The Formation Constants and the Rate Constants of the Electrode Processes of Thiocyanato-Indium(III) Complexes with the Dropping Mercury Electrode*

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Few authors[1,2] have reported investigations of the formation constants of indium(III) thiocyanate complexes. Sunden[1] has, however, determined the formation constants of thiocyanato-indium(III) complexes potentiometrically. The potentiometric method and the polarographic method, though they have a wide applicability, generally include uncertainties arising from the estimations of a liquid junction potential and those of the activity coefficients of the complex ions present.

The polarographic method proposed by DeFord and Hume[3] for the formation constants, though it has an unknown liquid junction potential, is applicable when the electrode processes are reversible at the dropping mercury electrode.

In the present paper, the formation constants and rate constants of the electrode processes of thiocyanato-indium(III) complexes are presented. Analyses of the present data will show the existence of the mono-, di-, tri- and tetra-coordinated species in a solution, and each consecutive formation constant will be calculated. The rate constants, $(k_0)_B$ and $(k_1)_B$ at the standard potential and $k^0{}_{f,h}$ at 0 V. vs. NHE, will also be determined.

Experimental

Reagents. — A commercial sodium thiocyanate was dissolved in water and standardized against the standard silver nitrate solution by volumetric titration with uranin as the indicator. An appropriate amount of indium perchlorate, prepared from a commercial indium sesquioxide, was dissolved in water and standardized gravimetrically. A solution of sodium perchlorate was prepared by dissolving a commercial reagent and was standardized by the ion exchange method. A solution of geratine was freshly prepared every time it was used. All the other chemicals were of a reagent grade and were used without further purification. The composition of the solution was obtained by mixing indium(III) ions, perchlorate and variable amounts of thiocyanate solutions, the ingredients being so chosen

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1) N. Sundén, *Svensk Kem. Tidskr.*, **66**, 50 (1954).

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

3) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

that the total ionic strength was kept constant at 2.0 mol./l.

Apparatus.—A Yanagimoto PB-105 pen-recording polarograph was used for the measurement of the current-potential curves. The usual polarographic technique was used in this study. The capillary used was $m=1.28$ mg./sec., $\tau=3.74$ sec./drop and 1.47 mg$^{2/3}$ sec$^{-1/2}$ for $m^{2/3}\tau^{1/6}$ (where m is the flow rate of mercury and τ, the drop time) in a solution to be examined at -0.7 V. vs. SCE at a height of 70 cm. of the mercury reservoir. The sample solution was connected to the reference electrode through the series of successive bridges of an agar-sodium nitrate, a saturated sodium nitrate solution, and an agar-potassium chloride. The resistance of the cell was found to be 95 ohms when measured by an a. c. bridge. This resistance is very small and it did not change noticeably as the composition of the thiocyanate-perchlorate mixture was varied, so it was neglected in measuring the half-wave potential. Toa-Dempa HM-5 pH meter was used for pH measurements. The pH of the solution of this system measured was about 3.0. All polarographic measurements were made at 25±0.1°C unless otherwise stated. Purified hydrogen gas was used for removing oxygen from a solution before polarograms were obtained.

Measurements of the Half-Wave Potential. — The polarograph was always set with an initial voltage of -0.4 V. vs. SCE and a span voltage of 0.5 V. The sensitivity used was 0.06 μamp./mm., without condenser damping. Using the Leeds and Northrup K-type potentiometer as an external potentiometer, the inital and final potentials were measured to within 0.5 mV. All the current measurements used in the calculations were of the average current of an individual oscillation of the polarogram. The average current was taken simply as one-half of the oscillation (the maximum pen excursion).

The half-wave potentials were found by plotting the logarithm of $\bar{i}/(\bar{i}_d-\bar{i})$ (where $\bar{i}$ is the current corresponding to a given potential and $\bar{i}_d$, the diffusion current corrected for the residual current) versus the applied potential. A point was plotted for each individual small oscillation on the polarogram, and at least twelve values were used along the mid-portion of the curve. The plots of the $\log\bar{i}/(\bar{i}_d-\bar{i})$ versus the applied potentials yielded a slightly curved line in a lower half and a straight line in an upper half in perchlorate and/or thiocyanate media (see Fig. 1). These curves of the log-plot are typical of those obtained for the "quasi"-reversible electrode processes. The reversible half-wave potential, $E_{1/2}{}^r$, was calculated by applying the Matsuda-Ayabe theory.[4] Duplicate experiments showed that the reproducibility of the half-wave potential was within 1 mV. Measurements were made with four separately-prepared samples containing 1.09 mmol./l. indium(III) ion, 0.5 mol./l. thiocyanate, 1.5 mol./l. perchlorate and 0.005% gelatine; the individual half-wave potentials obtained were -0.5670, -0.5688, -0.5688 and -0.5692 V. vs. SCE respectively. The observed half-wave potentials involve an unknown liquid junction potential. The junction potential is a composite of the potential across the saturated potassium chloride - saturated sodium nitrate boundary and the saturated sodium nitrate - sodium perchlorate, sodium thiocyanate boundary. Although the correct value is unavailable, it will be taken into consideration in the future if it is determined for this system.

Results

The Effect of Maximum Suppressors and of the Concentrations of the Supporting Electrolyte. —When the total ionic strength of the solution was 2.0 mol./l. indium(III) simple ion and thiocyanato-indium(III) complexes, in perchlorate and in thiocyanate media respectively, showed pronounced maxima which could be depressed in the presence of 0.005 per cent gelatin, and "well-defined" waves were obtained. When the concentration of the supporting electrolyte (sodium thiocyanate) was smaller than 0.1 mol./l., the maximum appeared even in the presence of 0.005 per cent gelatine. That the maximum does not appear in the presence of positively-charged gelatine in an acid solution of the pH 3 when the concentration of thiocyanate is greater than 0.1 mol./l., while in the concentration of thiocyanate lower than 0.1 mol./l., the fact that the maximum which appears in the positive branch of the electrocapillary curve can not be eliminated by gelatine means that the maximum is of the first kind.

The Effect of Mercury Height. — A typical limiting diffusion current should be proportional to the square root of the effective height of the mercury.[5] At four various applied heights of the mercury column, 70, 60, 50 and 40 cm., the value of $\bar{i}_d/h_{\text{corr}}{}^{1/2}$ (where h_{corr} is an effective height of mercury) was found to be 0.785±0.005 μamp./cm$^{1/2}$ for a solution of 1.09 mmol./l. indium(III), 0.5 mol./l. thiocyanate, 1.5 mol./l. perchlorate and 0.005 per cent gelatine. In these experiments the half-wave potentials were constant within ±0.3 mV. These results indicate that the limiting current is diffusion-controlled.

The Effect of Temperature. — From the results with a solution of 2.0 mol./l. potassium thiocyanate, 0.941 mmol./l. indium(III) and 0.005 per cent gelatine, the temperature coefficient of limitting current near 25°C was calculated to be 1.37 per cent/deg.

This value is in fairly good agreement with the usual diffussion-controlled current[6]a. The

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[4] H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **63**, 1164 (1959).

[5] See, e. g., I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York (1952), p. 85.

[6] *a*, *b*, See, e. g., Ref. 5, pp. 92, 234.

half-wave potential became less negative with an increase in the temperature, and the value of $dE_{1/2}/dT$ was 3.4 mV./deg. The positive temperature coefficient which has been seen for the several hydrated metal ions implies that an appreciable activation energy is required in the electrode reaction.[6)b]

The Calculation of the Reversible Half-Wave Potential, $E_{1/2}{}^r$, According to the Matsuda-Ayabe Theory. — Figure 1 shows the plot of $\log \bar{i}/(\bar{i}_d-\bar{i})$ versus the applied potential, with a solution 1.09 mmol./l. indium(III) ion, 0.005 per cent gelatine and various thiocyanate concentrations of (0, 0.5 and 2.0 mol./l.). The plots of the upper halves of the curves show straight lines, while the lower halves of the plots are curved lines. The log-plots for all other cases were similar to those shown in Fig. 1. According to the Matsuda-Ayabe theory,[4)] the curves shown in Fig. 1 are considered to be typical of a "quasi"-reversible electrode process, and in such cases $\Lambda\sqrt{\tau}$ (where Λ is a kinetic parameter of an electrode process) is obtained from Eq. 1 and falls in the range between 30 and 10^{-2}. The reversile half-wave potential, $E_{1/2}{}^r$ can also be obtained as follows;

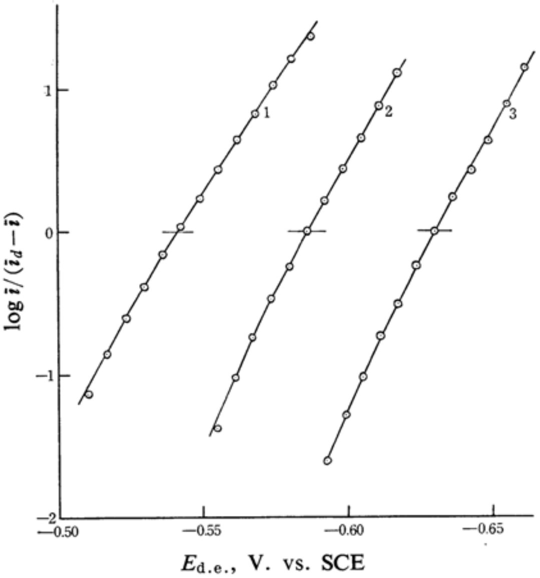

Fig. 1. A log-plot of 1.09 mmol./l. indium(III) ion in the presence of 0.005 per cent of gelatin and various thiocyanate concentration. Curves 1, 2 and 3: 0, 0.50 and 2.0 mol./l. C_{SCN^-}, respectively.

$$\log \Lambda = \frac{\alpha n\boldsymbol{F}}{2.3\boldsymbol{RT}}(E_{1/2}{}' - E_{1/2}{}^r) + \log(\bar{i}_l/\bar{i}_d) - \frac{1}{2}\log\tau + 0.053 \qquad (1)$$

$$E_{1/2}{}^r = E_{1/\nu+1} - 2.3\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\left\{\log\left[\nu - \exp\frac{\alpha n\boldsymbol{F}}{\boldsymbol{RT}} \times (E_{1/\nu+1} - E_{1/2}{}')\right] - \log(\bar{i}_l/\bar{i}_d)\right\} \qquad (2)$$

where $E_{1/\nu+1}$ and $E_{1/2}{}'$ are the potentials corresponding to $-\log\nu$ and zero on the ordinate respectively, $\bar{i}_l$ and $\bar{i}_d$ are average limiting and diffusion currents respectively, and α is the transfer coefficient in the electrode reaction. As the limitting current, $\bar{i}_l$ (7.02_0 μamp.), of simple indium(III) ions in 1.08_6 mmol./l. agrees fairly well with the value (7.09_2 μamp.) calculated from the original Ilkovic equation, assuming the diffusion coefficient D to be 5.97×10^{-6} cm^2/sec. (which is the average value calculated from the equivalent conductivity at an infinite dilution of many other trivalent ions such as ferric[7a)] chromic[7a)], aluminium[7a)] and rare earth metal ions[7b)]), the ratio of $\bar{i}_l$ to $\bar{i}_d$ must be unity. For complex ions, $\bar{i}_l$ gradually becomes smaller than $\bar{i}_d$ with an increase in the concentration of thiocyanate. Table I shows some of the experimentally-obtained potentials, $E_{1/2}{}'$, $E_{1/11}$ and the diffusion currents, together with the results calculated from Eqs. 1 and 2. As is shown in Table I $\Lambda\sqrt{\tau}$ was 0.3 to 0.1, which is in the range of 30 to 10^{-2}. This means that the electrode process of the indium(III)-thiocyanate system is "quasi"-reversible.

TABLE I. CALCULATIONS OF $E_{1/2}{}^r$ AND $\Lambda\sqrt{\tau}$

C_{SCN^-} mol./l.	$\bar{i}_l$ μamp.	α	$-E_{1/2}{}'$	$-E_{1/11}$ V. vs. SCE	$-E_{1/2}{}^r$	$\Lambda\sqrt{\tau}$
0	7.020	0.614	0.5415	0.5134	0.5213	0.238
0.01998	7.026	0.627	0.5477	0.5204	0.5286	0.250
0.4994	6.744	0.701	0.5870	0.5612	0.5664	0.180
0.9988	6.618	0.730	0.6081	0.5829	0.5863	0.149
1.498	6.594	0.730	0.6198	0.5949	0.5997	0.171
1.998	6.534	0.732	0.6309	0.6057	0.6090	0.145

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7) a) J. D'Ans and E. Lax, "Taschenbuch für Chemiker und Physiker" (1949), p. 1237.
b) F. H. Spedding, P. E. Porter and J. M. Wright, *J. Am. Chem. Soc.*, **74**, 2055, 2778, 2781 (1952); F. H. Spedding and I. S. Yaffe, ibid., **74**, 4751 (1952); F. H. Spedding and J. L. Dye, ibid., **76**, 879 (1954); F. H. Spedding and S. Jaffe, ibid., **76**, 882, 884 (1954).

The Relation between Half-Wave Potentials and Logarithms of Thiocyanate Concentration.—A relation of the half-wave potentials, $E_{1/2}{}^r$, to the logarithms of thiocyanate is given in Fig. 2; the ligand number can be estimated from the slope of the curve. Figure 2 also shows by a broken line the theoretical slopes corresponding to the ligand number. This indicates that the tetra-coordinated species is present in a solution of an ionic strength of 2.0 mol./l. The slope of the last part, 3.8, is slightly smaller than the theoretical value of 4; this deviation is considered to be due to overlapping with that of the lower ligand numbers, or with di- and tri-coordinated complexes.

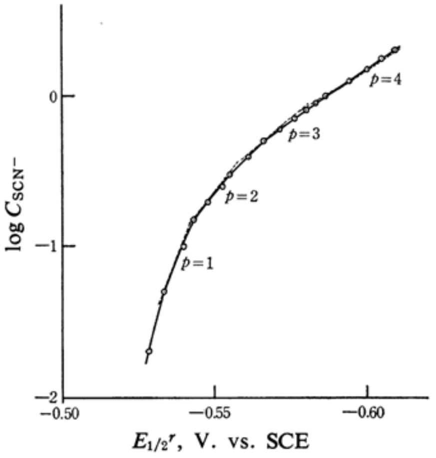

Fig. 2. A relation between $E_{1/2}{}^r$ and log C_{SCN^-}. The broken lines indicate the theoretical slopes corresponding to the respective ligand number.

An Analysis of the DeFord-Hume Function.—The following paragraph will describe the method of analysis of DeFord and Hume.[3]

The method is applicable when the following conditions are satisfied: (1) the electrode processes of a hydrated metal ion, as well as of a complex ion, are reversible at the dropping mercury electrode; (2) the metal reduced at the electrode is soluble in mercury, or forms an amalgam, and (3) the formation constants are not very large.

The indium(III)-thiocyanate system satisfies these conditions except that the electrode processes of the simple indium(III) ion, like those of complex ions, are "quasi"-reversible in the reduction at the electrode, and the method of DeFord and Hume[3] is supposed to be applicable for this system by the aid of the reversible half-wave potential, $E_{1/2}{}^r$, which is calculated from the experimentally-observable values according to the Matsuda-Ayabe theory.[4]

For the calculation of DeFord-Hume function $F_j(X)$, $E_{1/2}{}^r$ was taken as the half-wave potential of a simple or complex ions. According to the DeFord and Hume's theory,[3] $F_j(X)$ functions are defined as follows;

$$F_0(X)=\sum_{j=0}^{N}\frac{K_j(C_X)^j(f_X)^j}{f_{MX_j}}$$

$$=\text{antilog}\left[0.434\frac{n\boldsymbol{F}}{\boldsymbol{RT}}\{(E_{1/2}{}^r)_s-(E_{1/2}{}^r)_c\}+\log\frac{I_s}{I_c}\right] \qquad (3)$$

$$F_j(X)=[F_{j-1}(X)-(K_{j-1}/f_{MX_{j-1}})]/C_Xf_X \qquad (j=1,\ 2,\ \cdots\cdots,\ N) \qquad (4)$$

where K_j is the formation constant of complex MX_j, C_X is the concentration of ligands, f's are the activity coefficients of corresponding ions, I's are diffusion current constants, subscripts s and c refer to simple and complex ions, respectively, and other symbols are used with their usual significances. Substituting the experimentally-measurable quantity on the right-hand side of Eq. 3, the $F_0(X)$ function is calculated. The logarithm of I_s/I_c was so small in comparison with the first term of the bracket of Eq. 3 in the range of ligand concentrations from 0 to 2.0 mol./l. that it was disregarded in the calculation of the $F_0(X)$ function. Furthermore, the $F_j(X)$ functions were calculated from the previous $F_{j-1}(X)$ function by the aid of Eq. 4.

Figure 3 shows the plot of the $F_j(X)$ functions calculated from Eqs. 3 and 4 against the thiocyanate concentration, C_X.

By extrapolating the $F_j(X)$ function to $C_X=0$, the value of K_j is obtained as an intersection The formation constant, K_0, is the value of $F_0(X)$ corresponding to the zero concentration of ligand; it is unity. The extraporation of the plot of $F_1(X)$, $F_2(X)$, $F_3(X)$ and $F_4(X)$ to zero thiocyanate concentration yielded the values of K_1, K_2, K_3 and K_4 respectively. Besides, a value of $F_j(X)$ at zero thiocyanate concentration or a value of K_j is equal to the initial slope of the curve of a previous $F_{j-1}(X)$ function. Equation 4 indicates that $F_j(X)$ is a function of the concentration of ligands, C_X. When $F_{j-1}(X)$ is a function of the first power of C_X or is linear with a positive slope against C_X, $F_j(X)$ becomes parallel against the C_X axis, and the value of $F_j(X)$ gives that of K_j. As is shown in Fig. 3, a tetra-coordinated complex is explicitly present in the solution with the higher ligand concentration, in accordance with the result of Fig. 2. Bock[8] has shown the presence of the tetra-coordinated species $In(SCN)_4{}^-$ in diethylether by the distribution method. Accordingly, it

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[8] R. Bock, *Z. anal. Chem.*, **133**, 110 (1951).

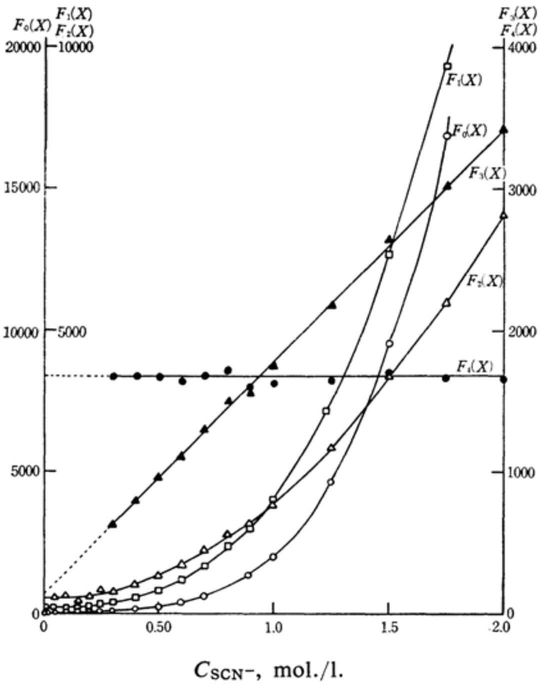

Fig. 3. A relation between $F_j(X)$ and C_{SCN^-}.

may be reasonable to assume the presence of $In(SCN)_4{}^-$ in an aqueous solution. The extrapolation of the plot of $F_1(X)$, $F_2(X)$, $F_3(X)$ and $F_4(X)$ to zero thiocyanate concentration yielded values of 50, 200, 120 and 1670 for K_1, K_2, K_3 and K_4 respectively. Moreover, the values of 45 to 55, 190 to 220, 110 to 130 and 1650 to 1660 for K_1, K_2, K_3 and K_4 were obtained from the initial slopes of the curves. These values are in good agreement with the extrapolated values.

Experimental errors in the determination of $\Delta E_{1/2}{}^r$ were cumulative in the successive calculations of $F_j(X)$; particularly for low concentrations (below 0.3 mol./l.) of a complexing agent, the values of $F_3(X)$ and $F_4(X)$ were so scattered that they were disregarded. As is shown in Fig. 3, however, these plots resulted in a linear relation with a higher thiocyanate concentration than 0.3 mol./l., and a better point at the intersection was obtained by extrapolation.

From the data of Fig. 3, the concentration distribution of each species may be calculated from the following equations.

Indium(III) ions are associated with the excess of thiocyanate as follows:

$$In_{aq}{}^{3+} + jSCN^- \rightleftarrows In(SCN)_j{}^{(3-j)+} \tag{5}$$

The formation constant K_j is given in the following equation:

$$K_j = \frac{[C_{MX_j} f_{MX_j}]}{[C_M f_M][(C_X)^j (f_X)^j]} \tag{6}$$

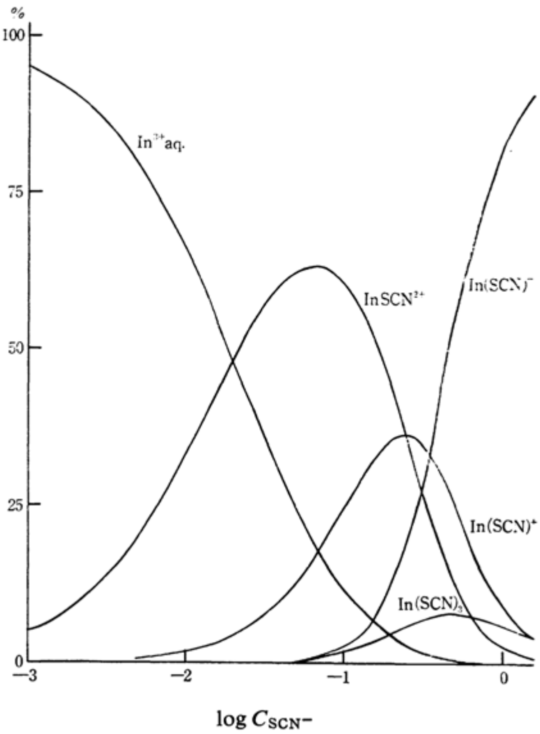

Fig. 4. Concentration distribution of each complex species.

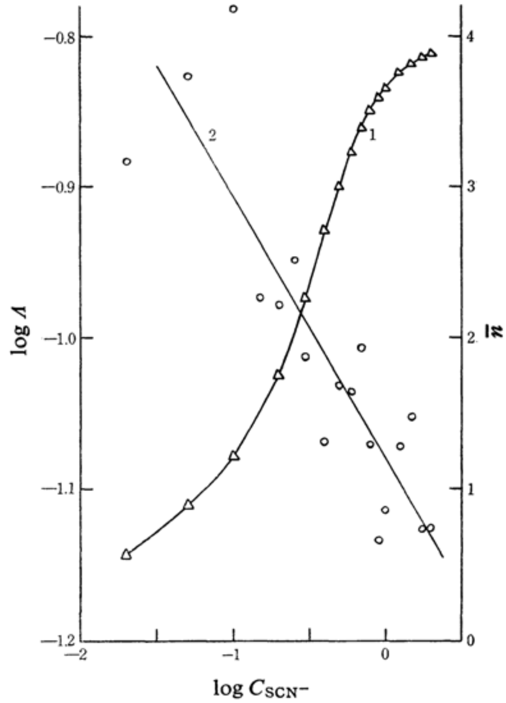

Fig. 5. The mean ligand number $\bar{n}$ (curve 1) and $\log \Lambda$ (curve 2) against $\log C_{SCN^-}$.

where $[C_M]$ is the simple indium(III) ion noncoordinated in the solution and is written as follows:

$$[C_M]=\frac{\sum_{j=0}^{N}[C_{MX_j}f_{MX_j}]}{\sum_{j=0}^{N}K_j[C_X]^j[f_X]^j[f_M]} \tag{7}$$

Therefore, the concentration of a complex species, $[C_{MX_j}]$, is written is the following equation:

$$[C_{MX_j}]=K_j[C_Mf_M][C_X]^j[f_X]^j/f_{MX_j} \tag{8}$$

In Fig. 4, the distributions of the concentration of all the species calculated from Eqs. 7 and 8 for $\sum_{j=0}^{N}[C_{MX_j}f_{MX_j}]=100\%$ are plotted against $\log C_{SCN^-}$. The activity coefficients, f's, were all assumed to be unity. As is obviously shown in Fig. 4, when the concentration of thiocyanate is greater than 1.5 mol./l, more than 90 per cent of all the species present in the solution exist as tetra-coordinated form $In(SCN)_4^-$. In Fig. 5, the mean values of the ligand number, $\bar{n}$, obtained from the data in Fig. 4 are plotted against $\log C_{SCN^-}$, and also the relation between $\log \Delta$ and $\log C_{SCN^-}$ is shown. The slope, -0.174, for the latter curve was obtained by the aid of the least-square method.

Discussion

Sundén[1)] has reported the overall formation constants obtained potentiometrically for K_1, K_2 and K_3 to be 3.8×10^2, 4.0×10^3 and 4.4×10^4 respectively, at an ionic strength of 2.0 mol./l. at 20.0°C. The polarographically-obtained values reported by Radhakrishnan et al.[2)] for K_1, K_2, K_3, K_4, K_5 and K_6 are 1.2×10^2, 1.6×10^3, 1.75×10^4, 1.7×10^4, 6.5×10^4 and 6.9×10^4 respectively, at an ionic strength of 2.0 mol./l. at 30°C. On the other hand, the K_1, K_2, K_3 and K_4 values obtained from the present data are 50, 200, 120 and 1670 respectively. This discrepancy from the values obtained by Sundén[1)] may be largely due to the adsorption of thiocyanate ions on the electrode surface. Furthermore, the slight enhancement of the limiting current, especially in the lower thiocyanate concentration, may be attributed to this adsorption of thiocyanate ions (see Table I). As is shown in Fig. 2, the tetra-coordinated species is evidently present in the higher ligand concentration. Moreover, as Fig. 3 shows, the value of the tetra-coordinated form, K_4, is obtained from the analysis of the DeFord and Hume function. Sundén[1)] has not obtained the value of K_4, and Radhakrishnan et al.[2)] have reported the values of K_5 and K_6. Though the values of K_5 and K_6 can be obtained by the analysis of DeFord and Hume function, they may include errors because of an obscurity in the half-wave potential measurement.

For the sake of simplicity, it is assumed that one of the complexes, $In(SCN)_p^{(3-p)+}$ ($p=4, 3, 1, 2, 0$), is present predominantly in a solution; it is reduced to an amalgam as follows:

$$In(SCN)_p^{(3-p)+}+3e^-+Hg \rightleftarrows In(Hg)+pSCN^- \quad (p=4,3,\cdots\cdots,0) \tag{9}$$

where the following consecutive dissociation and association reactions proceed very fast:

$$In(SCN)_p^{(3-p)+} \rightleftarrows In(SCN)_{p-1}^{(4-p)+}+SCN^- \quad (p=4,3,2,1) \tag{10}$$

The ligand number, p, in the electrode reaction is given by the following equation:[4)]

$$p=\beta N+\frac{\Delta \log \Delta}{\Delta \log (C_Xf_X)} \tag{10}$$

where $\beta=1-\alpha$, and N is the maximum value of the ligand number of a complex present in a given solution. By substituting the values $\beta=0.27$, $N=3.9$ and the slope $\Delta \log \Delta/\Delta \log (C_Xf_X)=-0.174$ obtained from Fig. 5 into the above equation, $p=0.88$ was obtained at $C_{SCN^-}\simeq2.0$ mol./l. On the other hand, at the concentration of about 0.02 mol./l., p was 0.03, which is nearly equal to zero. This means that two kinds of ions, $InSCN^{2+}$ and In^{3+}, are reduced at the D.M.E.

In fact, various complexes $In(SCN)_p^{(3-p)+}$ ($p=4, 3, \cdots\cdots, 0$) are present in a given solution and are reduced to an amalgam at different rates; therefore, the analysis of an individual rate constant is complicated.

According to the Matsuda-Ayabe theory,[9)] however, the rate constants, $(k_p)_B$, ($p=4, 3, \cdots\cdots, 0$) at the standard potential, $(E^0)_B$, can be calculated as follows:

$$\begin{aligned}\Delta \exp \frac{(1-\alpha)n\boldsymbol{F}}{\boldsymbol{RT}}&[(E_{1/2}{}^r)_s-(E_{1/2}{}^r)_c]\\ &=(1+\sum_{j=0}^{N}K_j)^{1-\alpha}(f_s/\sqrt{D_s})^{1-\alpha}(f_a/\sqrt{D_a})^{\alpha}\\ &\quad\times\sum_{p=0}^{N}(k_p)_B(f_XC_X)^p\end{aligned} \tag{12}$$

$$\begin{aligned}(E^0)_B=E_{1/2}{}^r-2.3\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\log\frac{f_N/\sqrt{D_N}}{f_a/\sqrt{D_a}}\\ -2.3N\frac{\boldsymbol{RT}}{n\boldsymbol{F}}\log(f_XC_X)\end{aligned} \tag{13}$$

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9) H. Matsuda and Y. Ayabe, *Z. Elektrochem., Ber. Bunsenges. physik. Chem.*, **66**, 469 (1962).

where D_s, D_N and D_a are the diffusion coefficients of simple indium(III) ions, indium(III) complex ions with the ligand number, N, and indium metal in mercury respectively, f's are activity coefficients, and the other symbols are used with the usual significance. Although the half-wave potential of simple indium(III) ions was determined to be −0.531 ±0.003 V. vs. SCE by Moorhead and MacNevin[10] from the analysis of the log-plot, it was found by the precise analysis of the present data that the reduction of indium(III) ions at the electrode implies some overpotentials. The value, $E_{1/2}{}^r$ $(=-0.5213$ V. vs. SCE), of the simple indium(III) ions obtained by taking the overpotential into consideration is more valid than that of Moorhead and MacNevin.[10] It is, however, not the standard potential of the reaction of $In^{3+}+3e^{-}+Hg \rightarrow In(Hg)$. The standard potential of the above reaction is unavailable; therefore, it is assumed to be closely equal to the potential (−0.5138 V. vs. SCE) calculated from Eq. 13, in which the concentration of thiocyanate is 0.02 mol./l.

As is obviously shown in Eq. 12, the logarithm of the left-hand side must be a linear function of $\log C_{SCN^-}$ if one complex species is present predominantly. In Fig. 6, $\log \Lambda + \{(1-\alpha)n\boldsymbol{F}/2.3\boldsymbol{RT}\}[(E_{1/2}{}^r)_s-(E_{1/2}{}^r)_c]$ are plotted in respect to $\log C_{SCN^-}$; as is shown, the linear relation was not obtained. This indicates that two or more complex species are involved in the electrode reaction.

Further, the left-hand side of Eq. 12 is the experimentally-measurable quantity, which is defined as the $H_0(X)$ function. By extrapolating the $H_0(X)$ function to $(f_X C_X)=0$, the limiting value is given as follows:

$$\lim_{f_X C_X \to 0} H_0(X) = (1+\sum_{j=1}^{N} K_j)^{1-\alpha} \times (f_s/\sqrt{D_s})^{1-\alpha}(f_a/\sqrt{D_a})^{\alpha}(k_0)_B \tag{14}$$

In general, $H_p(X)$ is defined as follows:

$$H_p(X) = [H_{p-1}(X) - \lim H_{p-1}(X)]/(f_X C_X) \tag{15}$$

By extrapolating $H_p(X)$ to $(f_X C_X)=0$, the following equation is obtained:

$$\lim_{f_X C_X \to 0} H_p(X) = (1+\sum_{j=1}^{N} K_j)^{1-\alpha} \times (f_s/\sqrt{D_s})^{1-\alpha}(f_a/\sqrt{D_a})^{\alpha}(k_p)_B \tag{16}$$

The relation of Eqs. 12 and 15 is shown in Fig. 7, in which $H_0(X)$ is linear with a positive slope with respect to the C_X axis. The slope and the intersection of the straight line

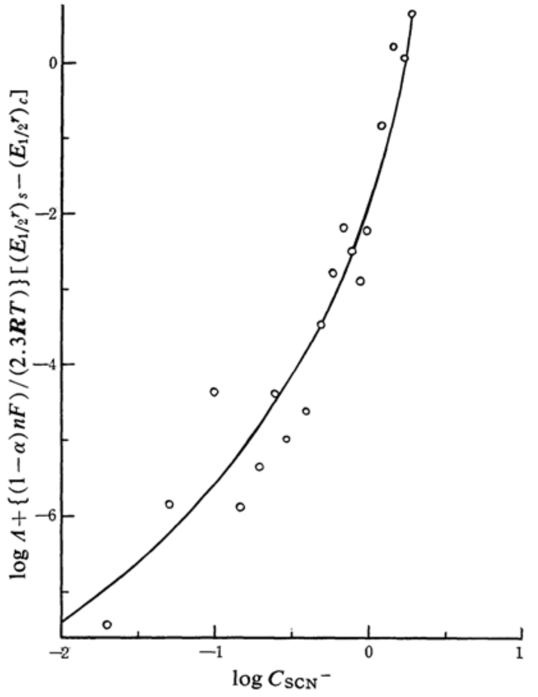

Fig. 6. The logarithmic relation of the left-hand side of Eq. 12 in respect to $\log C_{SCN^-}$.

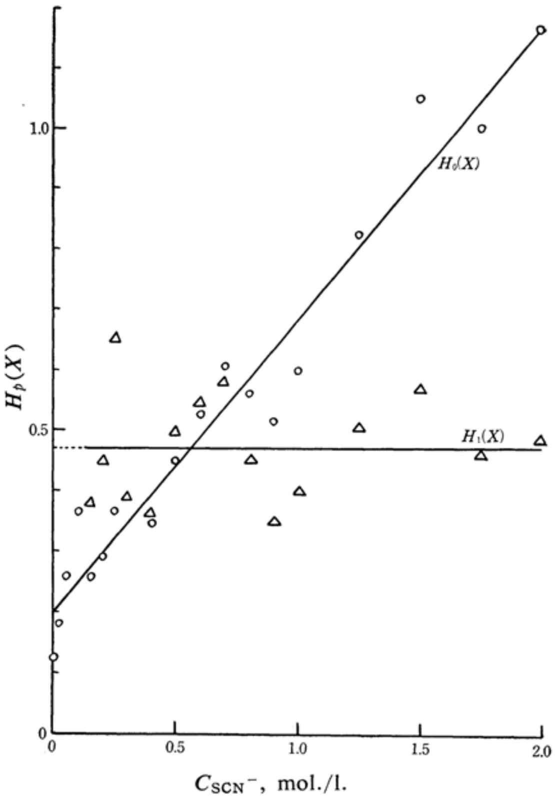

Fig. 7. The relation of $H_p(X)$ functions to C_{SCN^-}.

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[10] E. D. Moorhead and W. M. MacNevin, *Anal. Chem.*, **34**, 269 (1962).

with the ordinate were obtained by the least-square method. This relation indicates that $H_0(X)$ is a linear function of C_{SCN^-}; $H_1(X)$ is, therefore, constant irrespective of C_{SCN^-}, and higher $H_p(X)$ functions are equal to zero. By extrapolating $H_0(X)$ and $H_1(X)$ to $(f_X C_X)=0$, the following values were obtained:

$$\lim_{f_X C_X \to 0} H_0(X) = 0.20 \pm 0.05$$

$$\lim_{f_X C_X \to 0} H_1(X) = 0.47 \pm 0.06$$

$$\lim_{f_X C_X \to 0} H_p(X) \simeq 0 \qquad (p=2,\ 3 \text{ and } 4)$$

From Eqs. 14 and 16, $(k_0)_B$ and $(k_1)_B$ at the standard potential, $(E^0)_B = -0.2678$ V. vs. NHE, are calculated as follows;

$$(k_0)_B = (0.64 \pm 0.16) \times 10^{-4} \text{ cm./sec.}$$

$$(k_1)_B = (1.5 \pm 0.2) \times 10^{-4} \text{ (cm./sec.)/(mol./l.)}$$

$$(k_p)_B \simeq 0 \quad (p=2,\ 3 \text{ and } 4)$$

where the values of $D_s = 5.85 \times 10^{-6}$ cm²/sec., calculated from the Ilkovic equation, and $D_a = 1.47 \times 10^{-5}$ cm²/sec. (at 22°C)[11] were used, and f_s and f_a were assumed to be unity. The $(k_0)_B$ and $(k_1)_B$ values are the rate constants for $p=0$ and 1 respectively in the reaction given by Eq. 9. This means that two kinds of complexes, $\mathrm{In}_{aq}{}^{3+}$ and InSCN^{2+}, are reduced at the electrode; the presence of two kinds of complexes is in accordance with the results calculated from Eq. 11.

The logarithm of the forward rate constant, $k_{f,h}$, according to the Koutecky treatment[12] was plotted against the potential in NHE as is shown in Fig. 8 for the data of the simple indium(III) ion. As is shown in Fig. 8, the plot in a less negative potential deviates from a straight line. This deviation is due chiefly to the effect of the backward rate constant, $k_{b,h}$, in the range of this potential. In the range of the potential for the linear portion, however, $k_{b,h}$ may be neglected with respect to $k_{f,h}$.

By extrapolating the linear portion to the standard potential of -0.2678 V. vs. NHE and the potential of 0 V. vs. NHE, the logarithms of the rate constants, $(k_0)_s$ and $k^0{}_{f,h}$ respectively, are obtained from the following equation:

$$\log k_{f,h} = \log k^0{}_{f,h} - \frac{\alpha n \boldsymbol{F}}{2.3\boldsymbol{RT}} E \qquad (17)$$

The values of $(k_0)_s = 1.58 \times 10^{-4}$ cm./sec. and $k^0{}_{f,h} = 4.77 \times 10^{-12}$ cm./sec. were obtained by extrapolating the linear portion in Fig. 8 to -0.2678 V. and 0 V. vs. NHE respectively. The value of $(k_0)_B = (0.64 \pm 0.16) \times 10^{-4}$ cm./sec. is in good agreement with that of $(k_0)_s = 1.58 \times 10^{-4}$ cm./sec. when we consider that the scattering of the points in Fig. 7 is due largely to the errors of $E_{1/2}{}^r$, Λ and α. The latter value, 4.77×10^{-12} cm./sec., agrees fairly well with the walue of 4.7×10^{-12} cm./sec. (at 26.5°C) determined by Inouye and Imai[13] polarographically. Furthermore, from the slope of the straight line, αn was calculated to be 1.66, from which $\alpha = 0.55$ was obtained by assuming n to be 3. Although the agreement of $k^0{}_{f,h}$ was fairly good, the polarographic wave obtained by Inouye and Imai[13] was a totally irreversible one whose half-wave potential was about -1.0 V. and whose product αn was 0.66, while the wave obtained in the present paper is "quasi"-reversible, and the half-wave potential and the product αn are about -0.5 V. and 1.66 respectively. Inouye and Imai,[13] however, pointed out that when a chloride, iodide or acetate ion is added to the simple indium(III) ion, the irreversible wave, $E_{1/2} = -1.0$ V., is changed to a reversible one with $E_{1/2} = -0.5$ V. Likewise, the increase in perchlorate may cause the increase in the reversibility of the wave because the simple indium(III) ion in 2.0 mol./l. perchlorate is reduced at about -0.5 V. in the present paper.

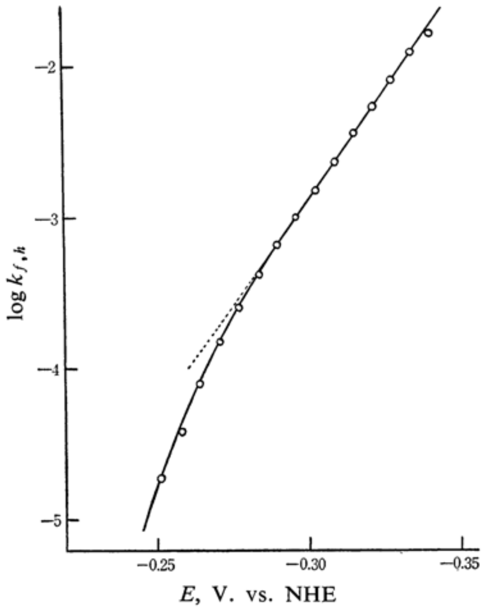

Fig. 8. The potential dependence of the rate constant of the electrode process for indium(III) simple ion in perchlorate medium.

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[11] M. von Stackelberg and V. Toome, *Z. Elektrochem.*, **58**, 226 (1954).

[12] See, e. g., P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, 2nd Ed., New York (1958), Chap. 4.

[13] S. Inouye and H. Imai, This Bulletin, **33**, 149 (1960).

Summary

The formation constants, $K_j = [\mathrm{In(SCN)}_j^{(3-j)+}]/[\mathrm{In}^{3+}][\mathrm{SCN}^-]^j$ ($j=1$, 2, 3, 4), have been determined to be 50, 200, 120 and 1670 respectively. The electrode reaction proceeds as follows:

(1) At a higher ligand concentration;

$\mathrm{In(SCN)}_p^{(3-p)+} \rightleftarrows \mathrm{InSCN}^{2+} + (p-1)\mathrm{SCN}^-$

(fast) ($p=2$, 3 and 4)

$\mathrm{InSCN}^{2+} + 3e^- + \mathrm{Hg} \rightarrow \mathrm{In(Hg)} + \mathrm{SCN}^-$

(rate constant $(k_1)_B$)

(2) At a lower ligand concentration:

$\mathrm{InSCN}^{2+} \rightleftarrows \mathrm{In}_{aq}^{3+} + \mathrm{SCN}^-$ (fast)

$\mathrm{In}_{aq}^{3+} + 3e^- + \mathrm{Hg} \rightarrow \mathrm{In(Hg)}$

(rate constant $(k_0)_B$)

The rate constants, $(k_0)_B$ and $(k_1)_B$, at the standard potential are $(0.64 \pm 0.16) \times 10^{-4}$ cm./sec. and $(1.5 \pm 0.2) \times 10^{-4}$ (cm./sec.)/(mol./l.) respectively. The rate constant, $k^0_{f,h}$, at 0 V. vs. NHE was 4.77×10^{-12} cm./sec.

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