Determination of the Stability Constants of the Bis(selenocyanato)mercury(II) and Tris(selenocyanato)mercurate(II) Complexes by a Polarographic Method

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Selenocyanate ions give an anodic polarographic wave with a half-wave potential of 0.033 V (*vs.* SCE) at 25°C and 0.044 V at 35°C for a 1 mM solution. The electrode process is: $Hg \rightleftarrows Hg^{2+}+2e$, $Hg^{2+}+2SeCN^- \rightleftarrows Hg(SeCN)_2$, $Hg^{2+}+3SeCN^- \rightleftarrows Hg(SeCN)_3^-$. By means of an equation which gives the relation between the anodic current and electrode potential, stability constants of the bis(selenocyanato)mercury(II) and tris(selenocyanato)-mercurate(II) complexes (β_2 and β_3, respectively) were calculated from the polarograms. Values of $\log \beta_2$ and $\log \beta_3$ at ionic strength 0.3 are, respectively, 21.4_3 and 25.6_6 at 25°C, and 20.4_4 and 24.4_8 at 35°C.

We reported in previous papers on the determination of stability constants of mercuric cyanide, the tri- and tetra-cyanomercurate(II) ions, and the tris(thiosulfato)mercurate(II) ion by a polarographic method.[1,2] This paper describes the determination of stability constants of the bis(selenocyanato)mercury(II) and tris(selenocyanato)mercurate(II) complexes by the same method. The constant of the tris complex was given by Toropova,[3] but that of the bis complex does not seem to have been reported.

Experimental

Commercial potassium selenocyanate (Koso Kagaku-Yakuhin) was used without purification. The concentration of the potassium selenocyanate stock solution was determined by argentometric titration.[4]

The stock solution of mercuric chloride was prepared by dissolving a weighed amount of the reagent of guaranteed grade.

The supporting electrolyte was 0.3 M potassium nitrate. For the amperometric titration of mercuric chloride, 0.002% Triton X-100 was added as a maximum suppressor.

All solutions were prepared with redistilled water.

The dropping mercury electrode had the following characteristics (in 0.3 M potassium nitrate solution at zero applied potential *vs.* SCE and at 25°C): the rate of flow of mercury (m), 1.978 mg/sec; the drop time (τ), 4.13 sec; $m^{2/3}\tau^{1/6}=2.00$.

The cell and the salt bridge were described previously.[2] To prevent interaction between the oxidation product and the mercury accumulated on the bottom of the cell, it was necessary to start measurements of the anodic wave as soon as the dropping mercury electrode was introduced into test solutions which had been degassed with nitrogen. The measurements were made at 25.0 and 35.0±0.1°C. All potentials were corrected for the internal resistance (*iR* drop) across the cell.

Polarograms were measured by a Yanagimoto PA-102 polarograph operated manually. The bridge of the polarograph was calibrated by a precise potentiometer.

Results and Discussion

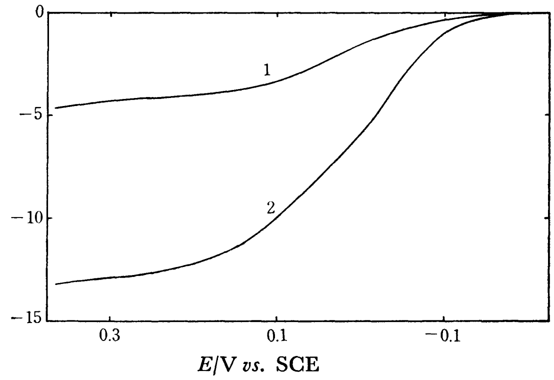

Fig. 1. Polarograms of the selenocyanate ion at 25°C. Corrected for the residual current. Supporting electrolyte, 0.3 M potassium nitrate. Concentration of potassium selenocyanate: 1; 1.142 mM, 2; 3.42_6 mM.

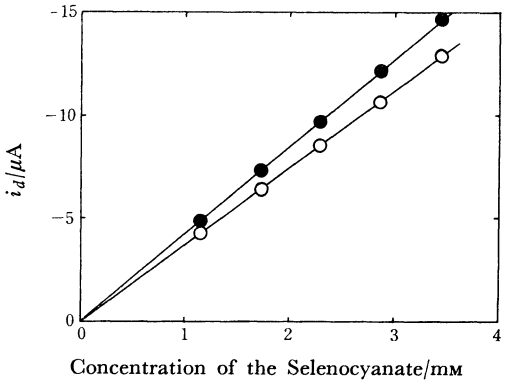

Fig. 2. Dependence of the diffusion current on the concentration of the selenocyanate. Temperature: ○; 25°C, ●; 35°C.

Fig. 1 shows anodic waves of the selenocyanate ion. The half-wave potential is 0.033 V *vs.* SCE at 25°C and 0.044 V at 35°C when the concentration of selenocyanate ions is 1 mM. The limiting current measured at a potential of 0.300 V *vs.* SCE is directly proportional to the concentration of selenocyanate ions, as shown in Fig. 2. The temperature coefficient of the limiting current is 1.2%.

By analogy with other anodic processes in which mercuric complexes are produced,[1,2,5] the overall electrode process of the selenocyanate ion may be

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[1] T. Murayama, *Sci. Rep. Tohoku Univ., Series I*, **45**, 84 (1961).

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

[3] V. F. Toropova, *Zhur. Neorg. Kihm.*, **1**, 243 (1956); *Chem. Abst.*, **51**, 4192i (1957).

[4] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, New York, N. Y. (1947), p. 280.

[5] N. Tanaka, K. Ebata, and T. Murayama, This Bulletin, **35**, 124 (1962).

considered to be composed of an electron transfer step

$$\mathrm{Hg} = \mathrm{Hg}^{2+} + 2\mathrm{e} \qquad (1)$$

and complex formation reactions:

$$\mathrm{Hg}^{2+} + 2\mathrm{SeCN}^- = \mathrm{Hg(SeCN)_2} \qquad (2)$$

$$\mathrm{Hg}^{2+} + 3\mathrm{SeCN}^- = \mathrm{Hg(SeCN)_3}^- \qquad (3)$$

Reactions (1), (2), and (3) are assumed to be reversible. The formation of $\mathrm{Hg(SeCN)_4}^{2-}$ and higher complexes are not considered here, because the polarographic behavior of the anodic wave is fully explained with reactions (1), (2), and (3) as shown in the following.

The potential E of the dropping mercury electrode is given by

$$E = E^0 + \frac{2.303RT}{2F}\log\frac{2\gamma_1\kappa_4}{\beta_2\kappa_2} + \frac{2.303RT}{2F}\log\frac{10^{-3}y}{(1+rx)x^2} + \frac{6.909RT}{2F} \qquad (4)$$

where E^0 is the standard potential of mercuric-mercury electrode, R the gas constant, T the absolute temperature, F the Faraday constant, γ_1 the activity coefficient of the mercuric ion, β_2 the stability constant of the bis(selenocyanato)mercury(II) complex, κ_2 the Ilkovič constant for the same complex, κ_4 the Ilkovič constant for the selenocyanate ion, x the concentration of selenocyanate ions at the surface of the dropping mercury electrode, and

$$r = \frac{\beta_3\kappa_3}{\beta_2\kappa_2} \qquad (5)$$

$$y = \frac{i}{2\kappa_4} \qquad (6)$$

Here β_3 and κ_3 are, respectively, the stability and Ilkovic constants of the tris(selenocyanato)mercurate(II) ion, and i is the anodic current. The value of x is calculated by

$$x = \frac{r(x_0-3y)-1+\sqrt{r^2(x_0-3y)^2+2r(x_0-y)+1}}{2r} \qquad (7)$$

where $x_0=i_d/\kappa_4$.[2] The value of κ_4 is 3.75 μA/mM at 25°C and 4.22 μA/mM at 35°C.

If the correct value of r is used, the logarithmic plot construed according to Eq. (4) should produce a straight line with a reciprocal slope equal to $2.303\,RT/(2F)$. By the method of trial and error the best value of r was determined to be 1.7×10^4 at 25°C, and 1.1×10^4 at 35°C. Figure 3 shows the logarithmic plot constructed from polarograms observed at 25°C. Table 1 shows the reciprocal slope of the plot constructed with these values of r and the potential e_0 where $\log 10^{-3}y(1+rx)^{-1}x^{-2}$ becomes zero. Fair agreement among the values in the respective columns is considered as evidence in support of the assumption that reactions (1), (2), and (3) are responsible for the anodic wave and that $\mathrm{Hg(SeCN)_4}^{2-}$ and higher complexes do not participate.

Values of β_2 and β_3 can be calculated from r and e_0, if E^0, γ_1, κ_2, and κ_3 are known. The standard electrode potential E^0 at 25°C was given as 0.8500 V *vs.* SHE (=0.6056 V *vs.* SCE) by Hietanen and Sillén.[6]

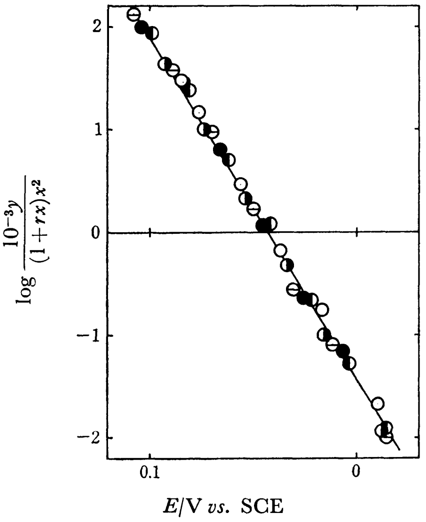

Fig. 3. Relation of $\log 10^{-3}y(1+rx)^{-1}x^{-2}$ *vs.* E at 25°C. $r=1.7\times10^4$. Concentration of the selenocyanate: ○; 1.142 mM, ●; 1.713 mM, ◑; 2.28_4 mM, ◐; 2.85_5 mM, ⊖; 3.42_6 mM.

TABLE 1. RECIPROCAL SLOPES OF LOGARITHMIC PLOTS CONSTRUCTED ACCORDING TO Eq. (4)

Temperature, 25°C; $r=1.7\times10^4$

Concentration of the selenocyanate mM	Reciprocal slope mV	e_0[a] *vs.* SCE V
1.142	30	0.041
1.713	30	0.042
2.28_4	30	0.044
2.85_5	30	0.041
3.42_6	29	0.044
	average	0.042

Temperature, 35°C; $r=1.1\times10^4$

Concentration of the selenocyanate mM	Reciprocal slope mV	e_0[a] *vs.* SCE V
1.142	31	0.050
1.713	31	0.051
2.28_4	31	0.050
2.85_5	30	0.053
3.42_6	30	0.051
	average	0.051

a) The potential where $\log 10^{-3}y(1+rx)^{-1}x^{-2}$ becomes zero.

The value at 35°C was calculated to be 0.6040 V *vs.* SCE from this and the entropy change of reaction (1) at 25°C.[7]

The activity coefficient of the mercuric ion was estimated through the Debye and Hückel equation without the extended term.[8]

$$\log\gamma_i = -\frac{Az_i^2(2I)^{1/2}}{1+Ba_i(2I)^{1/2}} \qquad (8)$$

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[6] S. Hietanen and L. G. Sillén, *Arkiv Kemi*, **10**, 103 (1956).

[7] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y. (1952), p. 30 and p. 176.

[8] G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y. (1961), p. 344.

In this equation γ_i, z_i, and a_i are the activity coefficient, the charge number, and the ionic size parameter, respectively, of the ion i, I is the ionic strength of the solution, and A and B are constants at a given temperature.[9] The value of a_i was assumed to be 5 Å for the mercuric ion.[10] The value of γ_1 was calculated to be 0.261 at 25°C and 0.255 at 35°C.

For the determination of κ_2 and κ_3, 25 m*l* of 0.260 mM mercuric chloride was titrated amperometrically with 11.42 mM potassium selenocyanate at a potential of -0.50 V *vs.* SCE. Figure 4 shows the titration curves. At first an approximate value of β_2 was estimated to be $10^{21.8}$ from Eq. (4) by introduction of the average value of e_0 at 25°C and of an approximate relation $\kappa_2=2\kappa_4$. From this and stability constants of chloro complexes of mercury(II),[11] it was concluded that the formation of the bis(selenocyanato)mercury(II) complex is quantitative if the total concentration of the selenocyanate is below 0.52 mM. The same holds at 35°C. Hence, 99% of the total mercury in the solution exists as bis(selenocyanato)mercury(II) when 1.13 m*l* of 11.42 mM potassium selenocyanate solution is added. From the diffusion current observed in the solution of this composition, the value of κ_2 was calculated to be 8.38 μA/mM at 25°C and 9.85 μA/mM at 35°C. Further addition of the selenocyanate causes little change in the diffusion current. This indicates that κ_3 is nearly equal to κ_2. In the following the ratio κ_3/κ_2 is assumed to be equal to unity. (At 35°C the ratio is not exactly equal to unity, but the discrepancy does not alter the result).

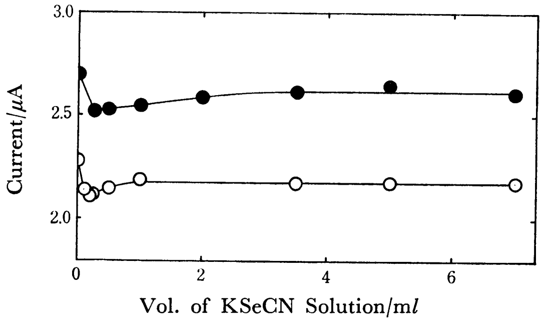

Fig. 4. Titration of 25 m*l* of 0.260 mM mercuric chloride with 11.42 mM potassium selenocyanate. Titrated at $E=-0.50$ V *vs.* SCE. Temperature: ○; 25°C, ●; 35°C.

By introduction of e_0 and other values given in the above into Eq. (4), the exact value of log β_2 was calculated to be 21.4_3 at 25°C and 20.4_4 at 35°C. From r, log β_2, and the relation $\kappa_3/\kappa_2=1$, the value of log β_3 was found to be 25.6_6 at 25°C and 24.4_8 at 35°C. Toropova gave 26.40 for log β_3 at 25°C.[3] Her value is greater than the value given in this study by about 0.7, the reason being not clear at present.

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[9] G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. II, Elsevier Publishing Co., Amsterdam (1951), p. 645.

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

[11] B. Lindgren, A. Jonsson, and L. G. Sillén, *Acta Chem. Scand.*, **1**, 475 (1947); *Chem. Abst.*, **42**, 2161 g (1948). Stability constants at 35°C were calculated from values at 25°C and enthalpy data given in the following: P. K. Gallagher and E. L. King, *J. Amer. Chem. Soc.*, **82**, 3510 (1960).