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Polarographic Anodic Wave of Hydrogen Peroxide in Alkaline Solutions

Kenji Kikuchi and Teisuke Murayama*
Shiga Prefectural Junior College, Hikone, Shiga 522
**Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432*

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The anodic reaction of hydrogen peroxide in alkaline solutions has been studied by the polarographic method. Polarograms were recorded in solutions with pH values ranging from 10.0 to 13.5. Hydrogen peroxide in alkaline solutions shows a one-step anodic wave at the dropping mercury electrode. The plot of half-wave potential against pH consists of three segments, each corresponding to a different value of $d(E_{1/2})/d(pH)$: -57 mV for the values of pH below 11.6, -29 mV for the pH range from 11.6 to 13.2, and 0 mV for the values of pH above 13.2 The limiting current is controlled by diffusion. It is concluded that the anodic wave corresponds to the formation of the species $[Hg(O_2H)(OH)]$.

Recently Honda *et al.* reported on the anodic reaction of hydrogen peroxide in alkaline solutions at the dropping mercury electrode.[1] They proposed a reaction mechanism given by:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (1)$$

$$HO_2^- \rightleftharpoons HO_2(a) + e^- \qquad (2)$$

$$OH^- \rightleftharpoons OH(a) + e^- \qquad (3)$$

$$HO_2(a) + OH(a) \rightleftharpoons O_2 + H_2O \qquad (4)$$

where (a) denotes the adsorbed state. Based on experimental observation, they concluded that the rate-determining step is Reaction 4. The present study, however, indicates that another interpretation is more appropriate.

Experimental

All chemicals used were of reagent grade. The water used for all solutions was prepared by distillation of deionized water with potassium permanganate. The concentration of hydrogen ions in solutions was controlled with acetate buffer (pH 3.5 to 5.6), phosphate buffer (pH 6.0 to 7.7 and 11.0 to 12.0), ammonia buffer (pH 8.8 to 11.0), and sodium hydroxide solution (above pH 12.0). Five one-thousandths of 1% gelatin was added as the maximum suppressor. The ionic strength of the test solutions was adjusted to 0.1 or 0.5 M with either sodium nitrate or sodium chloride. The pH value of the test solutions was measured by use of a TOA HM-5B pH meter with a TOA HG-4005 glass electrode. The concentration of hydrogen peroxide in the stock solution was determined by iodometry.[2]

Polarograms were recorded by a Yanagimoto Model P8 polarograph. The cell used was of a beaker type. A saturated calomel electrode (SCE) was used as a reference electrode. The dropping mercury electrode (DME) had the following characteristics (in 0.5 M sodium chloride solution at zero applied potential *vs.* SCE and at a mercury head of 80.0 cm): the rate of flow of mercury (m), 2.338 mg/s; the drop time (t), 3.88 s; the capillary constant ($m^{2/3}t^{1/6}$). 2.15 $mg^{2/3}s^{-1/2}$. All potentials reported in this paper were corrected for iR drop. The test solution was freed from oxygen by bubbling nitrogen through the solution for 50 minutes and thermostated at 20.0±0.1 °C. As soon as the DME was introduced into the test solution, the recording of polarograms was started; each was completed within 10 minutes. Changes in the concentration of hydrogen peroxide during the bubbling and the recording were found to be within 1% of the initial concentration.

Results

The anodic wave of hydrogen peroxide observed in the solutions with pH values below 10 was accompanied by a maximum, making any quantitative discussion impossible. Figure 1 shows typical polarograms obtained in solutions with pH values above 10. It illustrates that hydrogen peroxide produces a single anodic wave and that the wave shifts to negative potentials with increasing pH. Logarithmic plots of the wave are given in Fig. 2, where the experimental points form good straight lines with a reciprocal slope of 29 to 30 mV. In the construction of the plots the current was corrected by the residual current determined in the 0.1 or 0.5 M sodium nitrate solution, not by the one determined in a buffer solution as is usual. The reason for this procedure is that the buffer solution produces an anodic current due to the hydroxide ion which also participates in the anodic reaction of hydrogen peroxide, as will be shown later.

Figure 3 shows variations of the half-wave potential and limiting current with pH. The former consists of three segments with different slopes: -57 mV for values of pH below 11.7, -29 mV for the pH range from 11.7 to 13.2, and 0 mV for values of pH above 13.2. The limiting current decreases with increasing pH until the value of the pH becomes 11.7, then remains unchanged.

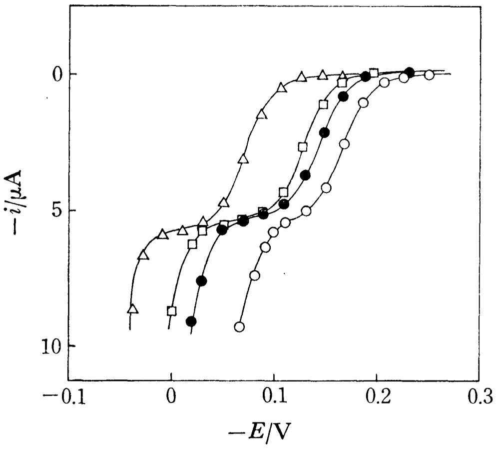

Fig. 1. Polarograms of 0.512 mM hydrogen peroxide. Ionic strengh, 0.5 M. pH: △, 10.08; □, 12.08; ●, 12.45; ○, 13.43.

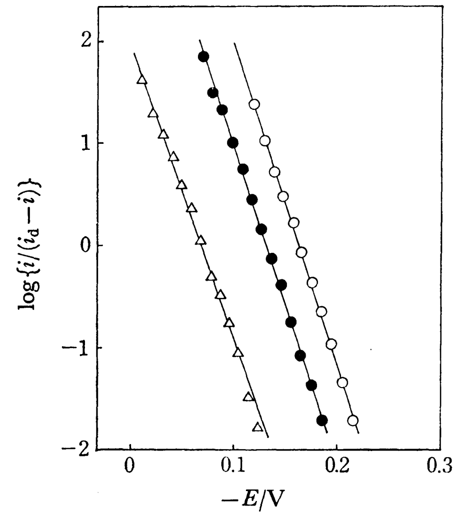

Fig. 2. Plot of $\log\{i/(i_d-i)\}$ *vs.* E.
Ionic strength, 0.5 M. Concentration of H_2O_2, 0.512 mM. pH: △, 10.82; ●, 12.26; ○, 13.43.

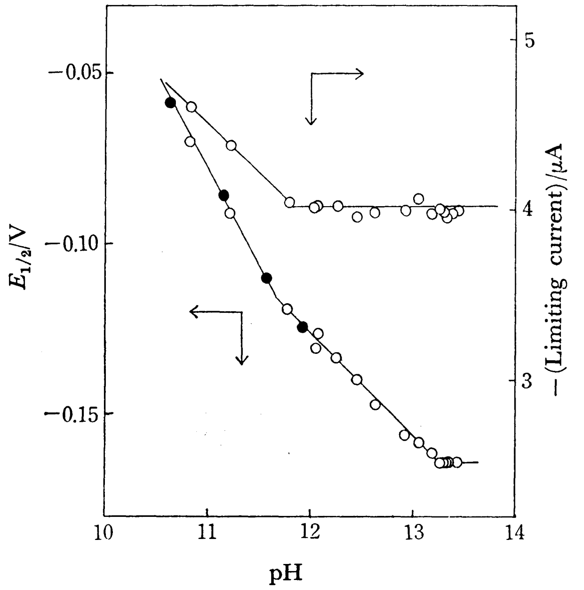

Fig. 3. Effect of pH on the half-wave potential and the limiting current.
Concentration of H_2O_2, 0.512 mM. Ionic strength: ○, 0.5 M; ●, 0.1 M.

When the pH of the solution was kept constant, the limiting current increased in proportion to the concentration of hydrogen peroxide and to the square root of the height of the mercury column. The temperature coefficient of the limiting current was $1.5\times 10^{-2}\ K^{-1}$. These facts indicate that the limiting current is controlled by diffusion. The diffusion current of 0.512 mM hydrogen peroxide, i_d (μA), can be represented by

$$i_d = -5.07 + 0.57\ (\mathrm{pH}-10) \tag{5}$$

for pH values below 11.7, as shown in Fig. 3.

Discussion

Honda *et al.* considered that the oxidation reaction of HO_2^- is responsible for the anodic wave of hydrogen peroxide. It is, however, much more natural to assume that this wave corresponds to the dissolution of electrode mercury and the formation of a mercury(II) complex, as given by

$$\mathrm{Hg} \rightleftharpoons \mathrm{Hg}^{2+} + 2e^- \tag{6}$$

$$\mathrm{Hg}^{2+} + \mathrm{HO_2}^- + \mathrm{OH}^- \rightleftharpoons [\mathrm{Hg(O_2H)(OH)}] \tag{7}$$

The species HO_2^- is supplied by the acid dissociation reaction of H_2O_2.

$$\mathrm{H_2O_2} \rightleftharpoons \mathrm{HO_2}^- + \mathrm{H}^+ \tag{8}$$

The potential of DME may be written as

$$E = E^\circ + \frac{RT}{2F}\ln\,[\mathrm{Hg}^{2+}]y \tag{9}$$

where E° is the standard potential of a mercuric-mercury electrode, R the gas constant, T the absolute temperature, F the Faraday constant, and y the activity coefficient of the mercuric ion. The concentration of mercuric ions at the electrode surface is given by

$$[\mathrm{Hg}^{2+}] = \frac{\left(\frac{[\mathrm{H}^+]}{K_a}+1\right)[\mathrm{H}^+][\mathrm{Hg(O_2H)(OH)}]}{\beta K_w([\mathrm{H_2O_2}]+[\mathrm{HO_2}^-])} \tag{10}$$

where K_a is the acid dissociation constant of H_2O_2, K_w the ionic product of water, and β the equilibrium constant of Reaction 7. Three equilibrium constants, K_a, K_w, and β, are defined as follows:

$$K_a = \frac{[\mathrm{H}^+][\mathrm{HO_2}^-]}{[\mathrm{H_2O_2}]}$$

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-]$$

$$\beta = \frac{[\mathrm{Hg(O_2H)(OH)}]}{[\mathrm{Hg}^{2+}][\mathrm{HO_2}^-][\mathrm{OH}^-]}$$

Introduction of Eq. 10 into Eq. 9 gives

$$E = E^\circ + \frac{RT}{2F}\ln\left\{\frac{y\left(\frac{[\mathrm{H}^+]}{K_a}+1\right)[\mathrm{H}^+]}{\beta K_w}\sqrt{\frac{D_1}{D_2}}\right\} + \frac{RT}{2F}\ln\frac{i}{i_d-i} \tag{11}$$

where i is the anodic current, i_d the anodic diffusion current, D_1 the common diffusion coefficient of species H_2O_2 and HO_2^-,[3] and D_2 the diffusion coefficient of the complex $[Hg(O_2H)(OH)]$. Equation 11 shows that a logarithmic plot should produce a straight line with the reciprocal slope of 29 mV if the solution is well-buffered with respect to hydrogen ions. Figure 2 shows that this is the case. The limiting current decreases with increasing pH in the range of pH values below 11.7. This indicates that the diffusion coefficient of HO_2^- is smaller than that of H_2O_2. A strong hydration caused by the charge on the HO_2^- ion may be responsible for this difference between the diffusion coefficients.

By introduction of the relation $i=i_d/2$ into Eq. 11 the half-wave potential at 20 °C becomes

$$E_{1/2} = E^\circ + \frac{0.058}{2}\log\left\{\frac{y\left(\frac{[\mathrm{H}^+]}{K_a}+1\right)[\mathrm{H}^+]}{\beta K_w}\sqrt{\frac{D_1}{D_2}}\right\} \tag{12}$$

When $[\mathrm{H}^+]\gg K_a$, Eq. 12 becomes

$$E_{1/2} = E^\circ + \frac{0.058}{2}\log\frac{y}{\beta K_a K_w}\sqrt{\frac{D_1}{D_2}} - 0.58\,\mathrm{pH} \tag{13}$$

where the activity coefficient of the hydrogen ion is assumed to be unity. Because of Eq. 5 and the proportionality of $D_1^{1/2}$ to i_d, Eq. 13 may be rewritten as

$$E_{1/2} = E^\circ + \frac{0.058}{2}\log\frac{\alpha y}{\beta K_a K_w D_2^{1/2}} - 0.059\mathrm{pH} \tag{14}$$

In this equation α is a proportionality constant. When $[\mathrm{H}^+] \ll K_a$, Eq. 12 becomes

$$E_{1/2} = E^\circ + \frac{0.058}{2}\log\frac{y}{\beta K_w}\sqrt{\frac{D_1}{D_2}} - \frac{0.058}{2}\mathrm{pH} \tag{15}$$

When pH is chosen as the independent variable, Eqs. 14 and 15 represent two straight lines. These straight lines intersect at the point whose pH value is equal to $\mathrm{p}K_a$.

Equations 14 and 15 agree well with the experimental results shown in Fig. 3, except for a few points obtained in the solutions with pH values above 13.2. The abscissa of the intersection is 11.65, consistent with the value 11.65 reported for $\mathrm{p}K_a$ of hydrogen peroxide by Evans and Uri.[4)]

Figure 3 shows that the half-wave potential deviates from the linear relation given by Eq. 13 above pH 13.2, although the points measured in this range are very few. Experimental difficulty prevented any measurements in solutions with higher pH values. Hence it is impossible to speculate on the electrode process above pH 13.2, at least at present.

References

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4) M. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 230 (1949).