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Cathodic Waves of *o*-Hydroxyphenylmercury Chloride in Aqueous Nitric Acid Medium. Inhibition by Reaction Product and Reduction of Precipitate

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Polarographic behavior of *o*-hydroxyphenylmercury chloride was examined in aqueous nitric acid medium. An abnormal first wave and a peculiar angular-shaped second wave were observed. Equations of the current-potential curves of the first and second waves are derived on the following assumptions: the first wave is inhibited by a reduction product adsorbed on the surface of the dropping mercury electrode as solid particles, the adsorbed precipitate being reduced at the second wave. The equations agree well with the observed results.

In a previous paper, inhibition of an electrode process by a reduction product of another electroactive species was discussed in relation to its current-time behavior.1) This paper reports inhibition of an electrode process by its own reduction product.

Polarographic behavior of *o*-hydroxyphenylmercury chloride (*o*-HPMC) in 80% ethanol solution was studied by Sato.2) He observed double one-electron waves of normal shape. This compound is soluble in water. We examined its polarographic behavior in aqueous solutions and observed an abnormal first wave and a peculiar angular-shaped second wave in aqueous nitric acid medium. It was revealed that the first wave is inhibited by a reduction product which is adsorbed on the surface of the dropping mercury electrode (DME) as solid particles, and that the adsorbed precipitate is reduced at the second wave.

Experimental

o-HPMC was prepared according to the method of Whitmore and Middleton,3) and recrystallized from water several times: mp 152 °C (lit.4) 152.5 °C). A stock solution was made by dissolving a weighed amount.

The nitric acid medium, used as a supporting electrolyte solution, was a mixture of 0.05 M nitric acid and 0.45 M sodium nitrate. Acetate buffer solutions, whose ionic strength was controlled to 0.50 with sodium nitrate, were also used as supporting electrolyte solution. All the supporting electrolyte solutions contained also 0.005% gelatin.

All solutions were prepared with redistilled water. Test solutions were degassed with nitrogen and thermostated at 25.0±0.1 °C.

The capillary constant ($m^{2/3}t^{1/6}$) of a DME was 1.810 mg$^{2/3}$ sec$^{-1/2}$ at zero applied potential *vs.* SCE and at mercury pressure of 1000 mm. The cell and salt bridge are described elsewhere.5) A manual instrument was used for the measurement of polarograms. Polarograms were corrected for the internal resistance (*iR* drop) across the cell and the residual current.

Results and Discussion

Figure 1 shows typical polarograms of *o*-HPMC in aqueous solutions. Polarograms in acetate buffer solutions have a normal shape and their diffusion currents increase linearly with increasing concentration of *o*-HPMC. The polarogram in the nitric acid medium, however, has a peculiar angular-shaped second wave. The first wave shifts to negative potentials with increasing concentration of *o*-HPMC in spite of its irreversibility. In the following discussion is confined to the behavior in the nitric acid medium.

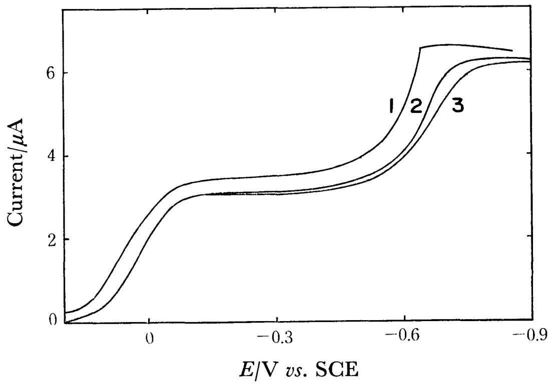

Fig. 1. Polarograms of *o*-HPMC.
Concentration of *o*-HPMC, 1.000 mM. Supporting electrolyte solution: 1, nitric acid medium; 2, acetate buffer (pH 4.38); 3, acetate buffer (pH 5.21).

The first wave in the nitric acid medium is preceded by a small wave, which does not exist in polarograms in acetate buffer solutions (Fig. 1). The height of this small wave increases slowly with degassing time. Dimroth decomposed *o*-HPMC by boiling with hydrochloric acid, and obtained phenol and mercuric chloride.6) Thus it seems that the small wave is due to mercuric ions produced by the protolysis of *o*-HPMC. The current measured at 0.20 V *vs.* SCE was identified as diffusion current of mercuric ions produced by the protolysis reaction, and subtracted from the current due to *o*-HPMC. The current corrected in this way is denoted by i^{I}.

Logarithmic plots of the first wave are given in Fig. 2, where $i_{\mathrm{d}}{}^{\mathrm{I}}$ is the diffusion current of the first wave.

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1) T. Murayama and A. Takayanagi, This Bulletin, **45**, 2233 (1972).

2) H. Sato, *Eisei Shikenjo Hokoku*, **75**, 50 (1957).

3) F. C. Whitmore and E. B. Middleton, *J. Amer. Chem. Soc.*, **43**, 619 (1921).

4) L. G. Makarova and A. N. Nesmeyanov, "Methods of Elemento-Organic Chemistry," Vol. 4, North-Holland Publishing Co., Amsterdam (1967), p. 83.

5) T. Murayama, T. Sawaki, and S. Sakuraba, This Bulletin, **43**, 2820 (1970).

6) O. Dimroth, *Ber.*, **31**, 2154 (1898).

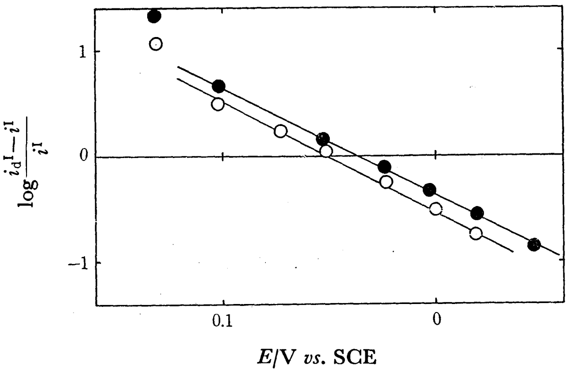

Fig. 2. Relation of log $(i_d^I - i^I)/i^I$ vs. E.
Mercury pressure, 1000 mm. Concentration of *o*-HPMC: ○, 0.400 mM; ●, 1.000 mM.

The slope of these plots indicates that the electrode process is totally irreversible. Thus the half-wave potential of the wave is expected to be constant and independent of the concentration of the electroactive species.[7] However, the half-wave potential shifts actually to negative with increasing concentration of *o*-HPMC. The first wave is abnormal in this respect.

The result of measurement of the electrocapillary curve indicates that a considerable adsorption takes place on the surface of DME in the range of potentials between the first and second waves (Fig. 3). This suggests that a reduction product of the first wave is adsorbed on the electrode surface and reduced further to non-adsorbable species at the potential of the second wave.

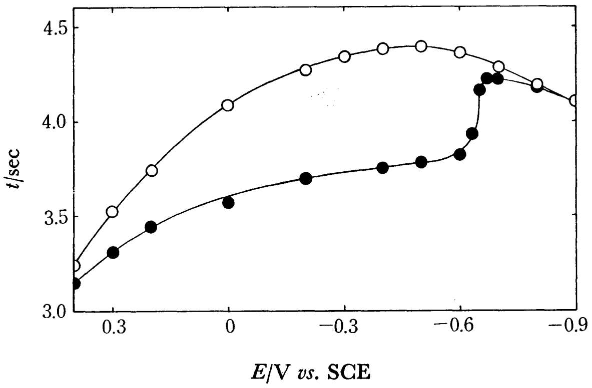

Fig. 3. Effect of *o*-HPMC on the electrocapillary curve. ○, nitric acid medium; ●, nitric acid medium+1.000 mM *o*-HPMC.

If this is the case, the electrode reaction at the second wave may be written as

$$\mathrm{A} + \mathrm{e} \xrightarrow{k_2} \mathrm{B} \tag{1}$$

where A is the reduction product of the first wave and adsorbable on the surface of DME, B the reduction product of the second wave and non-adsorbable, and k_2 the rate constant of the electrode process. The rate constant k_2 varies with the electrode potential E according to the equation

$$k_2 = k_2^\circ \exp\left[-\frac{\alpha_2 F}{RT}(E - E_2^\circ)\right] \tag{2}$$

where $E_2{}^\circ$ is the standard potential of reaction (1), k_2° the rate constant at E_2°, α_2 the transfer coefficient, F the Faraday constant, R the gas constant, and T the absolute temperature. The current of the second wave is given by

$$i^{II} = Fqk_2C_A{}^* \tag{3}$$

where i^{II} is $i^I - i_d{}^I$, q the mean surface area of DME, and $C_A{}^*$ the concentration of A at the electrode surface.

In order to account for the peculiar shape of the second wave we assume that A is a precipitate with very low solubility. Thus $C_A{}^*$ is given by

$$C_A{}^* = S_A \tag{4}$$

where S_A is the solubility of A. Introduction of Eqs. (2) and (4) into Eq. (3) results

$$i^{II} = FqS_Ak_2^\circ \exp\left[-\frac{\alpha_2 F}{RT}(E - E_2^\circ)\right]$$

This equation can be written in the form

$$E = E_2^\circ + \frac{2.303RT}{\alpha_2 F}\log FqS_Ak_2^\circ - \frac{2.303RT}{\alpha_2 F}\log i^{II} \tag{5}$$

It is evident from Eq. (5) that a plot of log i^{II} vs. E should produce a straight line with a reciprocal slope equal to $2.303\,RT/(\alpha_2 F)$. The plot constructed from observed polarograms is shown in Fig. 4. The reciprocal slope of the straight line is 0.167 V, consistent with the total irreversibility of reaction (1).

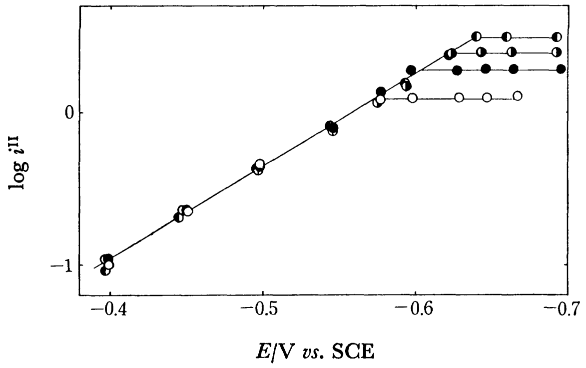

Fig. 4. Relation of log i^{II} vs. E.
Concentration of *o*-HPMC: ○, 0.400 mM; ●, 0.600 mM; ◑, 0.800 mM; ◐, 1.000 mM.

If A is a precipitate and is adsorbed on the electrode surface, it is expected that A inhibits the electrode process of the first wave. In the absence of inhibition the electrode reaction of the first wave may be written as

$$\mathrm{Z} + \mathrm{e} \xrightarrow{k_1} \mathrm{A} \tag{6}$$

where Z is *o*-HPMC, and k_1 is the rate constant of the electrode reaction in the absence of inhibition. The rate constant k_1 varies with E as given by

$$k_1 = k_1^\circ \exp\left[-\frac{\alpha_1 F}{RT}(E - E_1^\circ)\right] \tag{7}$$

where E_1° is the standard potential of reaction (6), k_1° the rate constant at E_1°, and α_1 the transfer coefficient. If k_1 varies according to Eq. (7), the electrode potential

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[7] J. Heyrovský and J. Kůta, "Principles of Polarography," Academic Press, New York, N. Y. (1966), p. 213.

is given by

$$E = E_1^\circ + \frac{RT}{\alpha_1 F}\ln 0.886k_1^\circ D_Z^{-1/2}t^{1/2} + \frac{RT}{\alpha_1 F}\ln\frac{i_d^I - i^I}{i^I} \qquad (8)$$

where t is the drop time of DME, and D_Z the diffusion coefficient of Z.[7)]

In the presence of inhibition the electrode reaction at the surface covered with A proceeds with the rate constant k_{1c}, differing from that at free surface. As a first approximation, the effective rate constant k_{ef} can be written as

$$k_{ef} = k_1(1-\Theta) + k_{1c}\Theta \qquad (9)$$

where Θ is the mean surface fraction of the electrode covered with A.[8)] The rate constant k_{1c} is given by

$$k_{1c} = k_{1c}^\circ \exp\left[-\frac{\alpha_{1c}F}{RT}(E-E_1^\circ)\right] \qquad (10)$$

where k_{1c}° is the rate constant at E_1°, and α_{1c} the transfer coefficient at the covered surface. Substituting k_{ef} for k_1 in the derivation of Eq. (8) one obtains

$$E = E_1^\circ + \frac{RT}{\alpha_1 F}\ln 0.886k_1^\circ D_Z^{-1/2}t^{1/2} + \frac{RT}{\alpha_1 F}\ln\left[1-\left(1-\frac{k_{1c}}{k_1}\right)\Theta\right] + \frac{RT}{\alpha_1 F}\ln\frac{i_d^I - i^I}{i^I} \qquad (11)$$

The half-wave potential is given by

$$E_{1/2} = E_1^\circ + \frac{RT}{\alpha_1 F}\ln 0.886k_1^\circ D_Z^{-1/2}t^{1/2} + \frac{RT}{\alpha_1 F}\ln\left[1-\left(1-\frac{k_{1c}}{k_1}\right)\Theta\right]_{1/2} \qquad (12)$$

where the subscript 1/2 indicates the value at the half-wave potential. The first and second terms in the right-hand side are independent of the concentration of *o*-HPMC, whereas the third term becomes zero by decreasing the concentration to zero.

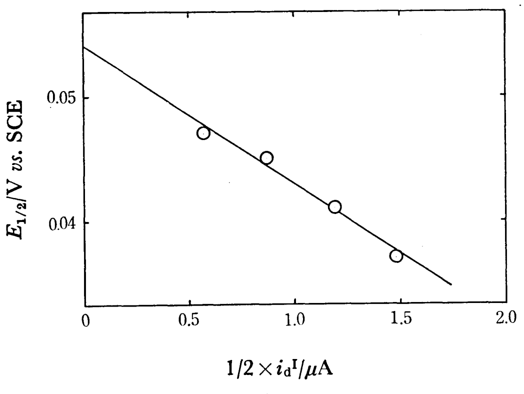

Fig. 5. Relation of $E_{1/2}$ *vs.* $i_d^I/2$.
Mercury pressure, 1000 mm.

The observed $E_{1/2}$ shifts linearly to negative by increasing the current at $E_{1/2}$, *i.e.* $i_d^I/2$, as shown in Fig. 5. One may write as

$$E_{1/2} = a + b(i_d^I/2) \qquad (13)$$

where a and b are constants. Comparison of Eqs. (12) and (13) results

$$b\left(\frac{i_d^I}{2}\right) = \frac{RT}{\alpha_1 F}\ln\left[1-\left(1-\frac{k_{1c}}{k_1}\right)\Theta\right]_{1/2} \qquad (14)$$

The fraction of covered surface increases proportionately with the amount of A on the surface of DME, which is proportional to $i^I t$. Hence Θ is given by

$$\Theta = \frac{si^I t}{q} \qquad (15)$$

where s is a proportionality constant.

By introducing Eq. (15) into Eq. (14), expanding the logarithm, and retaining only the first term, one get

$$b\left(\frac{i_d^I}{2}\right) = -\frac{RTst}{\alpha_1 Fq}\left[1-\left(\frac{k_{1c}}{k_1}\right)_{1/2}\right]\frac{i_d^I}{2} \qquad (16)$$

where

$$\left(\frac{k_{1c}}{k_1}\right)_{1/2} = \frac{k_{1c}^\circ}{k_1^\circ}\exp\left[\frac{(\alpha_1-\alpha_{1c})F}{RT}(E_{1/2}-E_1^\circ)\right] \qquad (17)$$

Division of Eq. (16) by $i_d^I/2$ results

$$b = -\frac{RTst}{\alpha_1 Fq}\left[1-\left(\frac{k_{1c}}{k_1}\right)_{1/2}\right] \qquad (18)$$

Since the half-wave potential of a totally irreversible wave is more negative than the standard potential of the reaction, $E_{1/2}-E_1^\circ$ is not equal to zero. Hence the right-hand side of Eq. (18) does not generally remain constant. To keep this remaining constant one must conclude that

$$\alpha_1 - \alpha_{1c} = 0 \qquad (19)$$

By expansion of the logarithm and introduction of Eqs. (15) and (19), the third term in the right-hand side of Eq. (11) can be approximately written as

$$\frac{RT}{\alpha_1 F}\ln\left[1-\left(1-\frac{k_{1c}}{k_1}\right)\Theta\right] = -\frac{RTst}{\alpha_1 Fq}\left(1-\frac{k_{1c}^\circ}{k_1^\circ}\right)i^I \qquad (20)$$

Combination of this with Eq. (11) yields

$$E = E_1^\circ + \frac{2.303RT}{\alpha_1 F}\log 0.886k_1^\circ D_Z^{-1/2}t^{1/2} - \frac{RTst}{\alpha_1 Fq}\left(1-\frac{k_{1c}^\circ}{k_1^\circ}\right)i^I + \frac{2.303RT}{\alpha_1 F}\log\frac{i_d^I - i^I}{i^I} \qquad (21)$$

The half-wave potential is now given by

$$E_{1/2} = E_1^\circ + \frac{2.303RT}{\alpha_1 F}\log 0.886k_1^\circ D_Z^{-1/2}t^{1/2} - \frac{RTst}{\alpha_1 Fq}\left(1-\frac{k_{1c}^\circ}{k_1^\circ}\right)\frac{i_d^I}{2} \qquad (22)$$

Rearranging Eq. (21) one has

$$E + \frac{RTst}{\alpha_1 Fq}\left(1-\frac{k_{1c}^\circ}{k_1^\circ}\right)i^I = E_1^\circ + \frac{2.303RT}{\alpha_1 F}\log 0.886k_1^\circ D_Z^{-1/2}t^{1/2} + \frac{2.303RT}{\alpha_1 F}\log\frac{i_d^I - i^I}{i^I} \qquad (23)$$

It is evident from Eq. (23) that a plot of log $(i_d^I - i^I)/i^I$ *vs.* $E + RTst(1-k_{1c}^\circ/k_1^\circ)i^I/(\alpha_1 Fq)$ should produce a straight line as far as q and t are kept constant. This is in agreement with results shown in Fig. 6, where a value of 0.011_1 V μA^{-1}, calculated from the slope of the straight line in Fig. 5, is used for $RTst(1-k_{1c}^\circ/k_1^\circ)/(\alpha_1 Fq)$. A value of 0.081 V is obtained for the reciprocal slope of the plot, which is given as $2.303RT/(\alpha_1 F)$ in Eq. (23). This is in accord with the assumption of total irreversibility of reaction (6).

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8) J. Heyrovský and J. Kůta, "Principles of Polarography," Academic Press, New York, N. Y. (1966), p. 307.

TABLE 1. COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE HALF-WAVE POTENTIAL OF *o*-HPMC[a)]

Mercury pressure mm	Drop time ratio[b)]	$i_d^{\mathrm{I}}/2$ μA	$\Delta E_{1/2}$[c)] V	$E_{1/2}$ *vs.* SCE, V Calcd	Obsd
1000	1	1.49	0	(0.036)	0.036
700	1.423	1.24	0.003	0.039	0.038
500	2.000	1.07	0.005	0.041	0.039

a) Concentration of *o*-HPMC, 1.000 mM.
b) The ratio of drop time to the one at mercury pressure of 1000 mm, calculated from the ratio of mercury pressure.
c) The difference between $E_{1/2}$ and the one at mercury pressure of 1000 mm, calculated according to Eq. (22).

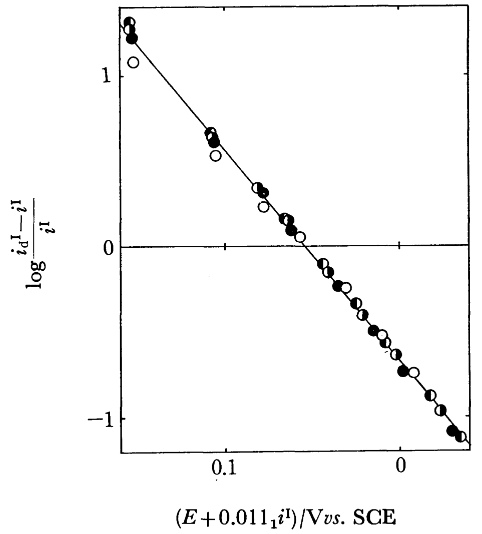

Fig. 6. Relation of log $(i_d^{\mathrm{I}} - i^{\mathrm{I}})/i^{\mathrm{I}}$ *vs.* $E+0.011_1\, i^{\mathrm{I}}$.
Mercury pressure, 1000 mm. Concentrations are same as in Fig. 4.

The half-wave potential shifts to positive when *t* increases. As shown in Table 1, the observed results are in good agreement with theoretical prediction given by Eq. (22).

The results support the assumptions that the first wave is inhibited by a reduction product adsorbed on the surface of DME as solid particles, and that the adsorbed precipitate is reduced at the second wave. Benesch and Benesch reported that an organomercury free radical RHg· is formed by one-electron reduction of organomercury compound RHgX.[9)] At present we are not certain whether $HOC_6H_4Hg\cdot$ corresponds to the sparingly soluble precipitate A or its dimer $(HOC_6H_4Hg)_2$ does. Because of its irreducibility $(HOC_6H_4)_2Hg$ should be excluded from possible reaction intermediates. However, a slow chemical reaction will produce $(HOC_6H_4)_2Hg$ from $HOC_6H_4Hg\cdot$ or $(HOC_6H_4Hg)_2$ as a final product at the first wave. These considerations lead to the following mechanism:

First wave

$$HOC_6H_4HgCl + e \longrightarrow HOC_6H_4Hg\cdot(\text{or } 1/2 \text{ mol of its dimer}) + Cl^-$$

$$2HOC_6H_4Hg\cdot(\text{or } 1 \text{ mol of its dimer}) \longrightarrow (HOC_6H_4)_2Hg + Hg$$

Second wave

$$HOC_6H_4HgCl + e \longrightarrow HOC_6H_4Hg\cdot(\text{or } 1/2 \text{ mol of its dimer}) + Cl^-$$

$$HOC_6H_4Hg\cdot(\text{or } 1/2 \text{ mol of its dimer}) + H^+ + e \longrightarrow C_6H_5OH + Hg$$

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9) R. Benesch and R. E. Benesch, *J. Amer. Chem. Soc.*, **73**, 3391 (1951).