Potentiometric Determination of the Formation Constants of Thiocyanato Complexes of Mercury(II)

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Although a number of investigations have been carried out on the formation constant of the tetrathiocyanatomercurate(II) complex, the values reported are not in satisfactory agreement with each other[1]. As for the formation constants of the dithiocyanatomercury(II) and trithiocyanatomercurate(II) complexes, only a few papers have been published[1].

In the present communication, the potentiometric determination of the formation constants of the dithiocyanatomercury(II) and tri- and tetrathiocyanatomercurate(II) complexes and some thermodynamic data for the formation reactions of these complexes are presented. Although Nyman and Alberts[2] reported the formation constants of these complexes during the course of this study, the scope of their study was limited to the determination of the formation constants at 25°C.

Experimental

A stock solution of 0.05 M mercury(II) was prepared by dissolving mercury(II) nitrate of a guaranteed reagent grade in 0.3 N nitric acid. Its concentration was determined by titrating with the standard solution of sodium chloride, using sodium nitroprusside as indicator[3]. A solution of potassium thiocyanate was obtained by dissolving

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[1] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes, Part II, Inorganic Ligands", Chemical Society, London (1958), p. 42.

[2] C. J. Nyman and G. S. Alberts, *Anal. Chem.*, 32, 207 (1960).

[3] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis", Vol. II. Interscience Publishers, New York (1947), p. 332.

an appropriate amount of potassium thiocyanate of a guaranteed reagent grade. The concentration of thiocyanate was determined by the Volhard method⁴⁾. All other chemicals used were also of a guaranteed reagent grade.

A conventional manual apparatus similar to that of Kolthoff and Lingane⁵⁾ was used for the measurement of the current-potential curve. The dropping mercury electrode used had an m value of 2.109 mg./sec. and a drop time t_d of 4.22 sec., being measured in a de-aerated 0.2 M potassium nitrate solution at −0.5 V. vs. SCE at 59 cm. of the mercury height. A saturated calomel electrode (SCE) with a large surface area was used for the reference electrode; to this the electrolytic solution was connected with a Hume and Harris type salt bridge⁶⁾. The measurements were carried out in the thermostat at 15, 25 and 35°C. The solutions prepared for the potentiometric determination contained 0.532 mM of mercury(II) and 0.016 to 0.03 M of thiocyanate, unless otherwise stated. The ionic strength of the solutions was adjusted to 0.2 with potassium nitrate. The residual current was obtained with a 0.2 M potassium nitrate solution. After the correction for the residual current and for the internal resistance (iR drop) across the electrolysis cell, the zero-current potential, i. e. the potential at which the current equals zero, was determined within the limits of ±0.5 mV.

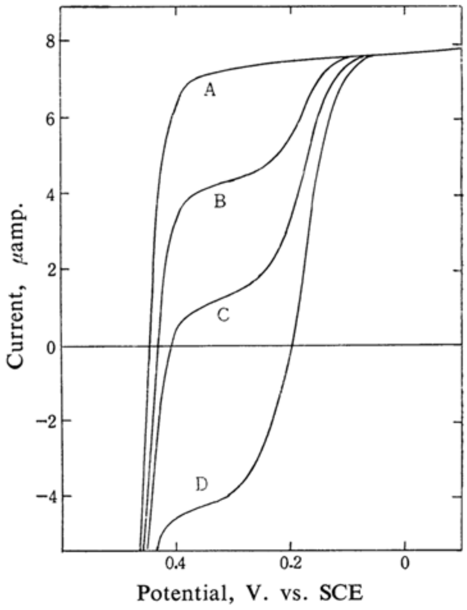

Fig. 1. Current-potential curves of 1.06_3 mM mercury(II) obtained at 25°C and $\mu=0.2$ without (curve A) and with 0.841 mM (B), 1.68 mM (C) and 2.94 mM (D) of thiocyanate. The residual current is not corrected.

Results

The current-potential curves of 1 mM mercury(II) obtained in the absence and in the presence of thiocyanate of various concentrations are reproduced in Fig. 1. The solution containing 1 mM of mercury(II) and less than 2 mM of thiocyanate gave a double wave. With the increasing concentration of thiocyanate at a constant concentration of mercury(II), the waves shifted to more negative potentials and the height of the first wave decreased, while the total height of both waves remained almost the same. The first wave was considered as due to the reduction of the free (hydrated) mercury(II) ion, and the second, to that of the thiocyanatomercury(II) complexes.

Since the limiting current of each wave was nearly completely dependent on the square root of the effective height of the mercury head, it was considered that the limiting currents are controlled by diffusion and are proportional to the concentrations of the hydrated and the complex mercury(II) ions in the bulk of solution respectively. The relation between the added concentration of the thiocyanate and the height of the wave showed that the complex which is formed under such conditions has two thiocyanate ions coordinating to the central metal ion. When the thiocyanate concentration exceeded 2 mM in the solution containing 1mM of mercury(II), the first wave became anodic, which is due to the dissolution of electrode mercury with the formation of thiocyanato complexes. These observations clearly showed that, in the concentration range employed in the present experiments, the presence of the mono-coordinated species $Hg(SCN)^+$ was negligible.

The relation between the zero-current potential ε and the thiocyanate concentration is given by the following equation:

$$\begin{aligned}\varepsilon = E^\circ &+ \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln f_{\mathrm{Hg}^{2+}} \\ &+ \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \sum_j [\mathrm{Hg(SCN)}_j^{2-j}] \\ &- \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \sum_j K_j^c [\mathrm{SCN}^-]^j, \ (0 \leqq j \leqq 4) \quad (1)\end{aligned}$$

in which E° is the standard potential of the reaction,

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

$f_{\mathrm{Hg}^{2+}}$ the activity coefficient of the species Hg^{2+}, and K_j^c the formation constant of the complex $Hg(SCN)_j^{2-j}$ in terms of concentration. (When j equals zero, K_j^c is unity.) At the potential ε, the concentrations of the ions at the electrode surface are the same as those in the bulk of the solution.

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4) I. M. Kolthoff and V. A. Stenger, ibid., Vol. II, p. 278.

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

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

In the absence of thiocyanate, the potential ε° is expressed as

$$\varepsilon^\circ = E^\circ + \frac{RT}{2F}\ln f_{\mathrm{Hg}^{2+}} + \frac{RT}{2F}\ln\,[\mathrm{Hg}^{2+}]. \quad (2)$$

Since the value of ε° could not be obtained experimentally, it was calculated by means of Eq. 2. The standard oxidation-reduction potential of the system Hg(0)-Hg(II) at 25°C was taken as 0.850 V. vs. NHE, which had been obtained by Hietanen and Sillén[7] taking into account the complex formation between mercury(II) and nitrate ions. The standard potentials at 15° and 35° were calculated using the value at 25°C and the enthalpy change of the system at 25°C[8]. The ε° values calculated are given in Table I.

At the constant concentration of total mercury(II), Leden's F_0 function[9] was obtained from Eqs. 1 and 2 as:

$$F_0 \equiv \sum_j K_j^c\,[\mathrm{SCN}^-]^j = \mathrm{antilog}\left[\,0.435\cdot\frac{2F}{RT}(\varepsilon^\circ - \varepsilon)\right] \quad (3)$$

TABLE I. VALUES OF ε° OF 0.532 mM MERCURY(II) NITRATE SOLUTION AT IONIC STRENGTH 0.2

Temperature °C	ε°, V. vs. SCE
15	0.493_3
25	0.492_9
35	0.492_6

Since the presence of hydrated mercury(II) and mono-coordinated thiocyanatocomplex ions was negligible compared to other species in the concentration range employed, the following F_2 function was obtained:

$$F_2 = \frac{F_0}{[\mathrm{SCN}^-]^2} = K_2^c + K_3^c\,[\mathrm{SCN}^-] + K_4^c\,[\mathrm{SCN}^-]^2 \quad (4)$$

If the values of F_2 obtained experimentally are plotted against $[\mathrm{SCN}^-]$, the value of K_2^c can be determined by extrapolation of the plot to a zero thiocyanate concentration. Using the K_2^c value thus obtained, the values of K_3^c and K_4^c can be determined by a similar graphical method with the aid of the following equation:

$$F_3 = \frac{F_2 - K_2^c}{[\mathrm{SCN}^-]} = K_3^c + K_4^c\,[\mathrm{SCN}^-] \quad (5)$$

In the above procedure the concentration of free (uncoordinated) thiocyanate $[\mathrm{SCN}^-]$ must

TABLE II. VARIATIONS OF ε, F_2 AND F_3 AS A FUNCTION OF THIOCYANATE CONCENTRATION

$[\mathrm{SCN}^-]_t$* mol./l.	ε V. vs. SCE	$[\mathrm{SCN}^-]$ mol./l.	F_2	F_3
0.0315	0.0451	0.0296	1.63×10^{18}	5.42×10^{19}
0.0263	0.0548	0.0243	1.13×10^{18}	4.53×10^{19}
0.0210**	0.0795	0.0173	6.55×10^{17}	3.64×10^{19}
0.0189**	0.0854	0.0152	5.34×10^{17}	3.33×10^{19}
0.0168**	0.0919	0.0131	4.31×10^{17}	3.07×10^{19}
0.0147**	0.0993	0.0111	3.38×10^{17}	2.80×10^{19}
0.0126**	0.1076	0.00910	2.65×10^{17}	2.61×10^{19}
0.00946	0.1052	0.00774	2.21×10^{17}	2.50×10^{19}
0.0105**	0.1182	0.00712	1.90×10^{17}	2.28×10^{19}
0.00841	0.1116	0.00673	1.77×10^{17}	2.24×10^{19}
0.00946**	0.1242	0.00614	1.60×10^{17}	2.16×10^{19}
0.00631	0.1261	0.00471	1.17×10^{17}	1.92×10^{19}
0.00525	0.1337	0.00371	1.04×10^{17}	2.08×10^{19}
0.00420	0.1456	0.00273	7.62×10^{16}	1.80×10^{19}
0.00273	0.1684	0.00140	4.90×10^{16}	1.57×10^{19}

* $[\mathrm{SCN}^-]_t$ is the added concentration of potassium thiocyanate.

** In these experiments the added concentration of mercury nitrate is 1.06_3 mM.

TABLE III. CONCENTRATION FORMATION CONSTANTS OF $\mathrm{Hg(SCN)}_n{}^{2-n}$ AT IONIC STRENGTH 0.2

Temperature °C	K_2^c	K_3^c	K_4^c
15	$(1.8\pm0.2)\times10^{17}$	$(7.1\pm0.3)\times10^{19}$	$(1.11\pm0.02)\times10^{22}$
25	$(2.7\pm0.2)\times10^{16}$	$(1.39\pm0.03)\times10^{19}$	$(1.32\pm0.02)\times10^{21}$
35	$(5.5\pm0.2)\times10^{15}$	$(2.43\pm0.05)\times10^{18}$	$(1.68\pm0.04)\times10^{20}$

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

[8] W. M. Latimer, "Oxidation Potentials", Prentice-Hall, New York (1952), p. 176.

[9] I. Z. Leden, *Z. phisik. Chem.*, **188A**, 160 (1941).

be known. Since the concentration of the thiocyanate that is consumed by complexing cannot be ignored, the free thiocyanate concentration must be calculated from the added concentrations of the thiocyanate and mercury(II) nitrate. At first, [SCN$^-$] was calculated with appropriate coordination numbers (2 or 3) assumed tentatively. When a set of approximate values of the formation constants were available, the concentration of free thiocyanate was computed again with those constants. Such a procedure of stepwise approximation was repeated until self-consistent values of the formation constants were obtained. As an example, the data at 25°C are presented in Table II. Similar sets of data are also obtained at 15 and 35°C, and the final values of K_2^c, K_3^c and K_4^c at 15, 25 and 35°C are given in Table III.

The plots of F_2 and F_3 versus [SCN$^-$] obtained at 25°C are given in Fig. 2. The solid line represents the theoretical curve which was calculated with the formation constants given in Table III. It is clearly seen that both F_2 and F_3 curves fit satisfactorily with the observed points plotted. This indicates that the formation constants obtained are proper ones.

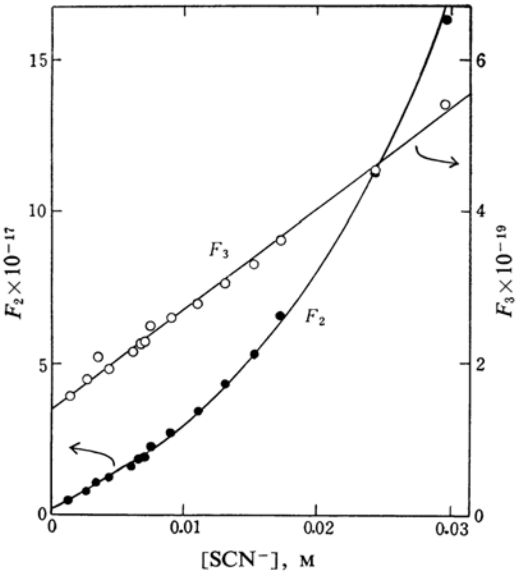

Fig. 2. F_2(Eq. 4) and F_3(Eq. 5) as functions of the thiocyanate ion concentration. (at 25°C). The solid line was calculated with the formation constants given in Table III.

Discussion

It is estimated from the experiments that, in a solution containing 0.532 mM of mercury(II) and 0.03 M thiocyanate, the mean coordination number with respect to thiocyanate ion is approximately 3.7 and that some 70 per cent of the mercury(II) in the solution exists in the form of $Hg(SCN)_4^{2-}$. Hence, the range of the thiocyanate concentration chosen in the present investigation is considered sufficient for the determination of the formation constants of the three complex species, $Hg(SCN)_2$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$. The measurements at higher thiocyanate concentrations were not taken into account, because it seemed better, for the following reasons, to avoid varying the composition of the medium widely:

1. The residual current was measured with a solution containing 0.2 M potassium nitrate. With a solution containing thiocyanate, the oxidation of the electrode mercury occurs at almost the same potential as when mercury(II) nitrate is added to the solution.
2. The liquid junction potential will not stay constant with the increase of thiocyanate concentrations.
3. The activity coefficient will not be the same with the change in the composition of medium, even though the ionic strength of the medium is held constant at 0.2.

Using the activity coefficients of the ions, the formation constants given in Table III were reduced to thermodynamic formation constants, which are given in Table IV. The activity coefficients were evaluated with the equation[10],

TABLE IV. THERMODYNAMIC FORMATION CONSTANTS OF $Hg(SCN)_n^{2-n}$

Temperature °C	K_2	K_3	K_4
15	1.2×10^{18}	4.6×10^{20}	4.1×10^{22}
25	1.8×10^{17}	9.3×10^{19}	4.9×10^{21}
35	3.8×10^{16}	1.7×10^{19}	6.8×10^{20}

$$\log f_i = \frac{-Az_i^2\sqrt{\Gamma}}{1+Ba_i\sqrt{\Gamma}}$$

in which A and B are constants at a given temperature[11], a_i is the mean distance of the nearest approach of the ions measured in Å, and Γ, the ionic concentration of the solution[11]. As for the mean distance of the nearest approach, the values given in Kielland's table[10] are used for the Hg^{2+} and SCN^- ions. For the $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ ions, the a_i values were estimated from the data given in the same table[10].

From the thermodynamic formation constants, the free energy change ΔF, the enthalpy

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

[11] G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry", Vol. II, Elsvier Publishing Co., New York (1951), p. 645.

change ΔH and the entropy change ΔS for the reaction,

$$Hg^{2+}(aq.) + n\,SCN^-(aq.) \rightleftarrows Hg(SCN)_n^{2-n}(aq.) \qquad (6)$$

were evaluated, as given in Table V.

TABLE V. THERMODYNAMIC DATA FOR REACTION 6 AT 25°C

	ΔH, kcal./mol.	ΔF, kcal./mol.	ΔS, cal./deg. mol.
$n=2$	−30	−23.6	−20
$n=3$	−29	−27.2	− 6
$n=4$	−36	−29.6	−20

In Table VI are presented the formation constants of thiocyanatomercury(II) complexes which are reported in the literature. Among them there are the formation constants K_2, K_3 and K_4 which were reported by Nyman and Alberts. They obtained those constants from the study of the polarographic anodic wave of mercury(II) which appeared in the presence of thiocyanate ions. Although the ionic strength of the solution in their study is not the same as that in our experiments, it is nevertheless reasonable to conclude that their values of the formation constants are in good agreement with ours. The values given by Korshunov and Shchennikova[13] and those by Yatsimirski and Tukhlov[16] are discussed by Nyman and Alberts in their paper[2]. Most of the formation constants given in Table VI were determined without taking into consideration the ionic strength of the medium. Therefore, those are not compared with the values obtained in this study. The constants k_3 and k_4 given by Gallais and Mounier[17] are the third and the fourth successive formation constants corresponding to the reactions

$$Hg(SCN)_2 + SCN^- \rightleftarrows Hg(SCN)_3^-$$
$$Hg(SCN)_3^- + SCN^- \rightleftarrows Hg(SCN)_4^{2-}$$

respectively. However, they are undoubtedly too small compared with the others.

Besides the values in Table VI, Toropova[12] reported the thermodynamic formation constant of $Hg(SCN)_4^{2-}$ at 25°C to be 7.8×10^{21}, which is greater than our value for K_4 by about 1.6 times. She also estimated the enthalpy change and the entropy change for reaction 6 to be −35 kcal./mol. and −20 cal./deg. mol. respectively for $n=4$ at 25°C; these figures are in good agreement with the values in Table V.

In the case of halo and pseudohalo complexes of mercury(II), it is known that the species with two anions coordinated, in general, are relatively more stable[19]. This tendency is clearly recognized in the formation constants of thiocyanato complexes of mercury(II) obtained in the present study.

Summary

The formation constants of dithiocyanatomercury(II) and tri- and tetrathiocyanatomercurate(II) complexes have been determined by the potentiometric method with a dropping

TABLE VI. FORMATION CONSTANTS OF THIOCYANATOCOMPLEXES OF MERCURY(II) OBTAINED BY VARIOUS INVESTIGATORS

Medium	Temp., °C	Method	K_2^c	K_3^c	K_4^c	Investigators
1 M $KClO_4$	25	polarography	1.18×10^{16}	8.9×10^{18}	8.7×10^{20}	Nyman and Alberts[2]
0.3 M $NaNO_3$	20	e. m. f.	—	—	4.68×10^{21}	Toropova[12]
	25	〃	—	—	1.70×10^{21}	
	30	〃	—	—	6.30×10^{20}	
var.	18	polarography	—	—	2.0×10^{19}	Korshunov and Shchennikova[13]
var.	18	e. m. f.	—	—	2.5×10^{22}	Grossmann[14]
var.	25	〃	—	—	9.7×10^{21}	Sherrill and Skowronski[15]
Br^-	25	Spectrophotometry	2.95×10^{17}	—	—	Yatsimirski and Tukhlov[16]
Cl^-	25	〃	1.32×10^{17}	—	—	
var.	16	Faraday effect	$k_3=4.78\times10$, $k_4=5.25$			Gallais and Mounier[17]
var.	20	e. m. f.	—	—	4.43×10^{21}	Golub and Tsitsurina[18]

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12) V. F. Toropova, *Zhur. Neorg. Khim.*, **1**, 243 (1956); *Chem. Abstr.*, **51**, 4192 (1957).

13) I. A. Korshunov and M. K. Shchennikova, *Zhur. Obshcheĭ Khim.*, **19**, 1820 (1949); *Chem. Abstr.*, **44**, 909 (1950).

14) H. Grossmann, *Z. anorg. Chem.*, **43**, 356 (1905).

15) M. S. Sherrill and S. Skowronski, *J. Am. Chem. Soc.*, **27**, 30 (1905).

16) K. B. Yatsimirski and B. D. Tukhlov, *Zhur. Obshcheĭ Khim.*, **26**, 356 (1956); *Chem. Abstr.*, **50**, 13643 (1956).

17) F. Gallais and J. Mounier, *Compt. rend.*, **223**, 790 (1946).

18) A. M. Golub and T. I. Tsitsurina, *Nauk. Zapiski, Kiïv. Derzhav. Univ. im. T. G. Shevchenka*, **16**, No. 15, *Zbirnik Khim. Fak.*, No. 8, 101 (1957); *Chem. Abstr.*, **53**, 9881 (1959).

19) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Willey & Sons, New York (1958), p. 4.

mercury electrode at ionic strength 0.2 and at 15, 25 and 35°C. The values obtained are:

at 15°C, $K^c_{\mathrm{Hg(SCN)_2}}=1.8\times10^{17}$,
$K^c_{\mathrm{Hg(SCN)_3}}=7.1\times10^{19}$,
$K^c_{\mathrm{Hg(SCN)_4}}=1.11\times10^{22}$;

at 25°C, $K^c_{\mathrm{Hg(SCN)_2}}=2.7\times10^{16}$,
$K^c_{\mathrm{Hg(SCN)_3}}=1.39\times10^{19}$,
$K^c_{\mathrm{Hg(SCN)_4}}=1.32\times10^{21}$;

at 35°C, $K^c_{\mathrm{Hg(SCN)_2}}=5.5\times10^{15}$,
$K^c_{\mathrm{Hg(SCN)_3}}=2.43\times10^{18}$,
$K^c_{\mathrm{Hg(SCN)_4}}=1.68\times10^{20}$.

The thermodynamic formation constants of these complexes and the free energy change, the enthalpy change and the entropy change of the formation reactions of these complexes have been calculated.

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