ M
at +0.25 V *vs.* SCE

Concn. of DTPA, C mM	Limiting current, i_d μA	i_d/C
1.00	5.28_0	5.28
1.25	6.56_1	5,25
2.50	13.19_0	5.28
5.00	26.28_9	5.26

Table 2. Limiting current and the effective pressure on DME
pH=4.80, $\mu=0.30$, $[\mathrm{Ac}]_t=0.10$ M
at +0.25 V *vs.* SCE
Concentration of DTPA=1.00 mM

Effective pressure, H_e cm	Limiting current, i_d μA	$i_d/H_e^{1/2}$
58.24	5.28_0	0.691
68.24	5.66_7	0.691
78.24	6.08_6	0.692
88.24	6.42_7	0.691

tion of DTPA, and also to the square-root of the effective pressure on the DME (Tables 1 and 2).

A plot of $\log i/(i_d-i)$ against the potential, E, gives a straight line with a slope of 30 mV over the entire range of pH values studied (Table 3). The half-wave potential of the anodic wave is independent of the bulk concentration of DTPA, provided that the pH of the solution is kept constant (Table 3).

Table 3. The half-wave potentials and pH
$\mu=0.30$, $[\mathrm{Ac}]_t=0.10$ M
Concentration of DTPA=1.00 mM

pH	Half-wave potential ($E_{1/2}$), V *vs.* SCE	$\frac{\Delta E}{\Delta \log i/(i_d-i)}$ mV	K_0 calcd. by means of (2) $\times 10^{-25}$
3.68	+0.163	30	13.80
3.70	+0.163	30	12.00
3.81	+0.158	31	9.33
4.00	+0.144	31	7.94
4.11	+0.135	30	7.76
4.80	+0.091	30	5.62
4.80*	+0.089	30	—
4.90	+0.086	30	4.27
5.45	+0.052	31	4.47

* Concentration of DTPA=2.00 mM

These facts may imply that the electrode reaction of DTPA in an acetate buffer solution proceeds reversibly in a usual polarographic sense, corresponding to a two-electron oxidation, and that DTPA forms exclusively a 1-to-1 chelate with mercury(II) at the electrode surface.

The reversibility of the electrode reaction was also checked a.c.-polarographically. Typical a.c. polarograms, the summit potential of which is nearly equal to the half-wave potential of the d.c. polarographic wave and the height of which can be compared to that of the cathodic wave of the Cu(II)-NTA chelate,[8] could be obtained (Fig. 2).

The effect of the concentration of the buffer re-

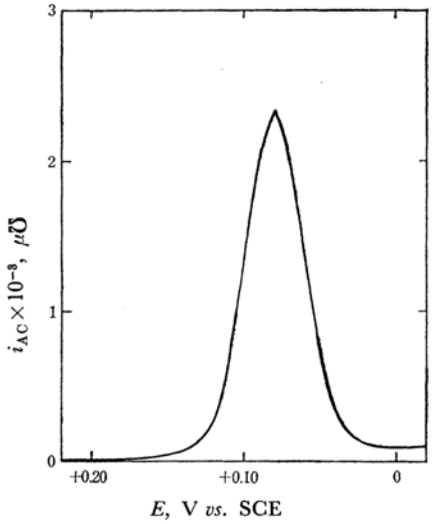

Fig. 2. A.C. polarogram of DTPA.
pH=4.80, $\mu=0.30$, $[\mathrm{Ac}]_t=0.10$ M
Concentration of DTPA=1.00 mM

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[8] M. Kodama and N. Abe, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **83**, 697 (1962).

TABLE 4. THE EFFECT OF THE CONCENTRATION OF BUFFER REAGENT ON THE HALF-WAVE POTENTIAL
$\mu=0.30$, Concentration of DTPA=1.00 mM

pH	Total concn. of acetate, M	Half-wave potential ($E_{1/2}$), V *vs.* SCE
3.70	0.10	+0.163
	0.50	+0.162
4.80	0.10	+0.091
	0.50	+0.092
5.45*	0.10	+0.052
	0.50	+0.050

* $\mu=0.50$

agent on the half-wave potential was also examined. As Table 4 shows, the half-wave potential was found to be independent of the concentration of acetate ions under the experimental conditions employed. This may mean that the mixed complex, HgZ-$(\mathrm{Ac})_n{}^{(3+n)-}$, is not involved in the electrode reaction. Therefore, remembering that the mercuric ion forms normal and hydrogen complexes with DTPA under the present pH conditions, one can safely assume the following electrode reaction for the anodic wave of DTPA:

$$\mathrm{Hg} + \mathrm{H}_n\mathrm{Z}^{n-5} = \underset{\substack{\| \\ \mathrm{HgHZ}^{2-}}}{\mathrm{HgZ}^{3-}} + n\mathrm{H}^+ + 2\mathrm{e}^- \quad (1)$$

The half-wave potential then become:

$$(E_{1/2})_z = E^0_{\mathrm{Hg}} - 0.0296[\log f_{\mathrm{Hg}^{2+}} + \log K_0 - \log \alpha_{\mathrm{H}}] \quad (2)$$

assuming that the diffusion coefficients of mercury(II)-DTPA chelates and of the various forms of DTPA ($\mathrm{H_5Z}$, $\mathrm{H_4Z^-}$, $\mathrm{H_3Z^{2-}}$, $\mathrm{H_2A^{3-}}$, $\mathrm{HZ^{4-}}$ and $\mathrm{Z^{5-}}$) are equal to one another.

Here, α_{H} is $1 + [\mathrm{H}^+]/k_5 + [\mathrm{H}^+]^2/k_4 \cdot k_5 + \dots + [\mathrm{H}^+]^5/k_1 \cdot k_2 \cdot k_3 \cdot k_4 \cdot k_5$, k_1, k_2, k_3, k_4, and k_5 refer to the successive acidity constants of DTPA, and E^0_{Hg} is the ordinary standard potential.[9]

The K_0 term in Eq. (2) can be expressed as:

$$K_0 = \frac{[\mathrm{HgZ}^{3-}] + [\mathrm{HgHZ}^{2-}]}{[\mathrm{Hg}^{2+}] \cdot [\mathrm{Z}^{5-}]} = K_{\mathrm{HgZ}}(1 + K^{\mathrm{H}}_{\mathrm{HgZ}} \cdot [\mathrm{H}^+]) \quad (3)$$

where K_{HgZ} and $K^{\mathrm{H}}_{\mathrm{HgZ}}$ are given by the following:

$$K_{\mathrm{HgZ}} = \frac{[\mathrm{HgZ}^{3-}]}{[\mathrm{Hg}^{2+}] \cdot [\mathrm{Z}^{5-}]}, \quad K^{\mathrm{H}}_{\mathrm{HgZ}} = \frac{[\mathrm{HgHZ}^{2-}]}{[\mathrm{HgZ}^{3-}] \cdot [\mathrm{H}^+]}$$

The relation (3) indicates that the plot of K_0 values calculated with the aid of Eq. (2) by using the value of $(E_{1/2})_z$ experimentally obtained; the numerical values for the equilibrium constants of DTPA against $[\mathrm{H}^+]$ should give a straight line with a slope of $K_{\mathrm{HgZ}} \cdot K^{\mathrm{H}}_{\mathrm{HgZ}}$, and the K_0 value obtained when $[\mathrm{H}^+]$ is equal to zero must be K_{HgZ}.

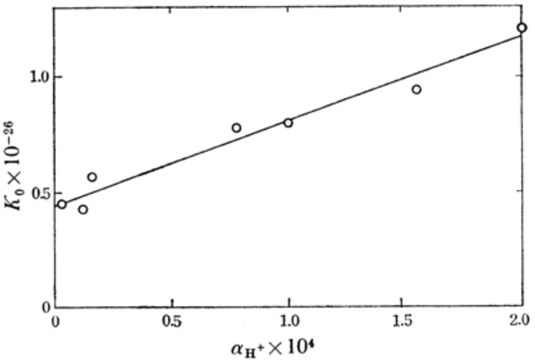

Fig. 3. The plot of K_0 against α_{H^+}.
$\mu=0.30$, $[\mathrm{Ac}]_t=0.10$ M
Concentration of DTPA=1.00 mM

This relation was examined in the light of the experimental data in Table 3. As is clear from Fig. 3, a linear relation was found between K_0 and $[\mathrm{H}^+]$. The values of $\log K_{\mathrm{HgZ}}$ and of $\log K^{\mathrm{H}}_{\mathrm{HgZ}}$ calculated from K_0 at $[\mathrm{H}^+]=0$ and the slope of the straight line in Fig. 3 were 25.63 and 3.93 respectively. By using these values and by considering the influence of the ionic strength, the $\log K_{\mathrm{HgZ}}$ and $\log K^{\mathrm{H}}_{\mathrm{HgZ}}$ values at an ionic strength of 0.10 were calculated to be 26.38 and 4.19 respectively; these values are in good agreement with those reported by Schwarzenbach *et al.*[1]

The numerical values of DTPA used for the calculations are given in Table 5. The values in Table 5 were calculated from the related dissociation constants and the formation constants in the solution with an ionic strength of 0.10 at 25°C,[10] while the activity coefficients of the ions were calculated by means of the well-known Davies equation.[11]

From the results of the theoretical analysis of the experimental data, it can be concluded that the electrode reaction for the anodic wave of DTPA

TABLE 5.

Dissociation constants of DTPA[10] (hybrid constants, $\mu=0.30$)

$\mathrm{p}K_1=1.75$, $\mathrm{p}K_2=2.45$, $\mathrm{p}K_3=4.23$, $\mathrm{p}K_4=8.50$
$\mathrm{p}K_5=10.02$

Formation constants of chelates[1] ($\mu=0.30$)

$K_{\mathrm{CaZ}}=10^{9.88}$, $K^{\mathrm{H}}_{\mathrm{CaZ}}=10^{5.77}$, $K_{\mathrm{Ca_2Z}}=10^{1.54}$
$K_{\mathrm{HgZ}}{}^*=10^{25.69}$, $K^{\mathrm{H}}_{\mathrm{HgZ}}{}^*=10^{3.94}$
$K_{\mathrm{HgZ}}{}^{**}=10^{25.95}$, $K^{\mathrm{H}}_{\mathrm{HgZ}}{}^{**}=10^{3.89}$

* Obtained by the present authors
** Reported by Schwarzenbach *et al.*[1]

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[9] W. M. Latimer, " Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J. (1959), p. 179.

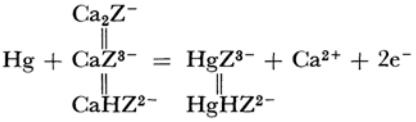
[10] S. Chaberek, A. E. Frost, M. A. Doran and N. J. Bicknell, *J. Inorg. Nucl. Chem.*, **11**, 184 (1959).

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

proceeds reversibly and by the mechanism represented by reaction (1).

Polarographic Behavior of DTPA in the Presence of Calcium(II) or Magnesium(II) Ions. Even when calcium(II) ions are present in a large excess over DTPA ions and when all the DTPA ions are considered to form stable chelates with calcium(II), the anodic reaction of DTPA at DME proceeds reversibly. This was confirmed by the facts that, even in the presence of an excess of calcium(II) ions, the plot of log $i/(i_d-i)$ against E gave a straight line with a slope of 30 mV and the limiting current is proportional to the square-root of the effective pressure on the DME. (The results are not shown here.)

Therefore, from thermodynamic considerations, in the presence of an excess of calcium(II) ions, the anodic reaction of DTPA should be expressed as:



$$\mathrm{Hg} + \begin{matrix}\mathrm{Ca_2Z^-}\\ \|\\ \mathrm{CaZ^{3-}}\\ \|\\ \mathrm{CaHZ^{2-}}\end{matrix} = \begin{matrix}\mathrm{HgZ^{3-}}\\ \|\\ \mathrm{HgHZ^{2-}}\end{matrix} + \mathrm{Ca^{2+}} + 2\mathrm{e^-} \qquad (4)$$

with a half-wave potential corresponding to:

$$\begin{aligned}(E_{1/2})_{\mathrm{CaZ}} = E^0_{\mathrm{Hg}} - 0.0296[&\log f_{\mathrm{Hg^{2+}}} - \log [\mathrm{Ca^{2+}}]\\ &-\log\{K_{\mathrm{CaZ}}(1+K^{\mathrm{H}}_{\mathrm{CaZ}}\cdot[\mathrm{H^+}]+K_{\mathrm{Ca_2Z}}\cdot[\mathrm{Ca^{2+}}])\}\\ &+\log\{K_{\mathrm{HgZ}}(1+K^{\mathrm{H}}_{\mathrm{HgZ}}\cdot[\mathrm{H^+}])\}] \qquad (5)\end{aligned}$$

assuming that the diffusion coefficients of calcium(II) and mercury(II) chelates of DTPA are equal.

$K_{\mathrm{Ca_2Z}}$ in Eq. (5) is given as:

$$K^{1)}_{\mathrm{Ca_2Z}} = \frac{[\mathrm{Ca_2Z^-}]}{[\mathrm{CaZ^{3-}}]\cdot[\mathrm{Ca^{2+}}]}$$

Hence, from Eqs. (2) and (5), it follows that the shift of the half-wave potential upon the addition of a large excess of calcium(II) ions should obey the following relation:

$$\begin{aligned}\Delta E_{1/2} &= (E_{1/2})_{\mathrm{CaZ}} - (E_{1/2})_{\mathrm{Z}}\\ &= 0.0296[\log [\mathrm{Ca^{2+}}] - \log \alpha_{\mathrm{H_2}}\\ &\quad +\log \{K_{\mathrm{CaZ}}(1+K^{\mathrm{H}}_{\mathrm{CaZ}}\cdot[\mathrm{H^+}]_1+K_{\mathrm{Ca_2Z}}\cdot[\mathrm{Ca^{2+}}])\}\\ &\quad +\log \{1+K^{\mathrm{H}}_{\mathrm{HgZ}}[\mathrm{H^+}]_2)/(1+K^{\mathrm{H}}_{\mathrm{HgZ}}[\mathrm{H^+}]_1)\}] \qquad (6)\end{aligned}$$

where $[\mathrm{H^+}]_1$ refers to the hydrogen concentration of a solution containing an excess of calcium(II) ions, and $[\mathrm{H^+}]_2$, to that of a solution not containing calcium(II) ions.

This relation was found satisfactory when examined with the experimental data. The $\Delta E_{1/2}$ values calculated by means of Eq. (6) are in very good agreement with those obtained experimentally. The numerical values used for the calculation are also listed in Table 5.

From the above theoretical analysis of the experimental data, it can be concluded that the anodic reaction of DTPA in the presence of an excess of calcium(II) ions is given by reaction (5).

TABLE 6. THE EFFECT OF CALCIUM(II) ION ON THE HALF-WAVE POTENTIAL OF DTPA ANODIC WAVE

Metal ion	pH	$(E_{1/2})$ V vs. SCE	$E_{1/2}$, mV	
			Obsd.	Calcd.
no	4.00	+0.144	−41	−37
0.1 M $\mathrm{Ca^{2+}}$	5.85	+0.103	0	0
no	4.90	+0.086	+17	+23
no	5.85	+0.019	+84	+82

$\mu=0.40$, $[\mathrm{Ac}]_t=0.10$ M
Concentration of DTPA = 1.00 mM

The influence of magnesium(II) ions on the anodic waves of DTPA at DME was also studied. The elongated shape of the wave (not shown here) and the results of a log-plot examination, *i.e.* an examination of a plot of log $i/(i_d-i)$ against E (Fig. 3), clearly indicates that the electrode reaction of the anodic wave of DTPA is quasi-irreversible under the pH conditions where the DTPA in the solution is considered to form chelates with magnesium-ions. This may be ascribed to the slow reaction of the magnesium(II) chelates of DTPA. Study of the influence of magnesium(II) ions on the anodic wave of DTPA is now in progress.

Amperometric Titration of Calcium(II) and Lanthanum(III) with DTPA. Calcium(II) ions in an alkaline medium have been reported to be titrated amperometrically with EDTA[4)] by measuring the height of the anodic wave of EDTA after the end point. Considering the magnitude of the $\log K_{\mathrm{MZ}}$ values of mercury(II)- and calcium(II)-DTPA chelates and the reversible polarographic behavior of DTPA in the presence and in the absence of calcium(II) ions, DTPA may also be expected to be a good titrant for the amperometric determination of calcium(II).

Provided that the chemical and electron transfer reactions at the electrode surface proceed at a rate much greater than the rate of the diffusion of chelon and its metal chelates to the electrode surface, for the successful amperometric determination of electroinactive metal ions by measuring the height of the anodic wave of free chelon after the end point, the following conditions should be established:

Under the pH conditions where the metal ion to be determined forms stable chelates with chelon:

i) the difference in half-wave potentials with and without the metal ion, *i.e.*, the difference in the $(E_{1/2})$'s of the anodic waves before and after the end point, is sufficiently great and the potential suitable for the accurate measurement of the height of the anodic wave of the free chelon after the end point can be selected successfully.

ii) the conditional formation constant for the chelate of mercury(II) must be sufficiently great, and the half-wave potential of the free chelon occurs at potentials more negative than the decomposition

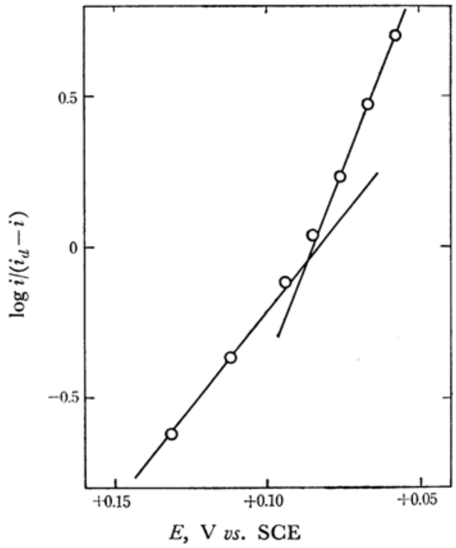


Fig. 4. The log-plot analysis of the anodic wave of DTPA in the presence of 0.10 M magnesium(II). pH=6.00, μ=0.30, $[\mathrm{Ac}]_t$=0.10 M Concentration of DTPA=1.00 mM

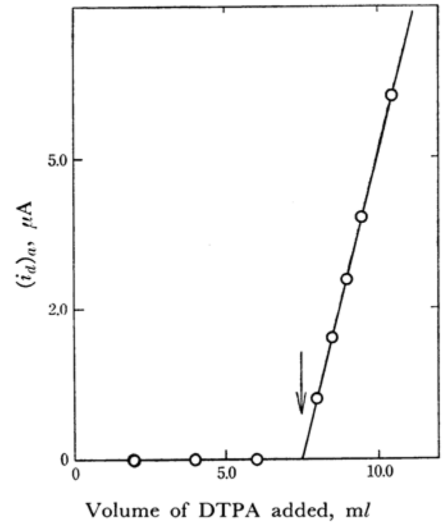


Fig. 5. Amperometric titration curve of 75.0 m*l* of 2.00 mM calcium(II) with 20.0 mM DTPA. pH=10.5 (ammonia buffer), at −0.05 V *vs.* SCE Equivalence point indicated by arrow.

potential of the background electrolyte.

From the forgoing theoretical consideration of the polarographic behavior of DTPA, these requirements may be expected to be fulfilled satisfactorily by the DTPA-calcium(II) system. The titration curve in Fig. 4 is a demonstrative example. The half-wave potential of the DTPA wave in an acetate buffer of pH 4.00 containing 1.00 mM lanthanum(III) is expected to occur at about +0.30 V *vs.* SCE from the theoretical observations based on the relation (5). Therefore, the lanthanum(III) in the solution with a pH of 4.00 can be expected to be titrated amperometrically with DTPA, as in the case of calcium(II). The titration curves obtained at pH 4.00 are shown in Fig. 5.

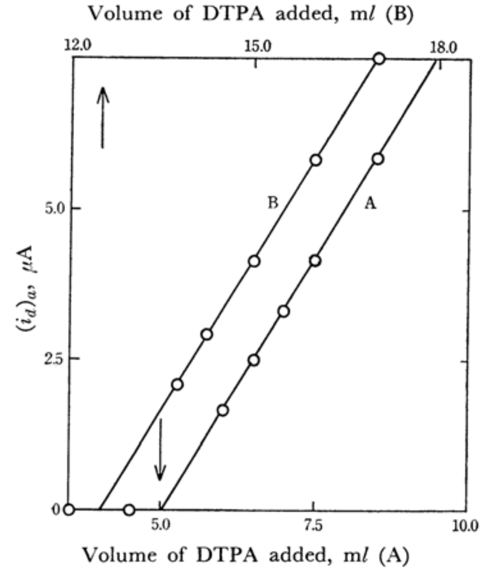


Fig. 6. Amperometric titration curves of 75.0 m*l* of lanthanum(III) with 20.0 mM DTPA. pH=4.00, μ=0.30, $[\mathrm{Ac}]_t$=0.10 M at +0.25 V *vs.* SCE
A) 1.60 mM lanthanum(III)
B) 4.00 mM lanthanum(III)
Equivalence points indicated by arrows.

Finally, it can also be pointed out that the use of DTPA as a titrant in the amperometric titration based on the appearance of an anodic wave has an advantage over that of EDTA when the sample solution contains substances such as halide ions which would interfere with the chelon anodic wave.

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