*The Reduction of Indium(III) in Thiocyanate Solutions at the Dropping Mercury Electrode**

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(Received June 4, 1964)

The effects of adsorbed ions or molecules on the rate of electrode processes have recently received considerable attention from many investigators. Frumkin was the first to point out the effect of adsorbed cations on the reduction wave of persulfate ions at the dropping mercury electrode. He discussed the dependence of the kinetics of the electrode processes on the surface layer structure.[1] Tamamushi et al. reported the apparent reversibility of the reduction of zinc(II), which increased with the increasing concentration of halide ions in the solution.[2,3]

The reduction wave of indium(III) at the dropping mercury electrode is irreversible and very much drawn-out in sodium nitrate or sodium perchlorate solutions. In potassium thiocyanate or potassium iodide solutions, on the other hand, indium(III) produces a reversible three-electron reduction wave in the potential region between -0.5 and -0.9 V. vs. saturated calomel electrode. Shirai[4,5] found that the polarographic behavior of an indium(III)-thiocyanate system was very peculiar; on the direct current (d. c.) polarogram of the system a minimum appeared at relatively negative potentials, and on the alternating current (a. c.) polarogram a negative admittance was observed in the potential region where the minimum appeared on the d. c. polarogram. However, she gave no explanation of the effect of thiocyanate ions on the reduction process of indium(III) at the electrode.

In the present paper, the acceleration effect of thiocyanate ions on the reduction of indium(III) at the dropping mercury electrode is presented, and the most plausible mechanism to explain the effect is proposed.

Experimental

D. c. and a. c. polarograms were obtained with a pen-recording polarograph, Yanagimoto Galvarecorder Y-GR 2 equipped with an automatic potential scanner. In the more accurate measurement of d. c. polarograms, a manual apparatus similar to that of Kolthoff and Lingane[6] was used. Current-time curves during the life of a mercury drop were recorded with a mechanical oscillograph, Yokogawa type N-6.[7] The faradaic impedance was determined by an impedance bridge used in the previous study.[8] The attachment of the bridge and the electrolysis cell were the same as described previously.[8] The impedance of the cell circuit was measured at the moment immediately before the detachment of the mercury drop. The electrode potential of the dropping mercury electrode (DME) was measured against a saturated calomel electrode (SCE), which was connected to the electrolytic solution through an agar-agar bridge containing 1 M potassium nitrate. In the impedance measurement, a Pt-spiral electrode of a large surface area was used as an auxiliary electrode. The rate of flow of mercury and the drop time of the DME used were 1.14 mg./sec. and 6.71 sec. respectively, being measured in an air-free 0.5 M sodium perchlorate solution containing 1×10^{-6} M polyoxyethylene lauryl ether (LEO) under an applied pressure of 50 cm. of mercury at open circuit. The dissolved oxygen in the electrolytic solution was removed by passing pure nitrogen gas through the solution for about 30 min. All measurements were carried out at 25.0±0.1°C.

A standard solution of indium(III) was prepared by dissolving a known amount of pure indium metal (Kanto Chemical Co. purity 99.99%) in a concentrated nitric acid. All the other chemicals were of an analytical reagent grade. Redistilled water was used for the preparation of solutions. Proper amounts of nitric acid were added to the electrolytic solutions (pH 2.7 to 3.7) to prevent indium(III) ions from the hydrolysis.

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* This was partly presented at the 18th International Congress of Pure and Applied Chemistry, Montreal (1961), under the title of "Minimum on the Current-potential Curve in Polarography," and also at the First Australian Conference on Electrochemistry, Sydney and Hobart (1963), under the title of "Effect of Adsorbed Ions and Molecules on the Rates of Electrode Processes at the Dropping Mercury Electrode."

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[1] A. Kalish and A. Frumkin, *J. Phys. Chem.* (*U. S. S. R.*), **28**, 1473 (1954).

[2] R. Tamamushi, K. Ishibashi and N. Tanaka, *Z. physik. Chem. N. F.*, **35**, 209 (1962).

[3] R. Tamamushi and N. Tanaka, ibid., **39**, 117 (1963).

[4] H. Shirai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1248 (1960).

[5] T. Takahashi and H. Shirai, *Rev. Polarog.* (*Kyoto*), **11**, 155 (1963).

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

[7] R. Tamamushi, S. Momiyama and N. Tanaka, *Anal. Chim. Acta*, **23**, 585 (1960).

[8] R. Tamamushi and N. Tanaka, *Z. physik. Chem. N. F.*, **28**, 158 (1961).

Results

D. c. polarograms of 1 mM of indium(III) which were obtained in the solutions containing various amounts of thiocyanate ions are given in Fig. 1, where $\bar{i}$ means the average current during the life of a mercury drop.* The ionic strength of the solution was adjusted to be 1.0 with sodium nitrate. In a sodium nitrate solution, the reduction wave of indium(III) was very much drawn-out, and a relatively small cathodic current was observed in the potential region of −0.5 to −0.9 V. vs. SCE (curve 1 in Fig. 1). The cathodic current in this potential region, however, was greatly increased by the addition of a minute amount of thiocyanate ions (curves 2 and 3 in Fig. 1).

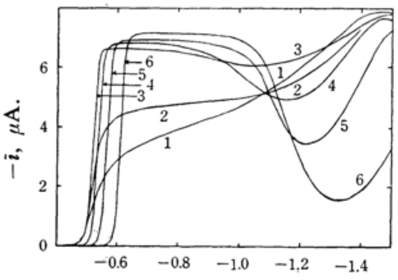

Fig. 1. Direct current polarograms of 1.0 mM In(NO$_3$)$_3$ in the solutions of ionic strength 1.0 (with NaNO$_3$) containing various concentrations of KSCN and 1×10^{-5} M LEO. The concentrations of KSCN are: (1) 0, (2) 0.0001, (3) 0.002, (4) 0.04, (5) 0.20, (6) 1.00 M.

The ionic species of indium(III) in the bulk of the solution do not change appreciably by the addition of such a small amount of thiocyanate ions.[9] Therefore, it is suggested that the effect of thiocyanate ions on the reduction of indium(III) at the dropping mercury electrode is mainly due to the change in the state of the electrode surface by the adsorption of thiocyanate ions. When the concentration of thiocyanate ions was larger than 0.02 M, a reversible three-electron reduction wave of indium(III) was completely developed in the potential region mentioned above. The half-wave potential $E_{1/2}$ of the reduction wave of indium(III) shifted to negative potentials with the increase in the concentration of potassium thiocyanate. Fig. 2 shows the relation between the $E_{1/2}$ and the logarithm of the concentration of potassium thiocyanate. The number of thiocyanate ions coordinated with an indium(III) ion was determined from the slope of this relation, with the result that two thiocyanate ions were coordinated in a 0.3 M potassium thiocyanate solution and four in a 0.8 M potassium thiocyanate solution.

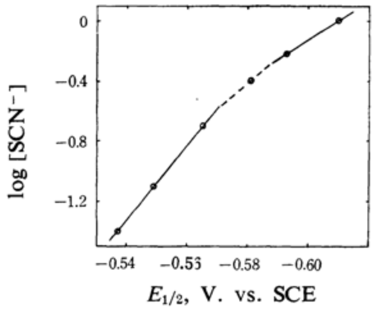

Fig. 2. Half-wave potentials of In(III)-SCN complexes as a function of the logarithm of the thiocyanate concentration.

At more negative potentials, a remarkable minimum appeared on the d. c. polarogram. It should be noticed that, in the In(III)-KSCN system, the minimum was observed in solutions of relatively high ionic strength. Therefore, the appearance of the minimum was unable to be explained on the basis of a simple electrostatic repulsion between the electrode surface and the depolarizing species.[10,11]

The current-time curves during the life of a mercury drop given in Fig. 3 were recorded with 1.0 mM indium(III) at 0.4 M potassium thiocyanate at various potentials in the region where the minimum appeared on the d. c. polarogram. These current-time curves were approximately represented by the relation:

$$\log|i| = k + \beta \log t$$

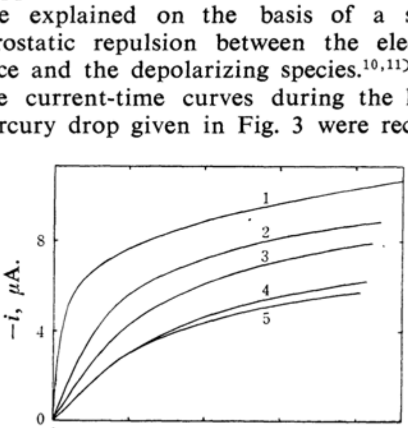

Fig. 3. Current-time curves of 1.0 mM In(NO$_3$)$_3$ in 0.4 M KSCN obtained at (1) −0.80, (2) −1.10, (3) −1.15, (4) −1.23, (5) −1.29 V. vs. SCE.

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* In this study, the sign of the cathodic current is taken as negative.

[9] T. P. Radhakrishnan and A. K. Sundaram, *J. Electroanal. Chem.*, **5**, 124 (1963).

[10] A. Frumkin, *Z. Electrochem.*, **59**, 807 (1955); *Trans. Faraday Soc.*, **55**, 156 (1959).

[11] A. Frumkin and N. Fedorovich, "Progress in Polarography," Vol. 1, Interscience Publishers, New York (1962), p. 223.

where i is the instantaneous current and k, the constant. The values of β were found to be beween 1/6 and 2/3. This suggests that the current in this potential region is partly controlled by some process of a kinetic nature.

An example of a. c. polarograms of 1.0 mM of indium(III) obtained in a 0.4 M potassium thiocyanate solution is shown in Fig. 4 (curve 1). A remarkable negative admittance was observed in the potential region where the d. c. current began to decrease. Such anomalies on the a. c. polarogram were also reported by Shirai for the In(III)-KSCN, Ni(II)-KSCN and $Cu(II)-NH_4NO_3$ systems.[3)] The negative admittance suggested the unique mechanism of the electroreduction of indium(III) at the electrode surface.

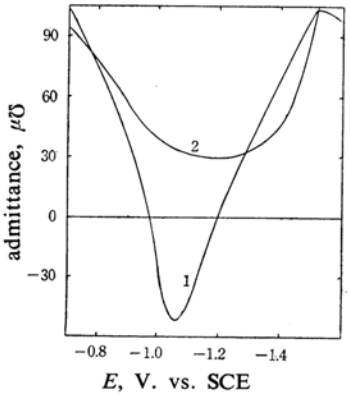

Fig. 4. Alternating current polarograms of (1) 1.0 mM $In(NO_3)_3$ in 0.4 M KSCN and (2) 0.4 M KSCN.

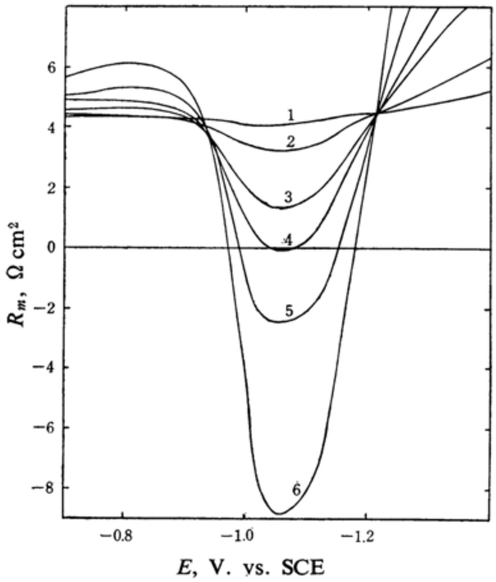

Fig. 5. The resistance component R_m of DME/ 1.0 mM $In(NO_3)_3-0.4$ M KSCN as a function of the electrode potential obtained at frequencies of (1) 1000, (2) 500, (3) 300, (4) 250, (5) 200 and (6) 150 cycles/sec.

The accurate measurement of the impedance of the electrode-solution interface, which was assumed to be represented with a series combination of the resistance, R_m, and the capacitance, C_m, was carried out by means of an impedance bridge. Fig. 5 shows the relation between the resistance component R_m of the impedance and the electrode potential. At relatively low frequencies, negative values of the resistance component were obtained in the potential region where the negative admittance was observed on the a. c. polarogram. The capacitance component C_m of the impedance was found to be almost the same as that of the supporting electrolyte solution in the whole potential region measured. From those measurements, it can be said that the anomalous negative admittance on the a. c. polarogram results from the negative value of the resistance component of the impedance.

Discussion

The electrical equivalent circuit of a polarizable electrode-solution interface can be represented with the circuit as shown in Fig. 6. If the impedance of the electrolytic cell is measured by an impedance bridge with the corresponding arm composed of the resistance R_m and the capacitance C_m in series, R_m is represented as follows:

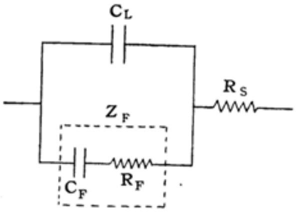

Fig. 6. Equivalent circuit of electrolytic system: C_L, double layer capacity; R_s, resistance of the cell; Z_F faradaic impedance; R_F, polarization resistance; C_F, electrolytic capacitance.

$$R_m - R_s = \frac{C_F{}^2 R_F}{\omega^2 C_L{}^2 C_F{}^2 R_F{}^2 + (C_F + C_L)^2} \qquad (1)$$

where ω is the angular frequency of the superimposed alternating current. In order to explain the experimental result that R_m is smaller than the resistance of the solution R_s, the polarization resistance R_F should be negative. The expression of R_F has been presented by Grahame[12,13)], and the simplest

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[12)] D. C. Grahame, *J. Electrochem. Soc.*, **99**. C 370 (1952).

[13)] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York (1954), p. 146.

expression is given as follows:

$$R_F=\left(\frac{\partial E}{\partial i}\right)(1+\kappa) \tag{2}$$

$$\kappa=\frac{1}{\sqrt{2}\,nFA\omega^{1/2}D^{1/2}}\left(\frac{\partial i}{\partial C_R}-\frac{\partial i}{\partial C_O}\right) \tag{3}$$

where D is the common diffusion coefficient of the oxidant and the reductant; A, the surface area of the electrode; C_O and C_R, the concentrations of the oxidant and the reductant at the electrode surface respectively; n, the number of electrons involved in the eletron-transfer process, and F, the faraday. Generally, the term $(1+\kappa)$ is positive because the sign of the cathodic current is taken as negative, and consequently the sign of R_F is the same as that of $(\partial E/\partial i)$.

The faradaic current, i, is represented as,

$$i=-nFA(k_cC_O-k_aC_R) \tag{4}$$

where k_c and k_a are the cathodic and the anodic rate constants, respectively. At sufficiently negative potentials compared to the standard potential of the system, the cathodic rate constant k_c is much larger than the anodic one k_a of the electrode reaction. At such potentials the current is given by the equation,

$$i=-nFAk_cC_O \tag{5}$$

Differentiating with respect to the electrode potential E,

$$\left(\frac{\partial i}{\partial E}\right)_{C_O}=-nFA\left(\frac{\partial k_c}{\partial E}\right)C_O \tag{6}$$

is obtained. Eq. 6 indicates that the sign of R_F depends on that of $(\partial k_c/\partial E)$.

As has been described above, it is considered that adsorbed thiocyanate ions on the electrode surface accelerate the reduction of indium(III) at the DME. This may be justified by the fact that the acceleration effect of the thiocyanate ion decreases and the minimum appears on the d. c. polarogram at potentials more negative than about −1.0 V. vs. SCE where thiocyanate ions desorb from the mercury electrode surface.* Therefore, the overall eletrode reaction under the influence of the adsorbed thiocyanate ions may be assumed to consist of two simultaneous processes in parallel:

$$\mathrm{O} + n\mathrm{e} + \mathrm{Hg(n)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R} \tag{I}$$

$$\mathrm{O} + n\mathrm{e} + \mathrm{Hg(c)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{R} \tag{II}$$

The reaction through path I proceeds at the naked part of the electrode surface, Hg(n), while the reaction through path II proceeds at the electrode surface which is covered with the adsorbed thiocyanate ions, Hg(c); k_1 (or k_{-1}) and k_2 (or k_{-2}) are the reduction (or the oxidation) rate constants of reactions through paths I and II respectively.

If it can be assumed that the reduction of indium(III) through one path proceeds independently of the other, the overall reduction rate constant k_c can be given by a linear combination of k_1 and k_2:

$$k_c=(1-\theta)k_1+\theta k_2 \tag{7}$$

where θ is the degree of coverage of the electrode surface by thiocyanate ions. Thiocyanate ions are electrocapillary active and are adsorbed on the mercury surface, particularly at the potentials in the positive branch of the electrocapillary curve, whereas, at relatively negative potentials in the negative branch of the electrocapillary curve, they markedly decrease in the degree of adsorption, and the electrode surface is gradually covered with some other species, such as water molecules or the hydrated cations present in the solution. In the region where thiocyanate ions are specifically adsorbed on the electrode surface, the contribution of the reaction at the covered surface to the overall process is so large that the electrode reaction of indium(III) virtually proceeds at the covered surface only. This explains the experimental result that, when the concentration of thiocyanate ions is greater than approximately 0.02 M, a reversible reduction wave is developed.

The contribution of the reaction at the naked electrode, however, is expected to increase as the potential becomes more negative. This results in the gradual decrease in the overall cathodic rate constant k_c with the increase in the negative potential; k_c might be comparable to, or smaller than, the rate of diffusion of the oxidant in a certain negative potential region. It is expected that, in this potential region, the actual d. c. current becomes smaller than that which would be expected for the diffusion-controlled current. When the potential is extremely negative, the electrode reaction of indium(III) proceeds only through path I. The decrease in the d. c. current at potentials more negative than −1.0 V. vs. SCE is considerable; the larger the decrease, the greater the concentration of thiocyanate ions in the solution is. This is probably due to the fact that the species of indium(III) in the bulk of the solution depends on the concentration of thiocyanate ions.

The shape of the current-time curve during the life of a mercury drop shown in Fig. 5

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* Detailed studies of the adsorption of thiocyanate ions on the mercury electrode will be reported elsewhere.

suggests that the cathodic current of indium(III) in a potassium thiocyanate solution at the negative potentials where the minimum appears on the d. c. polarogram is partly controlled by some processes of a kinetic nature. This is understandable if the rate of change in the state of the electrode surface during the life of a mercury drop is considered. The adsorption equilibrium of simple ions such as thiocyanate ions at the mercury surface is established almost instantaneously. The coverage θ of the electrode surface with the adsorbed ions is constant over the whole period of the life of a mercury drop, i. e.,

$$\left(\frac{\partial\theta}{\partial \ln t}\right)_E=0 \quad \text{and} \quad \left(\frac{\partial k_c}{\partial \ln t}\right)_E=0$$

At the potentials where k_c is smaller than the rate of diffusion, the characteristics of the current-time curve would be similar to those of the usual irreversible process, as is shown in Fig. 5.

The experimental result that the a. c. polarogram of the In(III)-KSCN system gives a negative admittance in a certain potential region can be explained as follows. As has been discussed earlier, this negative admittance results from the negative value of the polarization resistance R_F, the sign of which is opposite to that of $\partial k_c/\partial E$ in the potential region where the anomaly is observed. At such negative potentials, $\partial k_c/\partial E$ can be expressed from Eq. 7 as follows:

$$\frac{\partial k_c}{\partial E}=(k_2-k_1)\frac{\partial\theta}{\partial E}+(1-\theta)\frac{\partial k_1}{\partial E}+\theta\frac{\partial k_2}{\partial E} \quad (8)$$

In Eq. 8, both the second and the third term of the right-hand side have generally negative values, whereas the first term is considered to be positive because the condition,

$$k_2-k_1>0 \quad \text{and} \quad \frac{\partial\theta}{\partial E}>0 \quad (9)$$

may be satisfied in the present case. Therefore, the negative value of R_F and, in consequence, the negative admittance are expected when the relation:

$$\left|(k_2-k_1)\frac{\partial\theta}{\partial E}\right|>\left|(1-\theta)\frac{\partial k_1}{\partial E}+\theta\frac{\partial k_2}{\partial E}\right| \quad (10)$$

is statisfied. In the In(III)-KSCN system, it is plausible to assume that both k_2-k_1 and $\partial\theta/\partial E$ are so large that the relation of Eq. 10 holds in the potential region where the anomaly is observed on the a. c. polarogram.

Summary

The reduction process of indium(III) at the dropping mercury electrode in thiocyanate solutions has been investigated by direct current polarography, alternating current polarography and faradaic impedance measurements. The reduction current in the potential region between −0.5 to −0.9 V. vs. saturated calomel electrode is greatly increased by the addition of minute amounts of thiocyanate ions, when a remarkable minimum is observed on the diffusion current plateau at relatively negative potentials. On the alternating current polarogram, indium(III) in a potassium thiocyanate solution gives a negative admittance in the potential region where the minimum appears on the direct current polorogram. The analysis of impedance measurements has shown that the resistance component has a negative value in that potential region. The experimental results have been explained by assuming that the overall electrode process is composed of two simultaneous reactions, one of which proceeds at the naked electrode surface, and the other at the electrode surface covered with adsorbed thiocyanate ions, and by assuming that thiocyanate ions accelerate the reduction of indium(III) at the surface of the electrode.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

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