Studies on the Supplementary Reduction in Oscillographic Polarography

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A supplementary kink was found in the oscillographic potential-time curve of the metal ion such as Cd^{++} which exists in a neutral solution containing the dissolved oxygen. Vogel[1] was the first who reported the phenomenon, which was more recently assigned to a sudden decomposition of a metal hydroxide by Behr and Chodkowski[2].

In this paper are presented the results of detailed studies of the phenomenon by means of a current-potential oscillographic polarograph and a proposal of a new mechanism of the effect.

Experimental

The technique of the oscillographic current-potential curve introduced by Ševčik[3] was used with some modifications[4]. The arrangement is illustrated in Fig. 1. The cell used was a H-cell with double partitions made with sintered glass disks, and a supporting electrolyte solution was instilled in a compartment between a test solution and a saturated calomel electrode. Thus, the contamination of a test solution by chloride ion was avoided.

To prepare all test solutions reagent grade chemicals were recrystallized twice from their aqueous solutions.

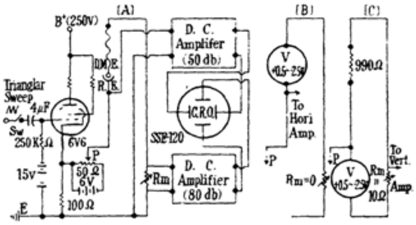

Fig. 1. Schematic diagram of measuring apparatus. (A) polarographic circuit, (B) and (C) calibrating circuit for horizontal and vertical deflection, respectively.

In the solution of Pb^{++}, Zn^{++}, Bi^{+++}, Al^{+++}, or Fe^{+++} no reproducible current was observed, owing to the irregular fluctuation of the lifetime of the D. M. E. (Sometimes it amounts to a variation as large as 10% of the mean life time.). Accordingly, Cd^{++} in N KCl was used for the quantitative measurements. The possible experimental error in measuring the polarographic current amounts to ±3%[5].

Results

1. Influence of the Dissolved Oxygen.— In an ordinary polarography the reduction of the metal ion such as Cd^{++} in a neutral

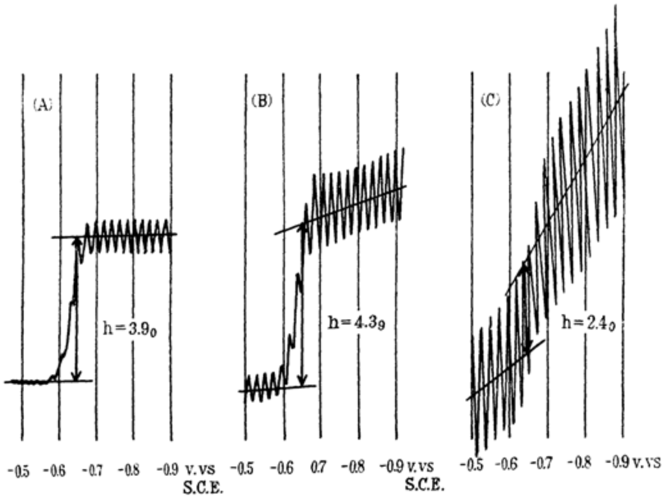

Fig. 2. Ordinary polarogram of $5\cdot3\cdot10^{-4}$ M/l. Cd^{++} in 0.5 N KCl (s=1/20, 24.6° C). (A) deaerated soln., (B) test soln. contg. atm. oxygen, (C) test soln. contg. conc. oxygen.

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[1] J. Vogel, Proc. 1st Intern. Polarog. Congr., Part III, 731 (1951); *C.A.*, 47, 11030 (1953).

[2] B. Behr and J. Chodkowski, *Rozniki Chem.*, 26, 650 (1950); *C.A.*, 48, 3816 (1954).

[3] A. Sevcik, *Collection Czechoslov. Chem. Commun.*, 13, 349 (1948).

[4] M. Shinagawa, H. Imai and S. Chaki, *J. Electrochem. Soc. Japan*, 23, 132, 187 (1955).

[5] H. Imai, *J. Electrochem. Soc, Japan*, 23, 530 (1955).

medium gives the current-potential curve irreversible to some degree. The limiting current increases as the concentration of oxygen increases. However, the presence of oxygen in its high concentration results in the reduction of the diffusion controlled current. The typical polarograms of these cases are illustrated in Fig. 2.

In the oscillographic current-potential polarogram a reduction peak and a reoxidation peak can be observed in the cathodic and anodic branches, respectively. Dissolved oxygen being present in a neutral Cd^{++} solution, the normal reduction peak, i. e. the reduction peak of an aquo cadmium ion, is lowered and it accompanies a supplementary reduction peak, while no remarkable change is observed in the anodic branch as is illustrated in Fig. 3.

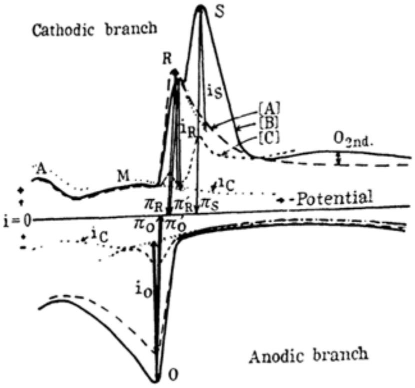

Fig. 3. Oscillographic polarogram of 1.10^{-3} M/l Cd^{++} in N KCl (20 c.p.s., v= 50 v/s): Full curve, interrupted curve and dotted curve correspond to (A), (B) and (C) of Fig. 2, respectively.

This effect can be observed not only in a multi-sweep method, but also in a single sweep method. As the concentration of the dissolved oxygen increases, at first the normal reduction peak lowers and, on the contrary, the supplementary reduction peak increases attaining a maximum value, then all peaks begin to decrease simultaneously, being extinguished ultimately.

Since, the shift of the initial sweep voltage toward more positive potential elongates the duration of the first oxygen reduction, the influence of the dissolved oxygen can be best realized by changing the initial sweep voltage.

The plot of the relation between the peak height and the initial sweep voltage is illustrated in Fig. 4. When the initial sweep voltage is shifted toward more positive potentials, at first the supplementary reduction peak remarkably increases and it amounts to a limiting value at −0.05 volts vs. S. C. E., which coincides with the half wave patential of the first oxygen reduction in N KCl*.

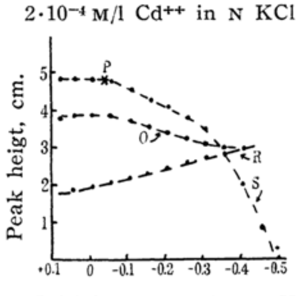

Fig. 4. Variation of the peak height with the initial sweep voltage. 20 c.p.s., v= 50 v/s, $2.0\cdot10^{-4}$ M/l Cd^{++}.

It must be recalled here that in the oscillographic technique the applied voltage sweeps during a single lifetime of the D.M.E., therefore, the electrode suffers from the hysteresis of a prior reduction (namely, the first reduction of the dissolved oxygen in this case.). Since the supplementary reduction does not affect the second oxygen reduction, it may be assumed that the hydroxide ion formed in the course of the first oxygen reduction plays a role in the supplementary reduction.

2. Influence of the Concentration of a Metal Ion.—The plot of the relation between the wave height and the concentration of Cd^{++} is illustrated in Fig. 5, where the full curve and the interrupted curve represent the plot in the cases of the deäerated and the undeäerated solutions, respectively. In the former case a good linearity is obtained by the ordinary polarograph concurring with Ilkovič's equation, while in the latter case the linearity deviates slightly. Likewise, in the deäerated solution a linear plot is obtained by the oscillographic technique, while in the undeäerated solution the supplementary reduction peak steeply increases at first as the Cd^{++} concentration increases, and it amounts to a limiting value at a certain Cd^{++} concentration (i. e., about 0.5 mM/l, which is

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* Behr and Chodkowski[2] coined the term "latent limiting current" for the first oxygen reduction in an potential-time oscillographic method. The present author has assigned the effect to its irreversible process and also to the fact that the cathodic current has probably been likely misjudged for a large charging current. The peak current of the dissolved oxygen was observed in the surfaceinactive supporting electrolyte such as nitrate, perchlorate or sulfate, while it was not observed in the solution containing halogen ion. The electrode reaction proceeds as follows:

1st reduction: $O_2+2H_2O+2e=H_2O_2+2OH^-$

2nd reduction: $H_2O_2+2e=2OH^-$

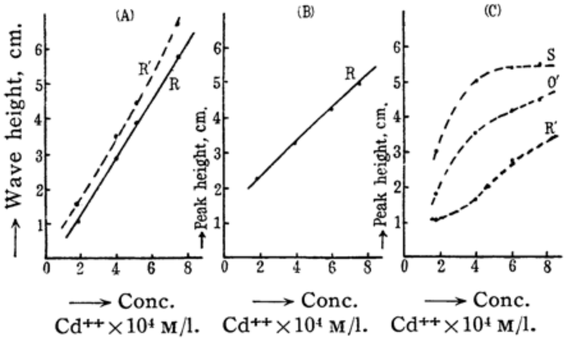

Fig. 5. Variation of the wave height with the conc. of Cd^{++}: (A); ordinary polarograph (s=1/20), (B) and (C): oscillographic polarograph (20 c.p.s., v=36 v/s): full curve; deäerated soln., interrupted curve; test soln. contg. atm. oxygen.

greater than the equivalent concentration of the dissolved oxygen (0.3_3 mM/l.)).

These results seem to indicate that the simultaneous reduction of Cd^{++} and oxygen does not affect the diffusion controlled current of Cd^{++} as the case is an ordinary polarograph, but in the oscillographic polarograph the hydroxide ion formed in the course of the first oxygen reduction changes an aquo Cd^{++} into cadmium hydroxide which pertains to the increment of the supplementary reduction.

3. Variation of the Peak Height with the Rate of Potential Change.—The peak height of Cd^{++} is linearly proportional to the square root of the rate of potential change in the range of 20–60 volts per second. The supplementary reduction behaves similarly, however, the gradient of the plot is about two and a half times greater than that of the normal reduction as is illustrated in Fig. 6. This effect is assigned to the fact that not only the reduction of Cd^{++} but also that of the dissolved oxygen increase with the increase of the rate of potential change, therefore, the increase of the supplementary reduction results from the conjoined effect of two reducible species, i. e. Cd^{++} and oxygen.

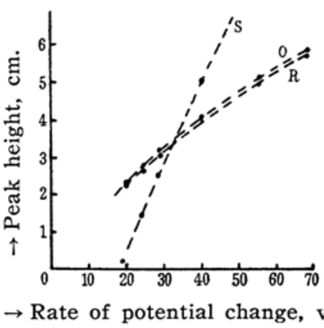

Fig. 6. Variation of the peak height with the rate of potential change, v. (20 c.p.s., $V_i=-0.30$ v. vs. S.C.E., $1\cdot10^{-3}$ M/l. Cd^{++}).

4. Influence of the Concentration of Hydrogen Ion.—The supplementary reduction can be observed in the neutral solution of bromide, chloride, rhodanate, nitrate or sulfate. However, there is a limit in an acidic or in an alkaline solution. The influence of pH on the supplementary reduction was persued in non-buffered media, and the results are illustrated in Fig. 7.

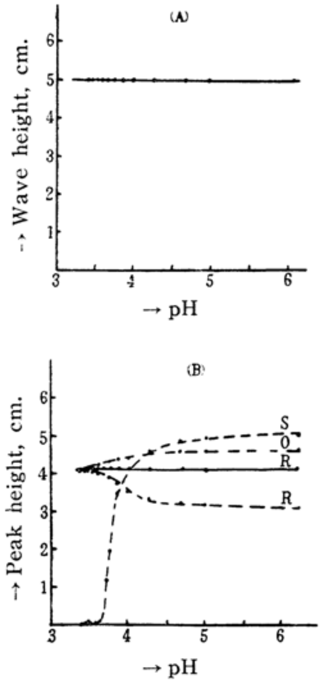

Fig. 7. Variation of the wave height with pH: (A) ordinary polarograph (s=1/20), (B) oscillographicp olarograph: full curve; deäerated soln., interrupted curve; test soln. contg. atm. oxygen.

In the ordinary polarography pH does not affect the diffusion controlled current of Cd^{++}. Also in the oscillographic work the normal reduction in the case of the deäerated solution is independent of pH. On the contrary, the effect is remarkable in the undeäerated solution. When pH of the test solution is less than 3.53 the supplementary reduction was not observed. In the pH range from 3.53 to 3.67 the supplementary reduction gradually increases as the D. M. E. drops repeatedly. Hence, the peak height recorded during the first single drop was taken into account. In Fig. 7 the supplementary reduction increases as pH increases, while the normal reduction varies vice versa. The supplementary reduction was not observed in the buffered solution containing N acetic acid and N sodium acetate.

As a result, it may be assumed that the variation of the solubility of a metal hydroxide in an acidic solution results in the variation of the supplementary reduction. This effect corresponds to the fact that the metal ion which gives rise to the supplementary reduction in a neutral medium is confined to its ability to form the sparingly soluble hydroxide. Only Cd^{++}, Pb^{++}, Zn^{++}, Bi^{+++}, Fe^{+++} or Al^{+++} was found to give the supplementary reduction.

From these results it is evident that the supplementary reduction results from the sparingly soluble metal hydroxide. It can not be elucidated, however, that not only the normal reduction but also the supplementary reduction decrease by the presence of oxygen in its high concentration. The following experiment was pursued to clarify this point.

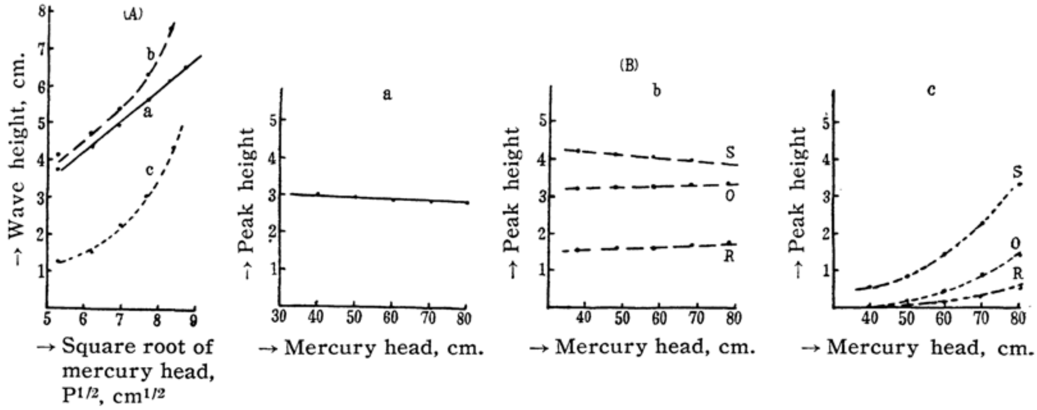

Fig. 8. Variation of the wave height with the mercury head: ($5.3 \cdot 10^{-4}$ M/l Cd^{++} in 0.5 N KCl), (A) ordinary polarograph, (B) oscillographic polarograph: full curve; deäerated soln., interrupted curve; test soln. contg. atm. oxygen, dotted curve; test soln. contg. conc. oxygen.

5. Variation of the Peak Height with the Mercury Head.—In an ordirnary polarography, the variation of the limiting current is linearly proportional to the square root of the mercury head as is illustrated in Fig. 8 Aa. However, in an oscillographic polarograph the peak height is practically independent of the mercury head (Fig. 8 Ba). These relations deviate in the case of the undeäerated solution (Figs. 8 Ab, 8 Bb), especially by the presence of oxygen in its high concentration (Figs. 8 Ac, 8 Bc).

The presence of oxygen in its high concentration results in the depletion of a reducible metal ion by the formation of a metal hydroxide at the electrode surface.

When the mercury head is raised, the rate of the drop growth of the D. M. E. increases in proportion to the mercury head, and accordingly, the expanding electrode surface can encounter the reducible metal ion which locates a little apart from the electrode surface.

From the fact that not only the normal reduction but also the supplementary reduction increase as the mercury head is raised, it is reasoned that the supplementary reduction is originated from an intermediate, i. e. a colloidal metal hydroxide, between an aquo metal ion and a metal hydroxide.

6. The Microscopic Observation of the D. M. E.—When the supplementary reduction arises, a smoky cloud is observed microscopically as the case is Pb^{++} or Fe^{+++}. The smoky cloud is formed at the vicinity of the

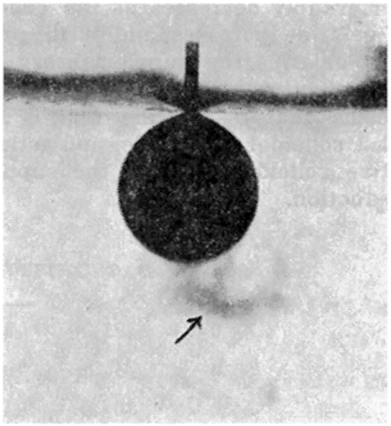

Fig. 9. Photomicrograph of metal hydroxide colloids repulsed from the surface of the D.M.E.

D. M. E. at an early stage of the lifetime, and some time after it is suddenly repulsed from the electrode surface prior to the drop of the D. M. E. The photomicrograph is illustrated in Fig. 9.

It may be assumed that a colloidal metal hydroxide is formed by the reaction of a metal ion with a hydroxide ion, and being deprived of the stabilizing ion as the result of the supplementary reduction, the metal hydroxide is repulsed by the negatively charged electrode. This assumption will be supported by the following experiment.

7. Influence of the Surface Active Reagent.—The variation of the peak height with the concentration of gelatine is illustrated in Table I.

TABLE I

VARIATION OF THE WAVE HEIGHT WITH THE GELATINE CONCENTRATION

A. Ordinary Polarograph: sensibility=1/20						
Gelatine conc., %		0	0. 005	0. 01	0. 05	0. 1
Wave height of Cd^{++} in deaerated soln., cm.		5.8_5	5.8_5	5.8_5	5.6_5	5.5_0
In the test soln. containing oxygen, cm.		6.4_3	5.9_2	5.9_2	5.7_8	5.7_8
B. Oscillographic Polarograph: v=50 v/s, 20 c.p.s.						
Gelatine conc., %		0	0. 005	0. 01	0. 05	0. 1
Peak ht. of Cd^{++} in deaerated soln., cm.	R	3.8_6	3.8_0	3.7_1	2.4_0	2.4_0
	O	3.8_7	3.9_0	3.9_0	3.8_0	2.8_0
In the test soln. contg. oxygen, cm.	R	3.1_1	3.7_6	3.8_0	3.2_1	2.9_9
	S	4.0_4	2.7_5	2.7_0	0	0
	O	4.3_9	3.9_2	3.7_4	2.8_3	2.6_2

In Table I, A the reduction of Cd^{++} is not hindered by the presence of 0.01% gelatine in the case of the deaerated solution, however, in the undeaerated solution the reduction is hindered even by the presence of 0.005% gelatine. In Table I, B the normal reduction is retarded only a little by the presence of gelatine. However, the supplementary reduction remarkably decreases as the concentration of gelatine increases, and by the presence of 0.05% gelatine the supplementary reduction is perfectly extinguished.

It seems that a gelatine film is formed around a colloidal hydroxide, and acting as a protective colloid it retards the supplementary reduction.

Both Triton X 100 and dodecyl-trimethyl ammonium chloride give the same results as that of gelatine.

Conclusion

From the above mentioned results the mechanism of the supplementary reduction can be given as follows.

At first the dissolved oxygen is reduced at the vicinity of the electrode surface to form a colloidal metal hydroxide with an aquo metal ion. When the cathodically produced hydroxide ion is not as much as the equivalent concentration of the metal ion, the excess metal ion is adsorbed around the colloidal metal hydroxide as the inner ion (i. e. the potential determining ion) of the colloid. This inner ion will give rise to the supplementary reduction. The potential required for the reduction of the inner ion will be greater than the aquo metal ion on account of its Coulombic attraction to the metal hydroxide. Thus, the supplementary reduction is observed at the more negative potential than the normal reduction.

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