Voltammetry of Nitrite at the Stationary and Rotated Platinum-Wire Electrodes

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The oxidation-reduction of nitrite-nitrate system has been investigated from the electrochemical standpoint[1]. Most of these investigations, however, were limited to the measurement and the discussion of equilibrium potentials of the system, but gave little information of the mechanism of the electrode reaction. Recently K. Vetter[2] studied the subject from the standpoint of electrode kinetics and proposed a mechanism for the electrode processes at the platinum electrode. He assumed the following steps:

$$H^+ + NO_3^- \rightleftarrows HNO_3 \qquad (1)$$

$$HNO_3 + HNO_2 \rightleftarrows N_2O_4 + H_2O \qquad (2)$$

$$N_2O_4 \rightleftarrows 2NO_2 \qquad (3)$$

$$NO_2 + e^- \rightleftarrows NO_2^- \qquad (4)$$

$$NO_2^- + H^+ \rightleftarrows HNO_2 \qquad (5)$$

and concluded that the reactions given in eqs. (2) and (4) must be rate-determining. Although his interpretation seemed fairly satisfactory as far as his experimental conditions were concerned, his data were restricted only to those obtained in nitric acid of more than 1 M in concentration.

Since his method was quite different from the conventional voltammetry, the investigation of the oxidation of nitrite at the platinum electrode was carried out from the voltammetric standpoint and has been presented in the present paper. From the theoretical consideration of observed current-voltage curves, the assumptions proposed by Vetter for the oxidation-reduction of nitrite-nitrate system have been verified in the solution with and without nitrate or nitric acid. The method was also applied to the determination of a minute quantity of nitrite in potassium nitrate with a good result.

Experimental

Apparatus.—A manual polarograph[3] was used for the measurement of current-voltage curves. The current was measured in terms of the iR drop across the 10,000 ohm precision fixed resistance in series with the electrolysis cell by means of potentiometer, or measured directly with

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[1] R. Ihle, *Z. physik. Chem.*, **19**, 577 (1896); W. C. Moore, *J. Am. Chem. Soc.*, **35**, 333 (1913); H. Pick, *Z. Elektrochem. angew. physik. Chem.*, **26**, 183 (1920); **28**, 56 (1922); A. Klemenc and E. Hayek, *Z. anorg. allgem. Chem.*, **186**, 181 (1930); H. Bode, ibid., **195**, 201 (1931); R. G. Monk and H. J. T. Ellingham, *J. Chem. Soc.* (*London*), **1935**, 125.

[2] K. Vetter, *Z. physik. Chem.*, **194**, 199 (1950).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Publishers, New York (1952) Vol. I, p. 297.

a galvanometer. Potentials were referred to a saturated caromel electrode (S. C. E). All experiments were carried out in a thermostat of 25.00±0.05°C. All current-voltage curves are corrected for the residual current.

Two platinum-wire electrodes of 0.6 mm. in diameter and approximately 5 mm. in length were used. One was used for the stationary electrode, which had 0.1033 cm^2 of geometrical surface area and gave a steady state diffusion current of 4.35 μ amp./millimole/l. for the oxidation of potassium ferrocyanide in deaerated 0.1 M potassium chloride solution. The other, which had 0.0944 cm^2 of geometrical surface area, was used for the rotated electrode. Being rotated at 650 r. p. m., it yielded diffusion currents of 9.90 μ amp./millimole/l. for the oxidation of ferrous ion in deaerated 0.1 M hydrochloric acid, and also 10.00 μ amp./millmole/l. for the reduction of ferric ion in the same medium.

Reagents.—A standard solution of nitrite was prepared by dissolving recrystallized potassium nitrite in distilled water free from oxygen, the concentration of which was determined volumetrically with the standardized solutions of potassium permanganate and sodium oxalate[4].

Pretreatment of Electrode.—The electrodes were treated in hot 10 M nitric acid for ten minutes and washed thoroughly with distilled water. Then, the electrodes were polarized at 0 volt vs. S. C. E. in the supporting electrolyte to eliminate the oxide film which might have formed on the surface upon the treatment with nitric acid[5].

Results

With Stationary Electrode.—Current-voltage curves were obtained with the stationary electrode in supporting electrolytes of pH between 0 and 9 in the absence of oxygen by measuring from negative to positive potentials. Typical examples obtained with 0.960×10^{-3} M potassium nitrite are given in Fig. 1. The half-wave potentials and the limiting currents are indicated in Table I. In the solutions of pH 0 to 3, the half-wave potentials were found to shift to more negative potentials by some 60 mV. with the increase of unit pH. At higher pH's, they tend to be independent of pH and approach to a limiting value. This fact, however, could not be clearly recognized, because the current-voltage curves were gradually drawn out with increasing pH of solutions. This may be attributed to the formation of the oxide film on the surface of platinum[5]. The potentials of the oxide film formation shift to negative potentials by 60 mV. with the increase of unit pH[5], whereas those of nitrite waves remain constant in solutions of higher pH.

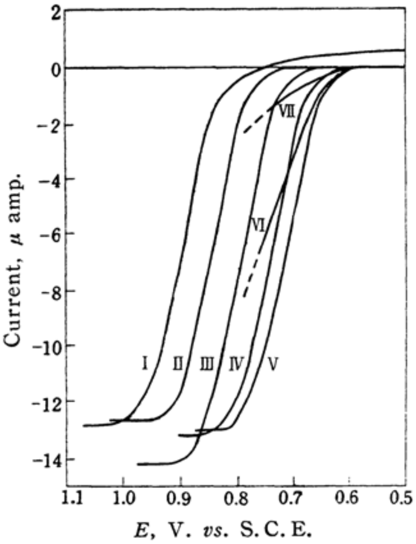

Fig. 1. Current-voltage curves of 0.960×10^{-3} M potassium nitrite obtained with the sationary electrode, being measured from negative to positive potentials in supporting electrolytes: I, 1 M HNO_3; II, 0.1 M HNO_3; III, 0.01 M NHO_3+0.09 M KNO_3; IV, citric acid-phosphate buffer of pH 3; V, acetate buffer of 4.75; VI, citric acid-phosphate buffer of pH 6 and VII, 0.05 M borax of pH 9.23.

TABLE I

ANODIC LIMITING CURRENTS AND HALF-WAVE POTENTIALS OF 0.960×10^{-3} M POTASSIUM NITRITE IN VARIOUS SUPPORTING ELECTROLYTES MEASURED WITH THE STATIONARY PLATINUM-WIRE ELECTRODE

Supporting Electrolyte	pH	i_l, μ amp.	$E_{1/2}$, V. $vs.$ S. C. E.
1 M HNO_3	0	−12.80	0.892
0.5 M HNO_3+0.5 N H_2SO_4	0	−13.50	0.885
0.1 M HNO_3+0.9 N H_2SO_4	0	−12.08	0.877
0.1 M HNO_3	1	−12.70	0.841
0.1 N H_2SO_4	1	−11.26	0.836
0.01 M HNO_3+0.09 M KNO_3	2	−14.14	0.786
Citric acid-phosphate buffer	3	−13.13	0.725
Acetate buffer	4.75	−13.0	0.719
Citric acid-phosphate buffer	6	−12.6	0.746

The oxide film formation also accounts for the difficulty in the measurement of limiting current. Even in 1 M nitric acid the limiting current plateau appeared at the potentials where the electrode surface can be oxidized. Although this difficulty was encountered, an almost linear relation was obtained between the limiting current and the concentration of nitrite added, as given in Fig. 2, which was obtained in 1 M nitric acid.

If it is assumed that the limiting current is controlled by the rate of diffusion of nitrite, it is possible to calculate the number of electrons involved in the electrode reaction, n, by the relation[6],

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[4] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", The MacMillan Co., New York (1952), p. 573.

[5] I. M. Kolthoff and Nobuyuki Tanaka, *Anal. Chem.*, **26**, 632 (1954).

[6] H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).

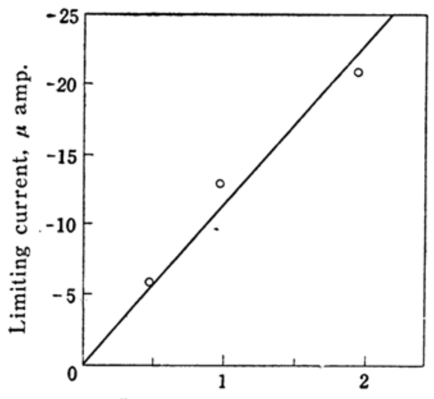

Fig. 2. Relation between limiting current and concentration of potassium nitrite in 1 M nitric acid measured with the stationary electrode.

$$i_a = \frac{AD}{l} nFC, \qquad (6)$$

where i_a represents the diffusion current, A, the surface area of the electrode, D, the diffusion coefficient, l, the effective thickness of diffusion layer, C, the concentration of the oxidizable or reducible substance and F, the Faraday constant. The diffusion coefficients of nitrite and ferrocyanide were calculated to be 1.92×10^{-5} and 0.74×10^{-5} cm²/sec., respectively, from the equivalent conductance at infinite dilution at 25°C. The diffusion current of nitrite was determined approximately 13 μ amp./millimole/l. averaging those obtained in various conditions, while that of ferrocyanide was 4.35 μ amp./millimole/l. in 0.1 M potassium chloride at the same electrode. Introducing those values into eq. (6) and assuming the identity of the effective thickness of diffusion layer for both electrode reactions[5], the number of electrons involved in the oxidation of nitrite was calculated to be approximately unity, from which electrode process of the oxidation of nitrite could be concluded as a one-electron reaction.

With Rotated Electrode.—Current-voltage curves were also obtained with the rotated electrode in supporting electrolytes of various pH's. Typical examples obtained with 0.960×10^{-4} M potassium nitrite are reproduced in Fig. 3, and the results are tabulated in Table II. A proportionality was found between the limiting current and the concentration as shown in Fig. 4.

TABLE II

ANODIC LIMITING CURRENTS AND HALF-WAVE POTENTIALS OF 0.960×10^{-4} M POTASSIUM NITRITE IN VARIOUS SUPPORTING ELECTROLYTES MEASURED WITH THE ROTATED PLATINUM-WIRE ELECTRODE AT THE RATE OF 650 R. P. M.

Supporting Electrolyte	pH	i_l, μ amp.	$E_{1/2}$, V. *vs.* S. C. E.
0.1 M HNO_3	1	−3.35	0.860
0.01 M HNO_3 + 0.09 M KNO_3	2	−3.36	0.810
Citric acid-phosphate buffer	3	−3.59	0.752
Acetate buffer	4.75	−4	—

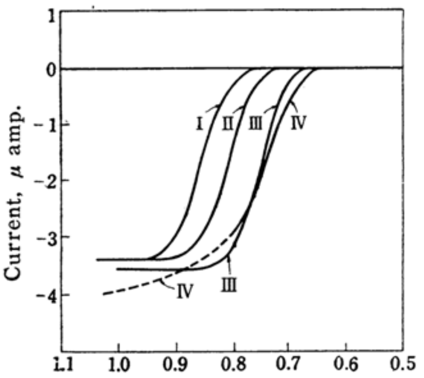

Fig. 3. Current-voltage curves of 0.960×10^{-4} M potassium nitrite obtained with the rotated platinum electrode at the rate of 650 r. p. m., being measured from negative to positive potentials in supporting electrolytes: I, 0.1 M HNO_3; II, 0.01 M HNO_3 + 0.09 M KNO_3; III, citric acid-phosphate buffer of pH 3 and IV, acetate buffer of pH 4.75.

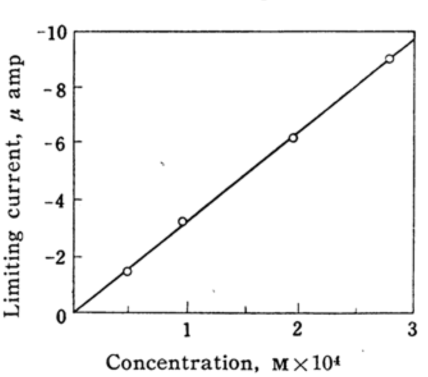

Fig. 4. Relation between limiting current and concentration of potassium nitrite in 0.1 N sulfuric acid measured with the rotated electrode at the rate of 650 r. p. m.

Discussion

The net reaction of oxidation-reduction of nitrite-nitrate system is represented as,

$$NO_2^- + H_2O \rightleftarrows NO_3^- + 2H^+ + 2e^-. \qquad (7)$$

The value of limiting current, however, suggested that the oxidation of nitrite at the platinum electrode must be a one-electron reaction. This can not be accounted for by eq. (7), but agrees with the findings by Vetter[2]. According to his proposal, the following reaction mechanism was set down:

$$HNO_2 \rightleftarrows H^+ + NO_2^-,\ K_{HNO_2} = 4.5\times10^{-4} \qquad (8)$$

$$NO_2 + e^- \rightleftarrows NO_2^-,\ E_0 = 0.650\ \text{V. } vs. \text{ S. C. E.} \qquad (9)$$

$$2NO_2 \rightleftarrows N_2O_4,\ K_2 = 8.79 \qquad (10)$$

$$N_2O_4+H_2O \rightleftarrows H^++NO_3^-+HNO_2,\quad K_1=2.82\times10^4 \tag{11}$$

where K_{HNO_2} is the dissociation constant of nitrous acid[7], K_2 and K_1 are the equilibrium constants of eqs. (10) and (11), respectively, and E_0 is the standard oxidation-reduction potential of $NO_2-NO_2^-$ system. The values of K_2, K_1 and E_0 were calculated from data given by Latimer[7].

In the electrode reactions represented with eqs. (8) to (11) the following conditions are considered:

(i) Nitrous acid and nitrite are in equilibrium at the surface of electrode according to eq. (8).

(ii) The potentials of oxidation of nitrite or nitrous acid are determined by the reaction given in eq. (9).

(iii) NO_2 formed by the oxidation of nitrite is in equilibrium with N_2O_4 at the surface of electrode according to eq. (10).

(iv) The reaction given in eq. (11) proceeds so slowly that the reproduction of nitrous acid at the surface of electrode can be neglected.

The reduction potential of reaction of eq. (8) is expressed with,

$$E=E_0+0.059\log\frac{[NO_2]}{[NO_2^-]}, \tag{12}$$

where, for simplicity, the concentration is employed rather than activity. If the sum of nitrous acid (i. e., potassium nitrite added) is represented with $\sum[HNO_2]$, the concentration of nitrite is given by

$$[NO_2^-]=\sum[HNO_2]\Big/\left\{1+\frac{[H^+]}{K_{HNO_2}}\right\}. \tag{13}$$

Introducing eq. (13) into eq. (12), the equation,

$$E=E_0+0.059\log\left\{1+\frac{[H^+]}{K_{HNO_2}}\right\}\frac{[NO_2]}{\sum[HNO_2]}, \tag{14}$$

is obtained. As NO_2 is in equilibrium with N_2O_4 at the surface of electrode, the following relations must be fulfilled when b mole/l. of total nitrite, $\sum[HNO_2]$, is oxidized at the electrode surface:

$$[NO_2]+2[N_2O_4]=b,$$
$$[N_2O_4]/[NO_2]^2=K_2,$$

then,

$$[NO_2]^2+\frac{[NO_2]}{2K_2}-\frac{b}{2K_2}=0. \tag{15}$$

The concentration of NO_2 calculated from eq. (15) would be introduced into eq. (14). When either nitrate or nitric acid is contained in the supporting electrolyte, some amounts of NO_2 and N_2O_4 which are formed by the reverse reactions of eqs. (10) and (9) may yield a reduction wave. This was proved from the current-voltage curve obtained in 1 M nitric acid, which gives a cathodic current as shown in Fig. 1. (Curve I in Fig. 1).

The consideration of the effect of nitric acid makes it possible to derive an equation for the composite wave of the oxidation-reduction of NO_2-NO_2^- system. If the total nitrite added, $\sum[HNO_2]$, is written as a, the concentration of nitrous acid $[HNO_2]$ is given by

$$[HNO_2]=a\Big/\left\{1+\frac{K_{HNO_2}}{[H^+]}\right\}. \tag{16}$$

In the electrolytic solution, HNO_2, NO_3^-, N_2O_4 and NO_2 are considered to be in equilibrium. Under the present conditions the concentration of N_2O_4 which is in equilibrium with NO_2 is negligibly small compared with that of NO_2 so that $\{2[NO_2]+[N_2O_4]\}$ equals approximately $2[NO_2]$. When x mole/l. of the total nitrite added (a) decreases to form N_2O_4 or NO_2 in equilibrium condition, the concentration of NO_2 is approximately equal to $2x$ mole/l., that is,

$$[NO_2]\fallingdotseq 2x, \tag{17}$$

and the total nitrite unchanged is equal to $(a-x)$ mole/l. Introducing these quantities into the product of equilibrium constants K_1 and K_2,

$$K_1\,K_2=\frac{[H^+][NO_3^-][HNO_2]}{[NO_2]^2}=\frac{[H^+][NO_3^-](a-x)}{(2x)^2\left\{1+\frac{K_{HNO_2}}{[H^+]}\right\}},$$

then

$$x^2+\frac{[H^+][NO_3^-]x}{4K_1K_2\left\{1+\frac{K_{HNO_2}}{[H^+]}\right\}}-\frac{[H^+][NO_3^-]a}{4K_1K_1\left\{1+\frac{K_{HNO_2}}{[H^+]}\right\}}=0 \tag{18}$$

are obtained.

Eq. (14) is now considered as a general formula of experssing the electrode potential of NO_2-NO_2^- system, if the values of $[HNO_2]$ and $[NO_2]$ therein are corrected for x, the latter being calculated from eq. (18). When neither nitrate nor nitric acid is contained in the supproting electrolyte, x becomes practially zero. Taking 0.960×10^{-3} M for a, the values for $E-E_0$ in eq. (14) were calculated at the point where the anodic current reaches one-tenth of the limiting current, i. e., $i=1/10\ i_l$, and where the concentration of the total nitrite $\{[NO_2^-]+[HNO_2]\}$ at the surface of electrode equals $9/10(a-x)$ and that of $\{2[NO_2]+[N_2O_4]\}$, $1/10\{(a-x)+2x\}$. These values are given in Table III. Introducing the potentials obtained experimentally at the point where $i=1/10\ i_l$ on the anodic

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[7] W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Inc., New York (1952), pp. 90-92.

TABLE III

STANDARD ELECTRODE POTENTIALS OF 0.960×10^{-3} M POTASSIUM NITRITE IN VARIOUS SUPPORTING ELECTROLYTES CALCULATED BY EQUATION (14)

Supporting Electrolyte	pH	$E-E_0$, V.	$E_{\text{obs.}}$, V. *vs.* S.C.E.	E_0, V. *vs.* S.C.E.
1 M HNO_3	0	0.154	0.839	0.685
0.1 M HNO_3	1	0.084	0.784	0.700
0.01 M HNO_3 + 0.09 M KNO_3	2	0.025	0.730	0.705
Citric acid-phosphate buffer	3	−0.026	0.682	0.708
Acetate buffer	4.75	−0.055	0.650	0.705
Citric acid-phosphate buffer	6	−0.056	0.663	(0.719)
			Mean,	0.701

part of the current-voltage curve, the values for E_0 were calculated as given in the last column of Table III. A constancy in E_0 values obtained in various supporting electrolytes apparently shows the electrode processes given in eqs. (8) to (11) correct.

A further confirmation of the electrode processes was attained in the comparison of current-voltage curves observed and those calculated theoretically. The potential values, E, at various points on the current-voltage curves were calculated at pH 0 and 2 with eqs. (14) and (18). For the values for E_0, +0.70 V. *vs.* S.C.E. was employed. The limiting current of theoretical curves is assumed to equal that of the observed one. A fair agreement between theoretical and observed curves is clearly seen in Fig. 5. The deviation of the experimental curve from the theoretical one is rather remarkable in the cathodic part of the current voltage curve. This has not been clearly understood, but may be due to other slow reactions involved.

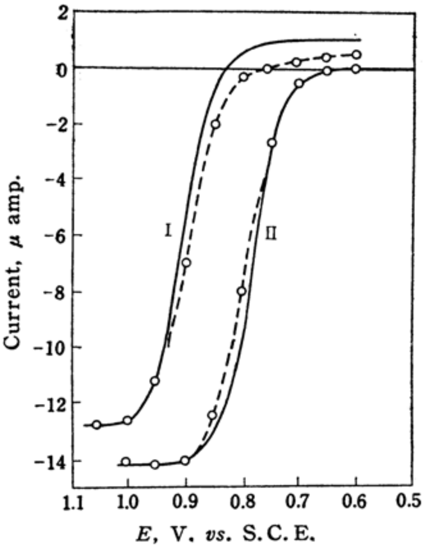

Fig. 5. Theoretical and observed current-voltage curves of 0.960×10^{-3} M potassium nitrite in supporting electrolytes: I, 1 M HNO_3 and II, 0.01 M HNO_3 + 0.09 M KNO_3. Solid lines indicate the theoretical curves and dotted lines, the observed ones obtained with stationary electrode.

It is predicted, from eq. (14), that at higher pH's the electrode potentials become independent of pH, because $\left\{1+\frac{[H^+]}{K_{HNO_2}}\right\}$ approaches to 1 with increasing pH of the solution. The half-wave potentials were calculated from eq. (14) with +0.70 V. *vs.* S.C.E. for E_0, which are plotted with pH as given in Fig. 6. A good agreement between the observed and calculated curves is clearly seen.

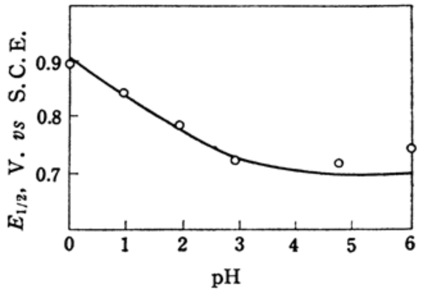

Fig. 6. Relation between the half-wave potential of anodic wave of 0.960×10^{-3} M potassium nitrite and pH of the solution: ○ indicate the experimental value observed with the stationary electrode.

In this calculation as well as in the calculation of the theoretical current-voltage curve, the value of +0.70 V. *vs.* S.C.E. was employed for E_0, which deviates by some 0.05 V. from the standard oxidation-reduction potential calculated with values given by Latimer[7]. The reason of deviation, however, has not been completely explained. The use of concentration instead of activity in the calculation could account for only a small part of the deviation. Some type of irreversibility seems to be involved in the electrode processes of the oxidation of nitrite.

When the electrode was rotated, the values of i_d/C for the anodic wave increased, whereas the slope of the current-voltage curves remained unchanged. S. S. Lord, Jr. and L. B. Rogers[8] stated, in their paper, that, if the electrode reaction is activation-controlled in nature, the value of i_d/C markedly increases and the current-voltage curve is drawn out when the electrode is rotated,

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[8] S. S. Lord, Jr. and L. B. Rogers, *Anal. Chem.*, **26**, 284 (1954).

while the rotation of the electrode gives only a small increase of i_a/C and also little influence to the slope of the current-voltage curve, if the electrode reaction is kinetic in nature. Since this criterion, however, has not been verified, no discussion should be presented here from this standpoint.

Analytical Application

The experimental result, that the limiting currents of the anodic wave obtained with the rotated electrode are proportional to the concentration of nitrite present, was applied to the determination of potassium nitrite contained in commercial potassium nitrate as impurity. A current-voltage curve of 1 M potassium nitrate was measured with the rotated electrode at the rate of 650 r. p. m. from negative to positive potentials. A small oxidation wave of nitrite was observed at +0.65 V. *vs.* S. C. E. to more positive potentials, the limiting current being 0.25 μ amp. measured at +0.95 V.

The measurement was also made in the same condition but after the addition of 0.960×10^{-5} M potassium nitrite with the limiting current of 0.62 μ amp. From the ratio of two values, the content of nitrite in potassium nitrate was calculated to be 0.0005_5% as potassium nitrate.

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