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Anodic Process of Thiosulfate at a Dropping Mercury Electrode

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In the anodic process of thiosulfate at a dropping mercury electrode, the formation of a species $Hg(S_2O_3)_3^{4-}$ is considerable even in dilute solution. An equation of current-potential curve is derived with proper consideration for the formation of the species. The successive stability constant of $Hg(S_2O_3)_3^{4-}$ was calculated to be 3×10^2 (at 25°C and an ionic strength of 0.2) by comparing the equation with experimental results.

A few decades ago, Kolthoff and Miller showed that the anodic wave of thiosulfate at a dropping mercury electrode (DME) corresponds to the formation of a complex ion $Hg(S_2O_3)_2^{2-}$.[1] More recently Nyman and Salazar investigated the same process.[2] They found that although a plot of log $i/(i_d-i)^2$ *vs.* E gave a straight line its reciprocal slope did not remain constant. The slope increased from 30 to 41 mV when the concentration of thiosulfate increased from 2×10^{-4} to 5×10^{-3} M. They attributed the slope increase to the formation of a species $Hg(S_2O_3)_3^{4-}$, which invalidated Eq. (9) in the paper by Kolthoff and Miller. Nyman and Salazar applied DeFord-Hume's method to evaluate stability constants of $Hg(S_2O_3)_2^{2-}$ and $Hg(S_2O_3)_3^{4-}$ from the observed shift in half-wave potential. However, they did not mention whether calculated values of constants were consistent with the behavior of the slope of the plot or not. In the following we have examined the relationship between the reciprocal slope of log plot and stability constants of the complex ions.

Results and Discussion

The potential of the dropping mercury electrode, E, may be written as

$$E = E^\circ + \frac{RT}{2F}\ln\gamma_1 + \frac{RT}{2F}\ln[Hg^{2+}] \qquad (1)$$

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[1] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, **63**, 1405 (1941).

[2] C. J. Nyman and T. Salazar, *Anal. Chem.*, **33**, 1467 (1961).

where E^0 is the standard potential of mercuric-mercury electrode, γ_1 is the activity coefficient of mercuric ion, and $\boldsymbol{R}$, T, and $\boldsymbol{F}$ are molar gas constant, absolute temperature, and Faraday, respectively. Square brackets indicate the concentration at the surface of DME. Mercuric ions are produced by an electrode process

$$\mathrm{Hg} = \mathrm{Hg}^{2+} + 2\mathrm{e} \tag{2}$$

and consumed by chemical reactions

$$\mathrm{Hg}^{2+} + 2\mathrm{S_2O_3}^{2-} = \mathrm{Hg(S_2O_3)_2}^{2-} \tag{3}$$

$$\mathrm{Hg}^{2+} + 3\mathrm{S_2O_3}^{2-} = \mathrm{Hg(S_2O_3)_3}^{4-} \tag{4}$$

which follow the electrode process. Formation of $\mathrm{Hg(S_2O_3)_4}^{6-}$ is not considered here, because its high negative charge forbids it. In the following we assume that reactions (2), (3), and (4) are reversible.

The average anodic current, i, may be written as

$$i = i_2 + i_3 \tag{5}$$

where i_2 and i_3 are the current parts relating to concentration of $\mathrm{Hg(S_2O_3)_2}^{2-}$ and $\mathrm{Hg(S_2O_3)_3}^{4-}$ at the electrode surface through

$$i_2 = \kappa_2[\mathrm{Hg(S_2O_3)_2}^{2-}]$$

$$i_3 = \kappa_3[\mathrm{Hg(S_2O_3)_3}^{4-}]$$

where κ_2 and κ_3 are the Ilkovic constants for $\mathrm{Hg(S_2O_3)_2}^{2-}$ and $\mathrm{Hg(S_2O_3)_3}^{4-}$, respectively. Because $[\mathrm{Hg}^{2+}]$ is too small compared with $[\mathrm{Hg(S_2O_3)_2}^{2-}]$ and $[\mathrm{Hg(S_2O_3)_3}^{4-}]$ at the potential of thiosulfate wave, the current part relating to $[\mathrm{Hg}^{2+}]$ is neglected in Eq. (5).

Equation (5) may be rewritten as

$$i = (\beta_2\kappa_2 + \beta_3\kappa_3 x)x^2[\mathrm{Hg}^{2+}] \tag{6}$$

where β_2 and β_3 are stability constants of $\mathrm{Hg(S_2O_3)_2}^{2-}$ and $\mathrm{Hg(S_2O_3)_3}^{4-}$, respectively, and x is the concentration of thiosulfate ions at the surface of DME. After rearrangement, we obtain the equation for $[\mathrm{Hg}^{2+}]$:

$$[\mathrm{Hg}^{2+}] = \frac{2\kappa_4 y}{\beta_2\kappa_2(1 + rx)x^2} \tag{7}$$

In the above κ_4 is the Ilkovic constant for thiosulfate ion, and

$$r = \frac{\beta_3\kappa_3}{\beta_2\kappa_2} \tag{8}$$

$$y = \frac{i}{2\kappa_4} \tag{9}$$

Combination of Eqs. (1) and (7) gives

$$E = E^0 + \frac{2.303\boldsymbol{R}T}{2\boldsymbol{F}}\log\frac{2\gamma_1\kappa_4}{\beta_2\kappa_2} + \frac{2.303\boldsymbol{R}T}{2\boldsymbol{F}}\log\frac{10^{-3}y}{(1 + rx)x^2} + \frac{6.909\boldsymbol{R}T}{2\boldsymbol{F}} \tag{10}$$

The last term of the right-hand side is added in order to compensate the factor 10^{-3} in the third term, which is introduced to displace the zero point of ordinate of the log plot for convenience. The third term represents the contribution by the current. For construction of a log plot according to Eq. (10) it is necessary to know numerical values of x at given potentials. This can be done as follows.

Fluxes of out-going species, $\mathrm{Hg(S_2O_3)_2}^{2-}$ and $\mathrm{Hg(S_2O_3)_3}^{4-}$, at electrode surface are given by

$$f_2 = \frac{i_2}{2\boldsymbol{F}} = \frac{\kappa_2[\mathrm{Hg(S_2O_3)_2}^{2-}]}{2\boldsymbol{F}} \tag{11}$$

$$f_3 = \frac{i_3}{2\boldsymbol{F}} = \frac{\kappa_3[\mathrm{Hg(S_2O_3)_3}^{4-}]}{2\boldsymbol{F}} \tag{12}$$

The flux of in-coming species $\mathrm{S_2O_3}^{2-}$ is given by

$$f_4 = \frac{i_d - \kappa_4 x}{\boldsymbol{F}} \tag{13}$$

where i_d is the diffusion current. There is no accumulation of $\mathrm{S_2O_3}$ group at the surface of DME. Hence

$$f_4 = 2f_2 + 3f_3 \tag{14}$$

Substituting Eqs. (11), (12), and (13) into Eq. (14) we obtain

$$i_d - \kappa_4 x = \kappa_2[\mathrm{Hg(S_2O_3)_2}^{2-}] + \frac{3}{2}\kappa_3[\mathrm{Hg(S_2O_3)_3}^{4-}]$$

$$= \frac{1}{2}\beta_2\kappa_2(2 + 3rx)x^2[\mathrm{Hg}^{2+}] \tag{15}$$

Combining this with Eq. (7), we get

$$x_0 - x = \frac{2 + 3rx}{1 + rx}y \tag{16}$$

where $x_0 = i_d/\kappa_4$.

Equation (16) is solved for x.

$$x = \frac{(x_0 - 3y)r - 1 + \sqrt{(x_0 - 3y)^2r^2 + 2r(x_0 - y) + 1}}{2r} \tag{17}$$

Numerical values of x can be calculated by this equation if r is known. However, it is not and we adopted the following procedure as we did previously.[3] First, values of x are calculated by Eq. (17) with a value of r arbitrarily chosen, and $\log 10^{-3}y/(1+rx)x^2$ is plotted against E. With an

TABLE 1. RECIPROCAL SLOPES OF LOG PLOTS CONSTRUCTED ACCORDING TO EQ. (10)
$r = 3\times10^2$

Concentration of thiosulfate ions mM	Reciprocal slope mV	e_0* *vs.* SCE V
0.522	30	0.143
1.044	30	0.143
1.566	30	0.141
2.088	30	0.142
3.17	29	0.145
4.23	30	0.144
5.29	30	0.143

* Potential at which $\log 10^{-3}y/(1+rx)^2$ becomes zero.

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[3] T. Murayama, *Sci. Rep. Tohoku Univ., Series I*, **45**, 98 (1961).

arbitrary value of r, the plot does not necessarily produce a straight line. Then the whole process is repeated with a slightly different value of r which is chosen to lessen deviation of the plot from a straight line. The process is repeated until the plot yields a straight line. It was found that the plot constructed from polarograms obtained at 25°C gave a straight line when a value of 3×10^2 was substituted for r. The accompanying table shows the reciprocal slope of plots constructed with this value of r and the potential at which $\log 10^{-3}\cdot y/(1+rx)x^2$ becomes zero. Fair agreement may be considered as an evidence in support of Eq. (10) and underlying assumptions.

The value of r is related to a stability constant ratio β_3/β_2, which is the successive stability constant of the tris complex, through Eq. (8). Evaluation of a ratio κ_3/κ_2 is necessary for calculation of the successive constant. It seems possible to determine the ratio by observing the change of diffusion current of mercuric ion with increasing concentration of thiosulfate ions in supporting electrolyte. However, this is not possible because mercuric ions react with thiosulfate ions to precipitate mercuric sulfide. The difficulty was overcome by substituting mercuric ions by mercuric cyanide in a buffer solution of an appropriate pH. Although the stability constant of mercuric cyanide, having a value of $10^{35.2}$ (activity constant),[4] is much larger than that of bis(thiosulfato)mercurate(II), it is still possible to convert the most part of mercuric cyanide to the bis complex, without precipitation of mercuric sulfide, by selecting pH of the buffer.

Measurement of diffusion current was carried out for 1 mM mercuric cyanide in the buffer of pH 5.26 with varying thiosulfate concentrations. Results are shown in Fig. 1 as the ratio of the diffusion current to that in the absence of thiosulfate. With a value of $10^{29.27}$ for the stability constant (activity constant) of bis(thiosulfato) complex,[2] the mole ratio of $Hg(S_2O_3)_2^{2-}$ to $Hg(CN)_2$ was calculated to be not less than 100 when the concentration of thiosulfate was 4.5 times as much as that of mercuric cyanide. Accordingly, the decrease of diffusion current beyond this point is due to the formation of tris(thiosulfato) complex. The formation of the tris complex seems incomplete even in the presence of thiosulfate of the highest concentration employed in this experiment (see Fig. 1). Although it is impossible to determine exactly the ratio κ_3/κ_2 from this experiment, it does not seem to deviate much from unity. If it is assumed to be equal to unity, the successive stability constant of tris(thiosulfato)mercurate(II) is calculated to be 3×10^2 (concentration constant). The activity constant was calculated to be $3._4\times 10$ from this and activity coefficients estimated by the Debye and Hückel equation without the extended term.[5]

$$\log \gamma_i = -\frac{0.358 z_i^2 (2\mu)^{1/2}}{1 + 10^8 a_i 0.2325 (2\mu)^{1/2}}$$

In this equation γ_i, z_i, and a_i are the activity coefficient, the electrovalency, and the ionic parameter, respectively, of the ion i, and μ is the ionic strength of the solution. Values of a_i assumed for thiosulfate ion, and bis- and tris(thiosulfato)mercurate(II) ions are 4, and 4 and 5 Å, respectively. These values were chosen for respective ions to be in accord with ions listed in Kielland's table with respect to charge type.[5,6]

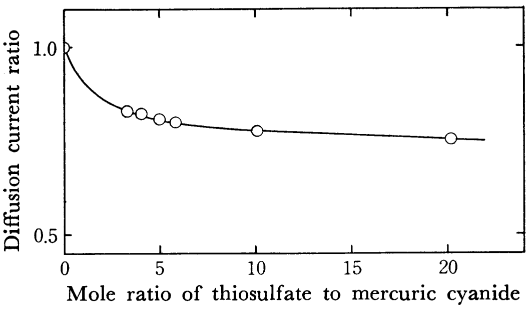

Fig. 1. Change of the ratio of the diffusion current of mercuric cyanide to that in the absence of thiosulfate.
Concentration of mercuric cyanide, 0.983 mM.

A value of 3×10 was calculated for the successive stability constant (activity constant) from β's at zero ionic strength given by Nyman and Salazar.[2] This is in good agreement with the value derived from the slope of the log plot in the present study.

Experimental

A manual polarograph was used for the measurement of the current-potential curve. The cell used was of a beaker type with a Hume and Harris type salt bridge.[7] To avoid contamination of chloride ion, the intermediate agar plug saturated with potassium chloride was replaced by one prepared with 1 M potassium nitrate. The dropping mercury electrode used had an m value of 1.865 mg/sec and a drop time of 4.28 sec, being measured in a deaerated 0.2 M sodium nitrate solution at the potential of the saturated calomel electrode with a head of mercury of 90.0 cm.

Stock solutions were prepared from redistilled water with chemicals of guaranteed grade. The sodium thiosulfate stock solutions were standardized against potassium iodate.[8] The mercuric cyanide stock solution

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[4] T. Murayama, *Sci. Rep. Tohoku Univ., Series I*, **45**, 111 (1961).

[5] G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. II, Elsevier Publishing Co., Amsterdam (1951), p. 680.

[6] J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

[7] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," Macmillan Co., New York, N. Y. (1952), p. 594.

was prepared by dissolving a weighed amount of solid salt in known volume of the solution. As supporting electrolyte, 0.2 M sodium nitrate solution was used for anodic wave, and an acetate buffer of pH 5.26, of which ionic strength was controlled to 0.2 with sodium nitrate, for cathodic wave. To the latter 0.005% gelatin was added as a maximum suppressor. The pH of the buffer was measured by a Hitachi-Horiba Model P pH meter.

All measurement were carried out in a thermostat kept at 25.0±0.1°C. All potentials were corrected for the internal resistance (iR drop) across the cell.