Alternating Current Polarization Titration with Two Hanging Mercury Drop Electrodes—Application to Chelatometric Titration of Cadmium

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Both potentiometry at a constant current and amperometry at a small constant applied voltage with two polarized platinum electrodes are widely used for the determination of the equivalent point in a large number of titrations. The relation between the two methods of titration mentioned above has been recently discussed by several authors on the basis of voltammetry[1-4].

On the other hand, conductometric titration using low frequency of 200~1000 c/sec. has been applied to the determination of the equivalent point in titrations involving acid-base neutralization reaction or precipitation reaction. However, alternating current polarization titration, which corresponds to the alternating current analogs of the two direct current method, situated between direct current polarization titration and conductometric titration has not been studied systematically. Recently Franck[5], Laitinen[6] and the present author[7] studied these methods, and applied them to redox, precipitation and complex formation reaction. The present author studied polarization titration fundamentally, applying to a pair of platinum microelectrodes a square wave or sine wave signal of constant current and measuring the alternating voltage (polarization voltage) in the course of a titration.

This is a suitable method which can be applied in redox reaction, complex formation reaction and neutralization reaction. It is impossible, however, that metal ion concentration is indicated by the platinum electrode, except in the case of some reversible system; for example, ferric-ferrous system. Hence when the chelatometric titration of metal ion is carried out by the polarization titration method, an excess of ethylenediaminetetraacetate (EDTA) solution of a known concentration is added, and the excess of EDTA is back-titrated with standard ferric solution. However, when the stability constant of metal ion titrated is much smaller than that of ferric ion, this titration method can not be used. Accordingly, only a few kinds of metal ion, ferric, indium and nickel, are titrated by this method[8]. For this reason, it seemed desirable and worth while to investigate the chelatometric titration of most metal ions by alternating current polarization titration with two mercury drop electrodes.

In this paper, the experimental results of the application to the cheltometric titration of the cadmium ion are presented, and the factors which affect this titration method are discussed.

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Experimental

Reagents. — A standard EDTA solution was obtained by dissolving the pure disodium ethylenediaminetetraacetate dihydrate (Wako Junyaku Co. Ltd.) in distilled water. The concentration was standardized against a standard copper solution by photometric titration using Murexide as indicator. The concentration was 0.100 M. A 0.01 M EDTA solution was prepared by dilution. Standard cadmium solution was prepared by dissolving cadmium nitrate in distilled water. The concentration was determined gravimetrically as cadmium oxinate. Standard mercuric ethylenediaminetetraacetate was prepared by mixing equivalent amounts of mercuric nitrate solution and EDTA solution. The concentration was 0.05 M.

All other chemicals were of analytical reagent grades. Redistilled water was used for the preparation of the solutions.

Apparatus.—Alternating current polarization titration apparatus is shown in Fig. 1. Kikusui Type CR oscillator was used for sine wave or square wave generator (20 ~2000 c/sec.). The circuit of measuring polarization voltage is shown in Fig. 2.

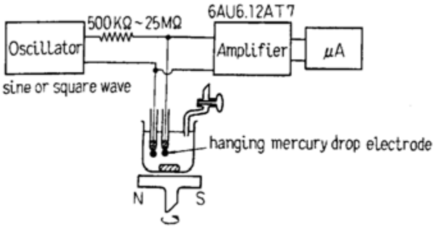

Fig. 1. Alternating current polarization titration apparatus.

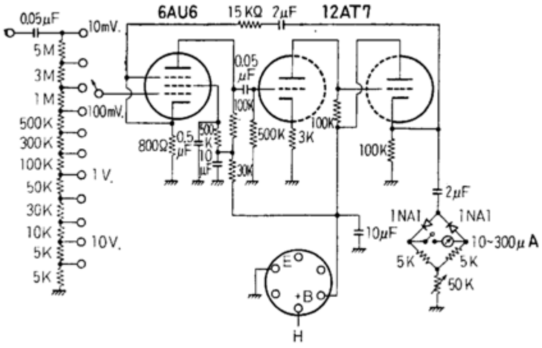

Fig. 2. Circuit of measuring polarization voltage.

The measurement was made at a small current using a large resistor in series with the electrolytic cell and an output voltage (12 volt) from the sine wave or square wave generator. The alternating voltage (polarization voltage) between two electrodes was measured as a function of the volume of reagent added.

The mercury drop electrode was prepared by fixing the mercury drop on the top of amalgamated platinum electrodes. Mercury can be deposited on the platinum electrode out of 1 M mercuric nitrate solution by the impression of an electromotive force of about 2 V. The surface area of the mercury drop was about 0.021 cm². A calibrated semimicroburet 5 ml. was used for all titrations.

Procedure.—About 50 ml. of the solution, which contained definite amounts of cadmium nitrate solution, 50 ml. of 1 M ammoium acetate-acetic acid buffer solution (pH 4.3~5.0), 1 ml. of 0.1% gelatine and 10 ml. of 0.05 M mercury (II) EDTA solution, was titrated with 10^{-1} or 10^{-2} M standard solution of EDTA. The frequency of square wave or sine wave was 25 c/sec. and the alternating current was 20~25 μA*. The polarization voltage was recorded at every 0.01 ml. of added titrant in the neighborhood of the equivalence point of this titration.

An example of this titration curve is shown in Fig. 3. In the course of this titration, the solution was stirred at a constant speed by a magnetic stirrer.

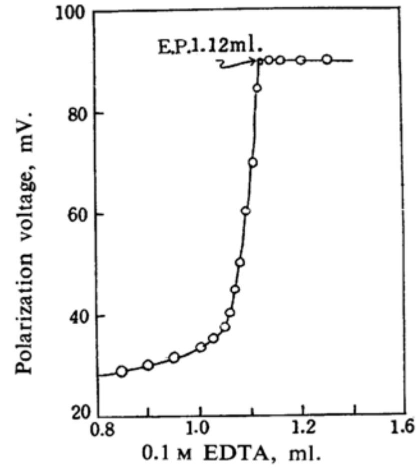

Fig. 3. Titration curve. Cd^{2+} 12.5 mg.

Results

In the procedure described above, the following factors were specially considered.

1) Relation between Polarization Voltage and Frequency.—Polarization voltage was measured at the equivalence point by the procedure described above. As shown in Fig. 4, a plot of polarization voltage against the reciprocal of square root of frequency gives a straight line at frequency 20~200 c/sec. Therefore, the frequency 20 c/sec. was used as a suitable frequency in this titration. In a frequency above 500 c/sec. it was impossible to apply this end point detection method, because the polarization voltage became very small.

2) Relation between Polarization Voltage and Alternating Current.—In the potentiometry at a constant direct current, the difference in potential between two identical indicator

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* Calculated value 12(V)÷500(KΩ)=24(μA)

electrodes becomes more extended with the increase of the current[2-4]. On the other hand, polarization voltage at alternating current polarization titration is proportional to the alternating current as shown in Fig. 4. Therefore, 25 μA was used for the suitable alternating current in this titration. If the alternating current becomes very small, it is impossible to use this titration method owing to the decrease of the polarization voltage.

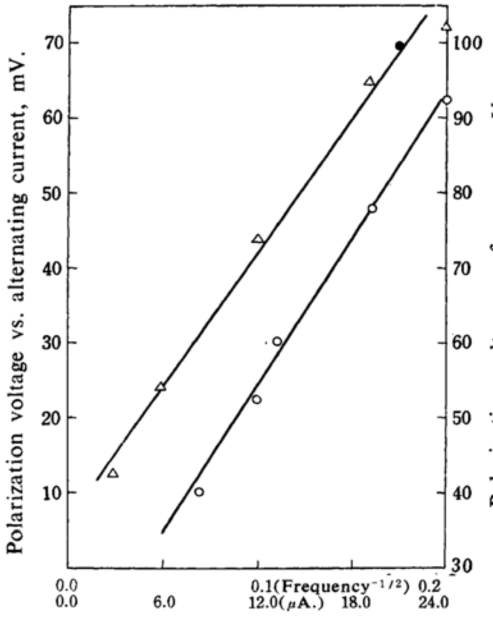

Fig. 4. A) Relation between polarization voltage and frequency (-○-).
B) Relation between polarization voltage and alternating current (-△-).

3) Effect of Surface Area of Mercury Drop.—The polarization voltage became smaller with the increase of the surface area of mercury drop as shown in Fig. 5. However, the area of the mercury electrode gave no effect on the experimental result. The pretreatment of the mercury electrode had also little effect on the shape of this titration curve and on the experimental results. Therefore, alternating current polarization titration has advantages in this point over the direct current polarization titration.

4) Effect of Gelatine. — In chelatometric titration of cadmium using potentiometry at a constant current and amperometry at a constant potential, the addition of gelatine was necessary[9] in order to suppress the kinetic current due to the dissociation of Cd-EDTA. Experimental results in the presence or the absence of gelatine in this method are shown in Table I. Although experimental results are not reproducible in the absence of gelatine, it is clear that the reproducible and precise results are obtained in the presence of gelatine. Therefore, the addition of 1 ml. of 0.1% gelatine is indispensable in this titration.

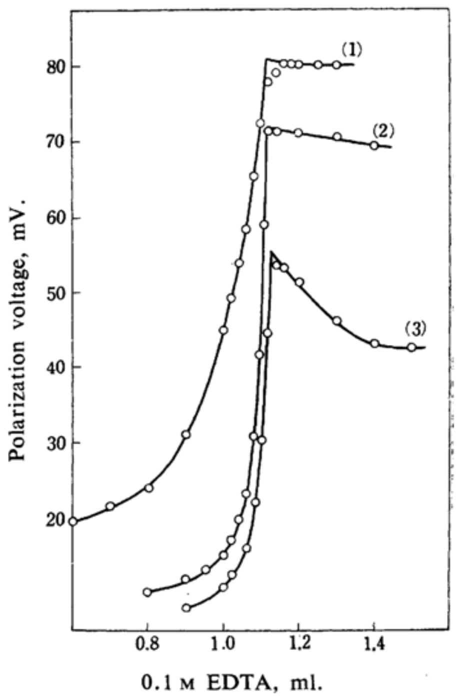

Fig. 5. Effect of surface area of mercury drop.
(1) surface area about 0.02 cm^2
(2) 〃 0.03 cm^2
(3) 〃 0.05 cm^2

TABLE I. EFFECT OF GELATINE ADDED

Cd taken mg.	0.1% Gelatine added ml.	Volume of 10^{-1}M EDTA titrated ml.	Cd found mg.
6.29	0	0.55_0	6.18
6.29	0	0.53_5	6.01
6.29	0	0.55_5	6.18
6.29	0.2	0.55_5	6.24
6.29	0.5	0.56_0	6.28
6.29	1.0	0.56_0	6.28
6.29	2.0	0.56_0	6.28

5) Effect of Wave Form.—The Effect of wave form to this titration (sine wave or square wave) was examined. Although polarization voltage was greater in the case of using sine wave than square wave, it was recognized that the wave form gave little effect on the experimental results.

6) Effect of Hg-EDTA Added.—To determine the optimum amount of Hg-EDTA to be added,

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[9] N. Tanaka et al., *Japan Analyst (Bunseki Kagaku)*, 6, 86 (1957).

various volumes of the Hg-EDTA solution were added to a constant volume of cadmium nitrate solution. In this case, all other conditions were kept constant according to the procedure described above. The results are shown in Table II. It was found that the amount of the reagent did not affect the determination of cadmium provided that it ranged from 5 to 15 ml.

TABLE II. EFFECT OF Hg-EDTA ADDED

Cd taken mg.	0.05 M Hg-EDTA added ml.	Volume of 10^{-1} M EDTA titrated ml.	Cd found mg.
12.58	0	1.11_0	12.48
12.58	1	1.12_0	12.56
12.58	2	1.12_5	12.60
12.58	3	1.12_0	12.56
12.58	4	1.12_5	12.60
12.58	5	1.12_5	12.60
12.58	10	1.12_0	12.56
12.58	15	1.12_5	12.60

7) *The Optimum Conditions for the Abovementioned Procedure.*—They have been concluded as follows: frequency, 20∼50 c/sec.; alternating current, 20∼25 μA., gelatine, 0.1% 1 ml.; pH of titration solution, 4.3∼5.0; the amounts of Hg-EDTA, 10 ml.

8) *Determination of Various Concentrations of Cadmium under the Optimum Conditions.*—Various concentrations of cadmium ions were determined by the procedure described above under the optimum conditions and the results are shown in Table III.

TABLE III. DETERMINATION OF VARIOUS CONCENTRATIONS OF Cd^{2+} AT THE OPTIMUM CONDITIONS

Cd taken mg.	Volume of EDTA titrated ml.	Cd found mg.	error %
	10^{-1} M EDTA		
12.58	1.12_0	12.56	−0.2
	1.12_5	12.60	+0.2
	1.12_5	12.60	+0.2
6.29	0.56_0	6.28	−0.2
	0.55_5	6.24	−0.9
	0.55_5	6.24	−0.9
	10^{-2} M EDTA		
0.62	0.55_5	0.62	−0.9
	0.55_5	0.62	−0.9
	0.55_5	0.62	−0.9

Discussion

Before the titration is initiated, some of the mercury(II) is displaced from its Hg-EDTA complex by the cadmium ion. The following substitution reaction occurs in the solution[10]

$$HgY^{2-} + Cd\ acetate \rightarrow Hg\ acetate + CdY^{2-}$$

In this case, complete substitution of the Hg-EDTA by the cadmium ion to be titrated is not necessary for successful titration. The end point of chelatometric titration of the cadmium ion in this procedure will be indicated by the change of polarization voltage based on the change of the mercuric ion concentration in the neighborhood of the end point. Accordingly, most metal ions will be titratid by this titration method using suitable solution conditions.

The principle on which alternating current polarization titration is based is the same as that of the direct current method. However, this is a more suitable method than the direct current polarization method in the point that the pretreatment of the mercury drop electrode is not necessary.

Summany

Cadmium was titrated with the EDTA by the alternating current polarization titration with two hanging mercury electrodes and the factors which affect this titration were examined. As a result, it is clear that the end point is indicated by the change of the mercuric ion concentration in the neighborhood of equivalence point. Pretreatment of the mercury drop electrode is not necessary. By this method, cadmium of 10^{-2}∼10^{-3} M were titrated with a relative error of 0.9%.

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