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Analytical Studies Using the Convection Electrode. XI. Cathodic Stripping Voltammetry of Chloride Ions with the Pushed-out Mercury Drop Convection Electrode

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The cathodic stripping voltammetry of chloride ions in a potassium nitrate or a nitric acid solution was studied by using the Pushed-out Mercury Drop Convection Electrode (PMDCE) (J. Suzuki and T. Ozaki, This Bulletin, **37**, 230 (1964)). The cathodic stripping peak current, i_p, depended upon the rotating rate of the disk, ω (600—1000 r. p. m.); the rate of voltage scan, v(100—300 mV./min.); the pre-electrolysis time, t (~3 min.), and the bulk concentration of chloride ions, C. It was concluded that the corresponding cathodic peak current, i_p, can be given by the equation:

$$i_p = kv\omega^{1/2}Ct^{2/3}$$

where k is the constant. In a 0.1 M nitric acid solution, it was possible to determine the chloride ions in so dilute a solution as 3×10^{-5} M with a good reproducibility.

A series of investigations of the stripping voltammetric analytical technique have shown that the method has a very high sensitivity in the determination of trace amounts of electroactive materials.

The anodic stripping analysis has been applied to the determination of those metal ions which can be deposited on the cathode as metals, and the cathodic stripping analysis, to the determination of those ions which can be precipitated on the surface of the anode as oxides or halides.

Recently, several applications of the mercury or silver electrode to the cathodic stripping analysis have been investigated for the determination of halide ions.[1-7] Ball et al.[1] and Shain and Perone.[5] reported that it was possible to determine chloride ions in solutions as dilute as 0.2 to 2γ/ml. with mercury electrode and iodide ions as dilute as 4×10^{-8} M by using the silver electrode. However, the reproducibilities obtained in these investigations were found not to be satisfactory. These unsatisfactory reproducibilities are considered to be caused by the irregularity of the flowing conditions of the solution during the electrolysis.

On the other hand, at the pushed-out mercury drop convection electrode (PMDCE), when a pulley-shaped disk was rotated near by, the reproducible flowing conditions of solution at the electrode surface were found to be achieved, as has been reported in the previous papers.[8]

In the present work, the PMDCE is applied to the cathodic stripping voltammetry in order to improve its reproducibility. The influences of the various factors upon the cathodic stripping peak current and the quantity of electricity involved in the reduction of the mercurous chloride produced on the surface of the electrode are investigated thoroughly. Also, the experimental equations of the peak current and the quantity of electricity at the PMDCE are derived. These results are described in detail below.

Experimental

Electrolytic Cell and Electrode.—The electrolytic cell used in the present experiment is the same as that described in the previous papers.[8] The electrode used is shown in Fig. 1.

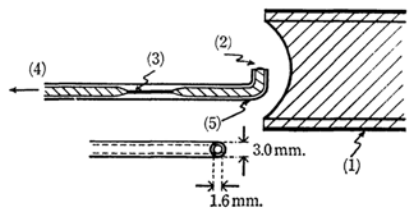

Fig. 1. Electrode and rotating disk.
(1) Rotating disk, (2) Electrode surface, (3) Capillary, (4) To the microsyringe, (5) Glass tube

1) R. G. Ball, D. L. Manning and O. Menis, *Anal. Chem.*, **32**, 621 (1960).
2) M. Ariel and U. Eisner, *J. Electroanal. Chem.*, **5**, 362 (1963).
3) W. L. Maddox, M. T. Kelley and J. A. Dean, ibid., **4**, 96 (1962).
4) K. Z. Braynina and E. M. Rozenblat, *Zavodskaya Lab.*, **28**, 21 (1962).
5) I. Shain and S. P. Perone, *Anal. Chem.*, **33**, 325 (1961).
6) W. Kemula, Z. Kublik and J. Taraszewska, *Acad. Poln. Sci.*, **8**, 269 (1960).
7) H. Specker and G. Schieve, *Z. anal. Chem.*, **196**, 1 (1963).
8) J. Suzuki and T. Ozaki, This Bulletin, **37**, 230, 789 (1964).

The renewal of the mercury drop surface of the electrode is carried out after each stripping analysis by pushing out one drop (volume: 0.0021 ± 0.0001 cc.) of mercury using a microsyringe. The peak height is found gradually to decrease when the same electrode surface is used repeatedly.

The cell and the saturated calomel reference electrode are connected through a salt bridge containing saturated potassium nitrate. Hence, cross-contaminations of the reference electrode and the sample can be prevented effectively.

The supporting electrolyte solution has a tendency to penetrate into the glass tube of the electrode. Therefore, the inside wall of the tube is coated with silicone film.

Apparatus.—The Shimadzu model RP-2 polarograph is employed for the measurements of stripping curves. The apparatus used for rotating the disk is the same as that used in the previous work.[8]

Reagents.—A nitric acid solution of an extra pure grade is used without further purification, and a potassium nitrate of an extra pure grade is purified by three recrystallizations. Also, a chloride solution is prepared from sodium chloride of an analytical reagent grade (99.99%). All the solutions are prepared with redistilled water.

Procedure.—About a 30-ml. portion of 0.1 M nitric acid or a 0.1 M potassium nitrate solution containing 3×10^{-5} M to 10×10^{-5} M of chloride ions is poured into the electrolytic cell.

The mercury surface of the electrode is renewed, and then mercurous chloride is deposited on the electrode surface by applying a potential of +0.4 V. vs. SCE for 1 min., while rotating the disk at 600 r. p. m. After this pre-electrolysis process, the disk is stopped and the electrolytic solution is allowed to stand for 15 sec.; then the deposited mercurous chloride is stripped polarographically by scanning the potential from +0.4 to 0 V. vs. SCE at a scanning rate of 200 mV./min., i. e., by a linearly-varying potential stripping method. A recorder sensitivity of 0.250 μamp./mm. is selected for recording the stripping curves. All the measurements are carried out at 25 ± 0.5°C.

The peak current, i_p, is measured as is illustrated in Fig. 2, and the quantity of electricity is obtained by measuring the area of the peak with a planimeter.

Results

The Reproducibility of the Peak Current.—A curve typical of those obtained is shown in Fig. 2. On the basis of the curve, the reproducibility of the peak current was investigated. A good reproducibility can always be obtained, with a mean error of $\pm 2\%$.

The Effect of the Pre-electrolysis Time.—By using a 0.1 M nitric acid solution containing 4×10^{-5} M chloride and a 0.1 M potassium nitrate solution containing 10×10^{-5} M chloride, the dependency of the peak current and the quantity of electricity on the pre-electrolysis time was investigated; the results are shown in Fig. 3 and Table I respectively. As can be seen from Fig. 3, the peak current gives a saturation curve with an increase in the pre-electrolysis time. As the pre-electrolysis time is longer than 5 min., the peak current is almost constant. However, in this case, it is necessary to remove the dissolved oxygen before the

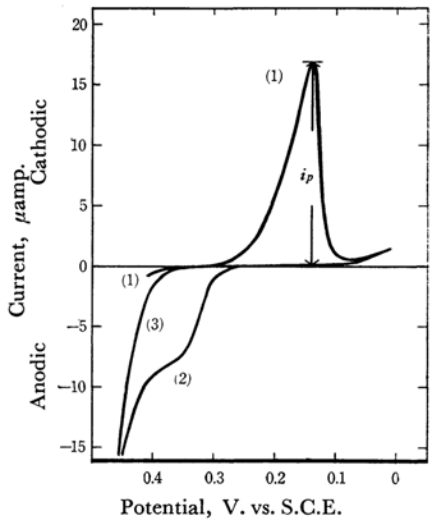

Fig. 2. Typical current-voltage curves of chloride ion in 0.1 M HNO_3 using the PMDCE.
(1) Cathodic stripping curve of 6×10^{-5} M Cl^-.
(2) D. C. polarogram of 1×10^{-4} M Cl^-.
(3) D. C. polarogram of 0.1 M HNO_3

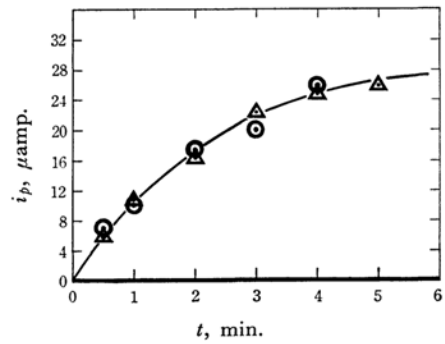

Fig. 3. Relations between the peak current i_p and the pre-electrolysis time t.
-△-: 4×10^{-5} M Cl^- in 0.1 M HNO_3
-⊙-: 1×10^{-4} M Cl^- in 0.1 M KNO_3

TABLE I. EFFECTS OF THE PRE-ELECTROLYSIS TIME (t) ON THE QUANTITY OF ELECTRICITY (Q) INVOLVED IN THE REDUCTION OF MERCUROUS CHLORIDE (SCANNING RATE: 200 mV./min.)

Pre-electrolysis time t, sec.	1×10^{-4} M Cl^- in 0.1 M KNO_3		4×10^{-5} M Cl^- in 0.1 M HNO_3	
	Q, μcoul.	Q/t	Q, μcoul.	Q/t
30	116.2	3.87	97.5	3.25
60	245.2	4.09	204.7	3.41
120	478.5	3.99	385.5	3.21
180	708.0	3.93	621.0	3.45
240	998.2	4.16	783.0	3.26
300	—	—	967.5	3.23

stripping, because the reduction of oxygen takes place before all the deposited mercurous chloride have been reduced.

The Influence of the Rotating Rate of the Disk during the Pre-electrolysis on the Peak Current and on the Quantity of Electricity.—The variations in the peak current and the quantity of electricity with the rotating rate (600—1000 r. p. m.) were investigated. The gradual increases in the peak current and in the quantity of electricity with the increase in the rotating rate were found to be as shown in Table II.

TABLE II. EFFECTS OF THE ROTATING RATE (ω) ON THE PEAK CURRENT (i_p) AND ON THE QUANTITY OF ELECTRICITY (Q) INVOLVED IN THE REDUCTION OF MERCUROUS CHLORIDE (SCANNING RATE: 200 mV./min.)

Stirring rate	1×10^{-4} M Cl^- in 0.1 M KNO_3		4×10^{-5} M Cl^- in 0.1 M HNO_3	
ω r.p.m.	i_p, μamp.	Q, μcoul.	i_p, μamp.	Q, μcoul.
600	9.93	245.3	11.18	204.8
800	11.17	294.8	12.73	261.8
1000	12.75	309.8	13.92	294.0

The Effects of the Voltage Scanning Rate on the Peak Current and on the Quantity of Electricity.—Three scanning rates, of 100 mV./min., 200 mV./min., and 300 mV./min., were investigated; the results are shown in Fig. 4. The figure shows that, as the rate of voltage scan was increased, the peak current increased linearly, but the quantity of electricity was almost constant at every scanning rate.

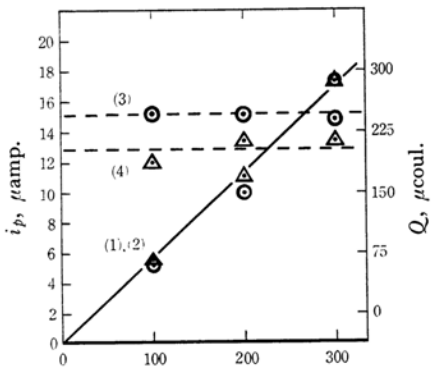

Fig. 4. Effects of the voltage scanning rate on the peak current i_p, and the quantity of electricity Q.
(1), (3): 1×10^{-4} M Cl^- in 0.1 M KNO_3
(2), (4): 4×10^{-5} M Cl^- in 0.1 M HNO_3
——: Peak current, ----: Quantity of electricity

Relations between the Concentration of Chloride and the Peak Current, and the Quantity of Electricity.—Several determinations of the peak current and the quantity of electricity were made at various concentrations of chloride; the results are shown in Fig. 5. It can be seen from the figure that satisfactory proportionalities between them are established.

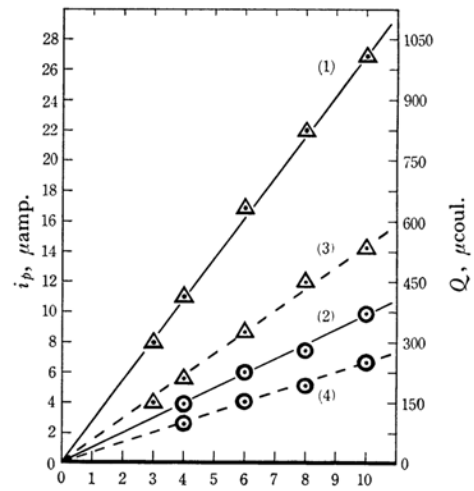

Fig. 5. Relations between the chloride concentration and the peak current i_p, and the quantity of electricity Q.
(1) (3): In 0.1 M HNO_3, (2) (4): In 0.1 M KNO_3
——: Peak current, ----: Quantity of electricity

Discussion

Pre-electrolysis Potential.—At any point on the anodic dissolution wave of mercury, the potential of mercury electrode can be expressed by:

$$E = E^0_{Hg} + 0.059/2 \log C^0_{Hg_2^{2+}} \quad \text{(at 25°C)} \quad (1)$$

where E^0_{Hg} is the standard potential of mercury-mercurous mercury couple (+0.553 V. vs. SCE) and $C^0_{Hg_2^{2+}}$ is the concentration of mercurous ions at the electrode surface. In the presence of chloride ions, however, the anodic wave of mercury shifts to more negative potentials. The anodic reaction can be expressed as follows:

$$2Hg + 2Cl^- = Hg_2Cl_2 + 2e \quad (2)$$

From the Nernst equation for the equilibrium potential[9] the following equation for the half-wave potential is obtained:

$$E_{1/2} = \text{const.} - 0.059 \log C_{Cl^-} \quad \text{(at 25°C)} \quad (3)$$

where C_{Cl^-} is the bulk concentration of chloride.

From Eq. 3, it follows that the $E_{1/2}$ value shifts to values more positive by about 60 mV. for each 10-fold decrease in the chloride concentration, until the chloride wave merges with the wave corresponding to the oxidation of mercury to mercurous

9) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience, New York (1952), pp. 577—581.

ions. Therefore, the lower limit of the determination of chloride with the mercury electrode is found to be about 10^{-6} M.

As the solubility product of mercurous chloride is 6×10^{-19} at 25°C, the critical concentration of mercurous ions in a 1×10^{-6} M chloride solution becomes 6×10^{-7} M. By substituting this value into Eq. 1, the potential of the mercury electrode at this concentration is calculated to be:

$$E=0.553+0.030\log 6\times10^{-7}=+0.36 \text{ V. vs. SCE}$$

Consequently, in low concentrations of chloride it is necessary to apply a pre-electrolysis potential of about +0.4 V. vs. SCE. In the present investigation, a pre-electrolysis potential of +0.4 V. vs. SCE was applied.

Peak Current and Voltage Scanning Rate.—Randles[10] and Sevcik[11] independently derived an equation for the cathodic peak height in oscillographic polarography:

$$i_{max} = kAn^{3/2}v^{1/2}D^{1/2}C \qquad (4)$$

where k is the constant; A, the electrode area; n, the number of electrons involved in the reduction; v, the rate of voltage scan; D, the diffusion coefficient, and C, the bulk concentration.

The application of the Randles and Sevcik relationship to the anodic peak current obtained by the stripping method was studied by Nikelly and Cooke.[12] They found that the relation between the anodic peak current and the scanning rate was the same as in the above Eq. 4. Namely, the anodic peak current obtained by the stripping method is proportional to one-half the power of the scanning rate.

Therefore, in the stripping analysis, the selection of a voltage scanning rate is important. In general, the more rapid the rate of voltage scan, the sharper the peak. It is preferable that the scanning rate should be as rapid as possible.

As can be seen from Fig. 4, in contrast with the above finding of Nikelly and Cooke, the present result indicates the linear relation between the peak current and the scanning rate. Further studies are, however, necessary before any definite conclusion recording the disagreement between the Nikelly and Cooke result and the present author's can be drawn.

The Rotating Rate of the Disk.—One of the most important factors affecting the magnitude of the peak current and the quantity of electricity is the amount of mercurous chloride deposited on the electrode during the pre-electrolysis process. The amount of mercurous chloride deposited is governed by the rate of the diffusion of chloride ions toward the electrode surface, that is, the rate of convection caused by stirring the solution. Therefore, the stirring rate should carefully be kept constant; a rapid stirring of the electrolytic solution gives a high sensitivity. However, the effects of the rotating rate on the peak current and on the quantity of electricity have never been investigated.

Using the data in Table II, the relations between the logarithm of the rotating rate and that of the peak current, and that of the quantity of electricity were investigated. It can be seen that both the peak current and the quantity of electricity are proportional to the square root of the rotating rate.

The Pre-electrolysis Time.—The amounts of mercurous chloride deposited are governed by the pre-electrolysis time. Therefore, the peak current and the quantity of electricity depend on the pre-electrolysis time. As Table I shows, the quantity of electricity changes linearly with the increase in the pre-electrolysis time. This indicates that the amounts of mercurous chloride deposited increase linearly with the increase in the pre-electrolysis time. On the other hand, the peak current increases, not linearly, but gradually with the increase in the pre-electrolysis time. This slight deviation from linearity can be explained as follows. The longer the pre-electrolysis time, the larger the amounts of mercurous chloride deposited on the electrode surface. Therefore, at a long pre-electrolysis time, the larger amounts of chloride ions released at the electrode surface during the stripping change the equilibrium potential,[5] and then the dissolution curve obtained becomes broader.

This explanation is supported by the fact that the

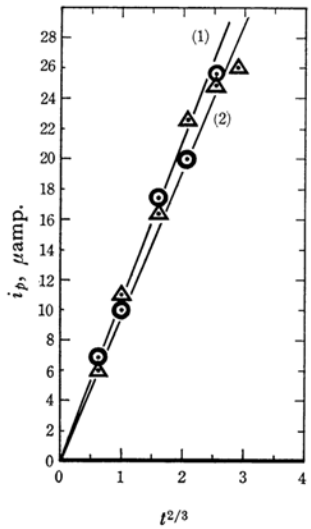

Fig. 6. Relations between the peak current i_p, and the two-thirds power of pre-electrolysis time t (min.).

(1) -△-: 4×15^{-5} M Cl^- in 0.1 M HNO_3
(2) -⊙-: 1×10^{-4} M Cl^- in 0.1 M KNO_3

10) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327, 334 (1948).
11) A. Sevcik, *Collection Czechoslov. Chem. Commun.* **13**, 349 (1948).
12) J. G. Nikelly and W. D. Cooke, *Anal. Chem.*, **29**, 933 (1957).

larger peak current was obtained on rotating the disk during the stripping in order to remove the chloride ions released and eliminate the effect on equilibrium potential.

Experimental Equations of the Cathodic Peak Current and the Quantity of Electricity at the PMDCE.—As is shown in Fig. 3, the peak current obtained by the PMDCE increases gradually with the increase in the pre-electrolysis time. When the peak current is plotted against two-thirds the power of the pre-electrolysis time, the plots are found to be straight lines, as Fig. 6 shows.

Consequently, considering the effects on the peak current mentioned above, the cathodic peak current, i_p, at the PMDCE may be expressed by the following equation:

$$i_p = k'v\omega^{1/2}Ct^{2/3} \quad (5)$$

Similarly, the quantity of electricity, Q, at the PMDCE may be expressed by:

$$Q = k''\omega^{1/2}Ct \quad (6)$$

where k' and k'' are the constants; v, the rate of the voltage scan; ω, the rotating rate of the disk; t, the pre-electrolysis time, and C, the bulk concentration.

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