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A.C. Polarographic Determination of Lanthanum(III), Nickel(II), Calcium(II), and Magnesium(II) by Using Diethylenetriaminepentaacetic Acid as a Titrant

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The a.c. polarographic determination of lanthanum(III), nickel(II), calcium(II), and magnesium(II) with diethylenetriaminepentaacetic acid was studied by using a dropping mercury electrode and a hanging mercury drop electrode as indicator electrodes. Lanthanum(III) and nickel(II) in an acetate buffer solution and calcium(II) and magnesium(II) in an ammonia buffer solution could be titrated with diethylenetriaminepentaacetic acid in the concentration range from 5×10^{-5} to 1×10^{-3} M by measuring the height of the a.c. polarographic wave of diethylenetriaminepentaacetic acid after the end point. The effect of the presence of calcium(II) ions on the a.c. polarographic determination of lanthanum(III) in an acetate buffer solution of pH 4.0 was also examined and discussed thermodynamically.

As has been reported previously,[1] diethylenetriaminepentaacetic acid (DTPA) gives a single well-defined anodic wave at a dropping mercury electrode (DME) and can be used as a titrant in the amperometric determination of electro-inactive

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

metal ions.[*1] DTPA also shows a well-defined a. c. polarographic wave, the peak-height of which is exactly proportional to the concentration of DTPA. Therefore, electro-inactive metal ions can also be determined successfully by measuring the a. c. peak-height of uncomplexed DTPA.

In this paper, the use of DTPA as a titrant in the a. c. polarographic determination of lanthanum(III), nickel(II), calcium(II), and magnesium(II) was studied by using a DME and a hanging mercury drop electrode (HMDE) as indicator electrodes. In the a. c. polarographic analysis, especially when a stationary electrode is employed, unfavorable interference caused by the contamination by surface-active substances is frequently observed. However, as the a. c. polarographic wave of DTPA occurs at potentials sufficiently positive with respect to the electrocapillary maximum (ECM), the present method, based on the measurement of the a. c. peak-height of DTPA, is free from the effect of contamination with uncharged or positively charged surface-active substances. In this connection, the effect of camphor on the a. c. polarographic determination of lanthanum(III) was also examined.

Experimental

Reagent. The standard solution of nickel(II) perchlorate was prepared by a procedure described previously.[2] Calcium(II) and magnesium(II) perchlorate solutions were prepared by dissolving pure calcium and magnesium carbonates into a dilute perchloric acid solution. Their concentrations were then standardized against the standard EDTA solution.[3] The standard solution of lanthanum(III) nitrate was prepared by dissolving a known amount of 99.9% lanthanum oxide in a reagent-grade nitric acid. The preparation and the standardization of diethylenetriaminepentaacetic acid (DTPA) solution have also been described in the previous paper.[1] All the other chemicals were of an analytical reagent grade and were used without further purification.

Apparatus and Procedure. The a. c. polarograms were recorded manually or automatically with a Yanagimoto PA-102 pen-recording polarograph. In the a. c. polarographic measurements, a 200-μF condenser was used to minimize the effect of the cell resistance.[4] For the accurate measurement of d. c. potential, a Shimadzu K-2-type potentiometer was used.

A dropping mercury electrode (DME) 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 0.1 M acetate buffer solution of pH 4.80 at -0.60 V *vs.* SCE was used.

The hanging mercury drop electrode (HMDE) was prepared by the method proposed by Ross, Demars, and Shain.[5] In the preparation of the HMDE, two drops of mercury from the DME were used.

The oxygen dissolved in the solution was removed by bubbling pure nitrogen gas through the solution; measurements were conducted on solutions with a constant ionic strength of 0.50 (Na_2SO_4).

Results and Discussion

A. C. Polarographic Behavior of DTPA in the Absence of Metal Ions. As is shown by the curves in Fig. 1, DTPA in an acetate buffer solution gave a single, well-defined a. c. polarographic wave at both the DME and the HMDE corresponding to the following anodic reaction:[1]

$$\begin{array}{c} \mathrm{Hg} + \mathrm{H}_n\mathrm{Z}^{n-5} \rightleftharpoons \mathrm{HgZ}^{3-} + n\mathrm{H}^+ + 2\mathrm{e}^- \\ \qquad\qquad \upharpoonleft\!\downharpoonright \mathrm{H}^+ \\ \qquad\qquad \mathrm{HgHZ}^{2-} \end{array} \tag{1}$$

where HgZ^{3-} and $HgHZ^{2-}$ refer to normal and mono-protonated mercury(II)-DTPA chelates respectively, and where H_nZ^{n-5} indicates the incompletely-dissociated DTPA anion.

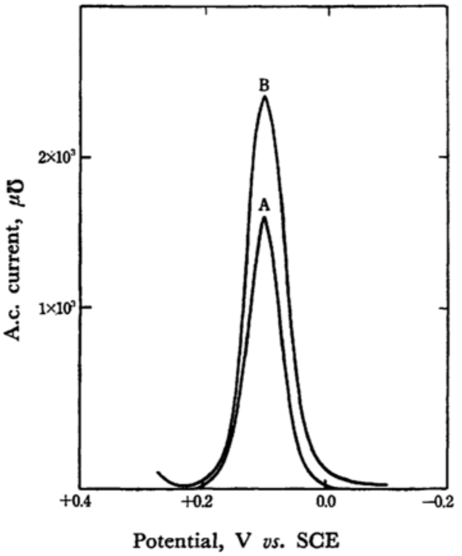

Fig. 1. A.c. polarograms of DTPA.
Concentration of DTPA = 1.0 mM, $\mu = 0.50$
pH = 4.0 (Acetate buffer, 0.10 M)
A: DME B: HMDE

A plot of $\log [(I_p/I)^{1/2} - ((I_p - I)/I)^{1/2}]$ against the d. c. potential, E,[6] gave a straight line with a slope of ±85 mV. Here, I_p and I indicate the a. c. peak-height and the height of the a. c. polarogram at E respectively. Some typical examples

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[*1] Here, "electro-inactive metal ion" means a metal ion which does not give a polarographic wave under the usual polarographic conditions.

[2] M. Kodama, C. Sasaki and M. Murata, This Bulletin, **41**, in press.

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

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

[5] J. W. Ross, R. D. Demars and I. Shain, *Anal. Chem.*, **28**, 1768 (1956).

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

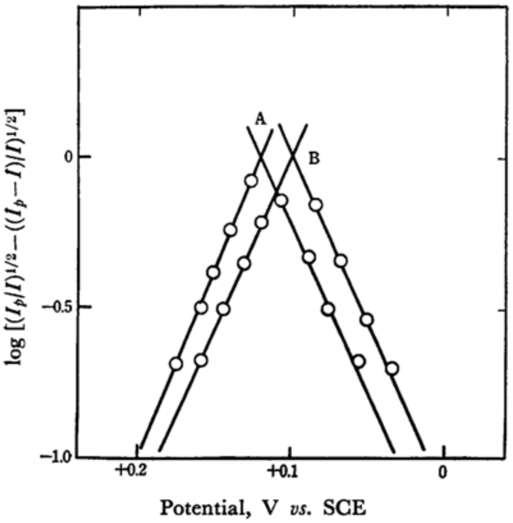

Fig. 2. The plot of $\log [(I_p/I)^{1/2}-((I_p-I)/I)^{1/2}]$ against d.c. potential, E.
Concentration of DTPA = 1.0 mM, $\mu = 0.50$
pH = 4.0 (Acetate buffer, 0.10 M)
A: DME B: HMDE

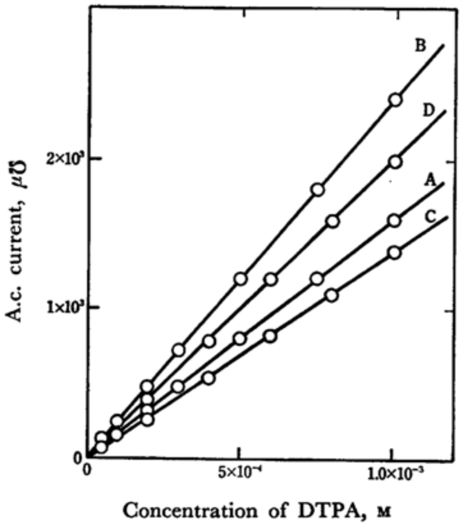

Fig. 3. The relation between the concentration of DTPA and a.c. peak-height.
$\mu = 0.50$
A: pH = 4.0 (Acetate buffer, 0.10 M), DME
B: pH = 4.0 (Acetate buffer, 0.10 M), HMDE
C: pH = 10.0 (Ammonia buffer, 0.10 M), DME
D: pH = 10.0 (Ammonia buffer, 0.10 M), HMDE

are shown in Fig. 2. This clearly indicates that the electrode reaction of DTPA at the mercury electrode is not perfectly reversible in the a.c. polarographic sense, but that it can be said to be reversible to an appreciable extent. The peak-height of DTPA can be compared with that for the reduction of the copper(II)-NTA chelate.[7]

As is illustrated by the calibration curves in Fig. 3, the a.c. peak-heights were found to be exactly proportional to the bulk concentration of DTPA in the concentration range between 5×10^{-5} and 1×10^{-3} M.

In an ammonia buffer solution of pH 10.0, quite similar results were also obtained with regard to the log-plot examination and the relation between peak-hight and DTPA concentration. These results are not shown here, however.

A. C. Polarographic Titration of Metal Ions with DTPA. A good linear relation between the a.c. peak-height and the concentration of uncomplexed DTPA strongly suggests the possibility that electroinactive metal ions, such as lanthanum(III), nickel(II), calcium(II), and magnesium(II) ions, can also be titrated with DTPA by measuring the a.c. peak-height of uncomplexed DTPA after the end point.

As had been attempted previously,[1] lanthanum(III) was titrated in an acetate buffer solution of pH 4.0. The titration curves in Fig. 4 are demonstrative examples. The end point obtained agrees well with the equivalence point, indicated by an arrow.

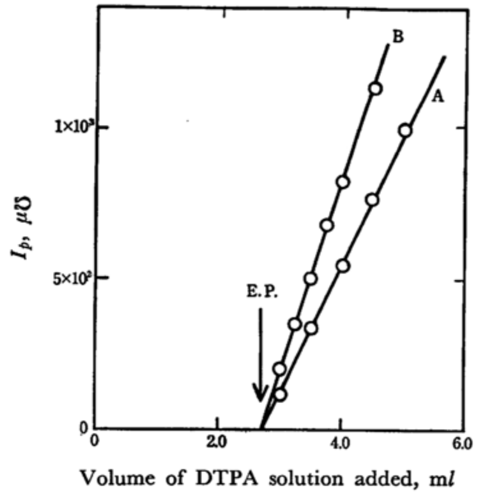

Fig. 4. Titration curves of 3.60×10^{-4} M lanthanum(III) solution with DTPA.
Volume of sample solution = 75.0 ml
Concentration of DTPA = 10.0 mM
pH = 4.0, $\mu = 0.50$
Equivalence point was indicated by an arrow.
A: DME, B: HMDE

The conditional stability constant of the nickel(II)-DTPA chelate, K', defined as:

$$K' = K_{\rm NiZ}(1+K^{\rm H}_{\rm NZi}[{\rm H}^+])/(\alpha_{\rm H})_{\rm Z} \qquad (2)$$

was estimated to be $10^{10.64}$ by using the numerical values in Table 1; the table shows that the complexation reaction between 1.0 mM nickel(II) and

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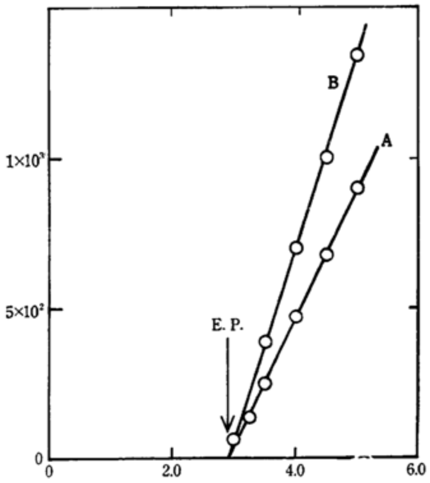
[7] M. Kodama and N. Abe, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 679 (1962).

TABLE 1. EQUILIBRIUM CONSTANTS
$\mu=0.50$

i) $\mathrm{p}K$ values of DTPA[7]			
$\mathrm{p}K_1=1.81$,	$\mathrm{p}K_2=2.64$,	$\mathrm{p}K_3=4.04$	
$\mathrm{p}K_4=7.64$,	$\mathrm{p}K_5=10.00$		
ii) $\log K_{\mathrm{MZ}}$ values			
Mg(II):[8]	8.30	Ca(II):[7]	9.89
Ni(II):[7]	19.32	La(III):[7]	18.96
iii) $\log K_{\mathrm{MZ}}^{\mathrm{H}}$ values[8]			
Mg(II):	6.60	Ca(II):	6.10
Ni(II):	5.30	La(III):	2.30
iv) $\log K_{\mathrm{M_2Z}}^{\mathrm{M}}$ values[7]			
Ca(II):	1.73		
Ni(II):	5.16		



Volume of DTPA solution added, m*l*

Fig. 5. Titration curve of 3.90×10^{-4} M nickel(II) lanthanum(III) solution with DTPA.
Volume of sample solution = 75.0 m*l*
Concentration of DTPA = 10.0 mM
pH = 4.0, $\mu=0.50$
Equivalence point was indicated by an arrow.
A: DME B: HMDE

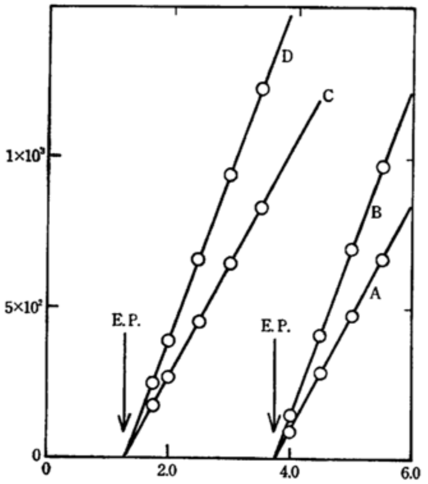
1.0 mM DTPA proceeds quantitatively at pH= 4.0. This value is considerably larger than that of the lanthanum(III)-DTPA chelate ($10^{8.96}$). K_{NiZ}, $K_{\mathrm{NiZ}}^{\mathrm{H}}$ and $(\alpha_{\mathrm{H}})_{\mathrm{Z}}$ in Eq. (2) have their usual meanings. The values in Table 1 were calculated from the related constants in the solution with an ionic strength of 0.10 at 25°C,[8,9] while the activity coefficients of the ions were calculated by means of the well-known Davies equation.[10] Therefore, as in the case of lanthanum(III), the nickel(II) ion in an acetate buffer solution of pH 4.0 is also expected to be titrated successfully with DTPA by measuring the a. c. peak-height of DTPA after the end point. Figure 5 shows typical titration curves. The experimental end point agreed well with the stoichiometric equivalence point, indicated by an arrow.

From the thermodynamic point of view, it is expected that calcium(II) and magnesium(II) ions will form stable chelates with DTPA at pH's higher than 10.0, and that the a. c. peak-potential of DTPA in the absence of any metal ion corresponding to that in Reaction (1) must be located at a potential very negative with respect to that in the presence of calcium(II) or magnesium(II) ions, corresponding to Reaction (3):

$$\begin{array}{ccccccc} & & \mathrm{M_2Z^-} & & & & \\ & & \Updownarrow{\scriptstyle \mathrm{M^{2+}}} & & & & \\ \mathrm{Hg} & + & \mathrm{MZ^{3-}} & = & \mathrm{HgZ^{3-}} & + \mathrm{M^{2+}} + 2e^- & \\ & & \Updownarrow{\scriptstyle \mathrm{H^+}} & & \Updownarrow{\scriptstyle \mathrm{H^+}} & & \\ & & \mathrm{MHZ^{2-}} & & \mathrm{HgHZ^{2-}} & & \end{array} \qquad (3)$$

where $\mathrm{M^{2+}}$ refers calcium(II) or magnesium(II) ions.

Therefore, at pH 10.0, it is considered that calcium(II) and magnesium(II) can be determined accurately by measuring the a. c. peak-height of



Volume of DTPA solution added, m*l*

Fig. 6. Titration curves of 5.00×10^{-4} M calcium(II) and 1.70×10^{-4} magnesium(II) solution with DTPA.
Volume of sample solution = 75.0 m*l*
pH = 10.0, $\mu=0.50$
Equivalence points were indicated by arrows.
A: Ca(II), DME B: Ca(II), HMDE
C: Mg(II), DME D: Mg(II), HMDE

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[8] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964), p. 693.

[9] A. Ringbom, "Complexation in Analytical Chemistry," Interscience, New York (1963), p. 333.

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

the uncomplexed DTPA after the end point. Titrations of calcium(II) and magnesium(II) with DTPA were conducted in an ammonia buffer solution of pH 10.0. Typical titration curves are shown in Fig. 6. There is good agreement between the experimental end points and the stoichiometric equivalence points.

The results of the a. c. polarographic titration of those metal ions with DTPA are given in Tables 2, 3, and 4.

Titration of Lanthanum(III) with DTPA in the Presence of Calcium(II) Ions. In an acid medium where the lanthanum(III) ions can form a stable chelate with DTPA, but, calcium(II)

TABLE 2. TITRATION OF LANTHANUM(III) WITH DTPA
volume of sample solution=75.0 m*l* concentration of DTPA=10.0 mM
acetate buffer (0.10 M) of pH 4.0 $\mu=0.50$

Concentration of lanthanum(III) M	Electrode	Volume of DTPA, m*l*		Error, % $(V_{\mathrm{obsd}}-V_{\mathrm{calcd}})/V_{\mathrm{calcd}}\times100$
		V_{calcd}	V_{obsd}	
2.40×10^{-5}*	DME	1.62	1.60	−1.0
4.80×10^{-5}*	DME	3.24	3.23	−0.3
1.70×10^{-4}	DME	1.28	1.28	0
	HMDE	1.28	1.26	−1.6
3.60×10^{-4}	DME	2.70	2.68	−0.7
	HMDE	2.70	2.71	+0.4
4.80×10^{-4}	DME	3.24	3.27	+0.9
	HMDE	3.24	3.27	+0.9
7.20×10^{-4}	DME	5.40	5.40	0
	HMDE	5.40	5.40	0

* Concentration of DTPA is 1.0 mM.

TABLE 3. TITRATION OF NICKEL(II) WITH DTPA
volume of sample solution=75.0 m*l* concentration of DTPA=10.0 mM
acetate buffer (0.10 M) of pH 4.0 $\mu = 0.50$

Concentration of nickel(II) mM	Electrode	Volume, m*l*		Error, % $(V_{\mathrm{obsd}}-V_{\mathrm{calcd}})/V_{\mathrm{calcd}}\times100$
		V_{calcd}	V_{obsd}	
0.130	DME	0.97	0.98	+1.0
	HMDE	0.97	0.98	+1.0
0.390	DME	2.91	2.90	−0.3
	HMDE	2.91	2.90	−0.3
0.780	DME	5.84	5.80	−0.7
	HMDE	5.84	5.80	−0.7

TABLE 4. TITRATION OF CALCIUM(II) AND MAGNESIUM(II) WITH DTPA
volume of sample solution=75.0 m*l* concentration of DTPA=10.0 mM
ammonia buffer (0.10 M) of pH 10.0, $\mu=0.50$

Metal(II)	Concentration of metal(II) mM	Electrode	Volume of DTPA, m*l*		Error, % $(V_{\mathrm{obsd}}-V_{\mathrm{calcd}})/V_{\mathrm{calcd}}\times100$
			V_{calcd}	V_{obsd}	
Ca(II)	0.25	DME	1.87	1.85	−1.1
		HMDE	1.87	1.89	+1.1
	0.50	DME	3.75	3.74	−0.3
		HMDE	3.75	3.70	−1.3
Mg(II)	0.17	DME	1.28	1.27	−0.8
		HMDE	1.28	1.29	+0.8
	0.42	DME	3.15	3.12	−1.0
		HMDE	3.15	3.17	+0.6

TABLE 5. TITRATION OF 75.0 ml LANTHANUM(III) SOLUTION OF 0.480 mM WITH DTPA IN THE PRESENCE OF CALCIUM(II)

concentration of DTPA=10.0 mM acetate buffer (0.10 M) of pH 4.0 $\mu=0.50$

Concentration of calcium(II) M	Electrode	Volume of DTPA, ml		Error, % $(V_{\text{obsd}}-V_{\text{calcd}})/V_{\text{calcd}}\times 100$
		V_{calcd}	V_{obsd}	
5×10^{-4}	DME	3.24	3.25	+0.3
	HMDE	3.24	3.25	+0.3
5×10^{-3}	DME	3.24	3.23	−0.3
	HMDE	3.24	3.25	+0.3
5×10^{-2}	DME	3.24	3.23	−0.3
	HMDE	3.24	3.23	−0.3
5×10^{-1}	DME	3.24	3.19	−1.6
	HMDE	3.24	3.19	−1.6

ions can not, the end point in the titration of lanthanum(III) with DTPA may be little affected by the presence of calcium(II) ions. However, even in an acid medium, when a large excess of calcium(II) ions is present in the solution, DTPA reacts partially with calcium(II) ions. Therefore, under such conditions, some positive error may be expected in the lanthanum(III)-DTPA titration. When 1.0 mM lanthanum(III) in a solution of pH 4.0 containing 0.10 M calcium(II) is 100% over-titrated with DTPA, the concentration of the calcium(II)-DTPA chelate is calculated to be 0.85 mM with the aid of the following relation, using the numerical values in Table 1.

$$[\text{CaZ}]_t = \frac{1}{1+\dfrac{1}{\dfrac{K_{\text{CaZ}}}{(\alpha_{\text{H}})_{\text{Z}}}(1+K^{\text{H}}_{\text{CaZ}}[\text{H}^+]+K^{\text{Ca}}_{\text{Ca}_2\text{Z}}[\text{Ca}^{2+}])}}\ \text{mM} \qquad (4)$$

where $[\text{CaZ}]_t=[\text{CaZ}^{3-}]+[\text{CaHZ}^{2-}]+[\text{Ca}_2\text{Z}^-]$, where K_{CaZ} is the stability constant of CaZ^{3-}, where $K^{\text{H}}_{\text{CaZ}}=[\text{CaHZ}^{2-}]/[\text{CaZ}^{3-}]\cdot[\text{H}^+]$, where $K^{\text{Ca}}_{\text{CaZ}}=[\text{Ca}_2\text{Z}^-]/[\text{Ca}^{2+}]\cdot[\text{CaZ}^{3-}]$, and where $(\alpha_{\text{H}})_{\text{Z}}$ corresponds to the $(\alpha_{\text{H}})_{\text{Z}}$ value defined as $1+[\text{H}^+]/k_5+\cdots+[\text{H}^+]^5/k_1\cdot k_2\cdot k_3\cdot k_4\cdot k_5$.

In the presence of calcium(II) ions, the a. c. polarographic titration of lanthanum(III) with DTPA was also carried out at pH 4.0. The results are given in Table 5.

Even when a large excess of calcium(II) ions is present in the solution, the error in the titration is very small and the agreement between the experimental end point and the stoichiometric equivalence point can be considered to be satisfactory. This is clearly in contrast to the above theoretical prediction. An alternative explanation is possible that, under the present experimental conditions, true equilibrium constants are much smaller than the numerical values in Table 4 used in the calculation of $[\text{CaZ}]_t$, and that the actual $[\text{CaZ}]_t$ is very small. However, it is also possible to ascribe the above fact to the facts that the peak-potential corresponding to the electrode reaction (1) and that corresponding to Reaction (3) occur at the same potential, and that the a. c. peak-heights per unit of concentration for these two reactions are the same. If the d. c. half-wave potential can be equated with the a. c. peak-potential, peak-potential difference between that in the absence of and that in the presence of a large excess of calcium(II) ions can be calculated with the aid of Relation (6) in Ref. 1. The peak-potential difference calculated for 0.10 M calcium(II) was 20 mV, and the a. c. peak-height ratio obtained experimentally was 0.95 (in an ammonia buffer solution of pH 10.0). These results may support the latter explanation.

The effect of camphor on the a. c. polarographic titration of lanthanum(III) with DTPA was also examined. The presence of 1.0 mM of camphor has little effect on the titration. This can be ascribed to the fact that camphor desorps completely from the mercury electrode[11] at the potential where the a. c. polarographic wave of DTPA is observed.

Finally, it can be mentioned here that the a. c. polarographic method established in this paper may be applied successfully to the determination of rare earths in the alloy of rare earth and alkaline earth oxide.[12]

The present authors thank the Ministry of Education for the financial support granted for this research.

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[11] B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York (1963), p. 128.

[12] T. N. Nazarchuk and S. R. Boremskaya, *(Inst. Maters. Sci. Probls., Kiev) Zh. Analit. Khim.*, **21**, (6), 745 (1966).