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The Complex Formation Between Mercury(II) and Thiocyanate Ions

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The equilibria between Hg^{2+} and SCN^- ions have been studied at 25°C in 1 M $NaClO_4$ ionic medium by potentiometric as well as by solubility measurements. The experimental data may be explained by assuming the formation of $HgSCN^+$, $Hg(SCN)_2$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ with equilibrium constants listed in Table VI.

Introduction

The complex formation between Hg^{2+} and SCN^- ions has been studied by several authors with different methods, but as yet there are no quantitative measurements of equilibria involving Hg^{2+}, $HgSCN^+$ and $Hg(SCN)_2$. The work on higher complexes is also scanty and contradictory. The aim of the present investigation is that of evaluating the stability constants of all the complex species in the mercury(II) thiocyanate system.

Previous work. In 1905 Sherrill and Skowronski[1] measured at 25°C the Hg^{2+} concentration with a Hg electrode in solutions of $Hg(SCN)_2$ in KSCN, and concluded that in the concentration range used, 0.251-1.53 M SCN^- and 0.0022-0.40 M $Hg(SCN)_2$, the predominant complex is $Hg(SCN)_4^{2-}$. These investigators calculated from the experimental data the equilibrium constant $\beta_4 = [Hg(SCN)_4^{2-}][Hg^{2+}]^{-1}[SCN^-]^{-4} = 10^{21.99}$. From potentiometric and solubility data Grossmann[2] arrived to similar conclusions and determined for β_4 a value of $10^{22.4}$ at 18°C. In his measurements this author used solutions containing also K^+ and NO_3^- ions in such amounts as to keep $[K^+] = 1$ M, namely a constant ionic medium. This is the first published investigation using the ionic medium method. Grossmann states however the method had before been suggested and used by Bodländer, his teacher, in unpublished works.

The presence of only $Hg(SCN)_4^{2-}$ was considered also by Korshunov and Shchennikova,[3] who calculated $\beta_4 = 10^{19.3}$ at 18°C from polarographic measurements, as well as by Toropova[4] who found from potentiometric data, extrapolated to zero ionic strength, a value of $\beta_4 = 10^{21.89}$ at 25°C.

(1) M. S. Sherrill and S. Skowronski, *J .Am. Chem. Soc.*, *27*, 30 (1905).
(2) H. Grossmann, *Z. anorg. Chem.*, *43*, 356 (1905).
(3) I. A. Korshunov and M. K. Shchennikova, *Zhur. obshchei Khim.*, *19*, 1820 (1949).
(4) V. F. Toropova, *Zhur. neorg. Khim.*, *1*, 243 (1956).

In addition to $Hg(SCN)_4^{2-}$, Golub and Romanenko[5] considered the presence of higher complexes such as $Hg(SCN)_5^{3-}$ and $Hg(SCN)_6^{4-}$ in concentrated, from 2.4 to 3.4 M, KSCN solutions, and calculated from potentiometric measurements $\beta_5 = [Hg(SCN)_5^{3-}][Hg^{2+}]^{-1}[SCN^-]^{-5} = 10^{22.05}$ and $\beta_6 = [Hg(SCN)_6^{4-}][Hg^{2+}]^{-1}[SCN^-]^{-6} = 10^{21.67}$. These authors give also values of β_5 and β_6 determined in water-methanol, water-ethanol and water-acetone mixtures.

From optical data Gallais and Mounier[6] found at 16°C $K_3 = [Hg(SCN)_3^-][Hg(SCN_2)]^{-1}[SCN^-]^{-1} = 10^{1.68}$, and $K_4 = [Hg(SCN)_4^{2-}][Hg(SCN)_3^-]^{-1}[SCN^-]^{-1} = 10^{0.62}$, while Yatsimirskii and Tukhlov[7] calculated at 25°C $\beta_2 = [Hg(SCN)_2][Hg^{2+}]^{-1}[SCN^-]^{-2} = 10^{17.47}$.

Czakis[8] measured the solubility of $Hg(SCN)_2$ in solutions of different SCN^- concentration at 20°C and 1.4 M NH_4NO_3 medium. She could explain the results by assuming only $Hg(SCN)_3^-$ with the equilibrium constant $[Hg(SCN)_3^-][SCN^-]^{-1} = 10^{0.13}$. If the solubility of $Hg(SCN)_2$ is assumed to be 3.4×10^{-3} M, the value given by Czakis, we calculate $K_3 = 10^{2.60}$.

Several authors have investigated the formation of $Hg(SCN)_2$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ by means of polarographic methods. Nymann and Alberts[9] found in 1 M $NaClO_4$ ionic medium at 25°C $\beta_2 = 10^{16.07}$, $K_3 = 10^{2.88}$, $K_4 = 10^{1.99}$, thus $\beta_4 = 10^{20.94}$. In solutions containing concentrations of KSCN ranging from 2×10^{-3} to 0.98 M Seth and Kapoor[10] determined $\beta_2 = 10^{17.60}$, $\beta_3 = 10^{20.40}$ and $\beta_4 = 10^{21.23}$, the temperature being not stated. Tanaka, Ebata and Murayama[11] studied the mercury(II) thiocyanate system in 0.2 M KNO_3 ionic medium in the temperature range 15-35°C and calculated for 25°C and zero ionic strength $\beta_2 = 10^{17.26}$, $\beta_3 = 10^{19.97}$ and $\beta_4 = 10^{21.69}$.

Notation

B = total concentration of Hg^{II}

b = concentration of Hg^{2+}

(5) A. M. Golub and L. I. Romanenko, *Zhur. neorg. Khim.*, *5*, 1085 (1960).
(6) F. Gallais and J. Mounier, *Compt. Rend.*, *223*, 790 (1946).
(7) K. B. Yatsimirskii and B. D. Tukhlov, *Zhur. obshchei Khim.*, *26*, 356, (1956).
(8) M. Czakis, *Roczniki Chem.*, *33*, 3 (1959).
(9) C. J. Nymann and G. S. Alberts, *Analyt. Chem.*, *32*, 207 (1960).
(10) T. D. Seth and R. C. Kapoor, *J. Polarog. Soc.*, *10*, 17 (1964).
(11) N. Tanaka, K. Ebata, and T. Murayama, *Bull. Chem. Soc. Japan*, *35*, 124 (1962).

M = total concentration of Hg^{I}

$B' = M+B$

m = concentration of Hg_2^{2+}

A = total concentration of SCN^-

a = concentration of SCN^-

$q = b^2m^{-1}$

$\bar{n}$ = average number of SCN^- per $Hg^{II} = (A-a)B^{-1}$

X = analytical excess of SCN^- over $Hg(SCN)_2$ and $Hg_2(SCN)_2$ $= A-2B-2M$

K_o = equilibrium constant for $Hg+Hg^{2+} \rightleftharpoons Hg_2^{2+}$

K = equilibrium constant for $Hg^{2+}+Hg(SCN)_2 \rightleftharpoons 2HgSCN^+$

K_{So} = solubility product of $Hg_2(SCN)_2$

K_n = equilibrium constant for $Hg(SCN)_{n-1}^{3-n}+SCN^- \rightleftharpoons Hg(SCN)_n^{2-n}$

β_n = equilibrium constant for $Hg^{2+}+nSCN^- \rightleftharpoons Hg(SCN)_n^{2-n}$

s = solubility of $Hg(SCN)_2$

In the equations, equilibrium constants and figures the unit M (moles/liter) is used throughout.

Method of Investigation

The equilibria between Hg^{2+} and SCN^- ions have been investigated at 25°C by measuring the concentration of Hg^{2+}, or the ratio $q = b^2m^{-1}$ in presence of solid $Hg_2(SCN)_2$, by potentiometric methods in a series of $Hg(ClO_4)_2$ –NaSCN mixtures. As a check a few solubility measurements of $Hg(SCN)_2$ in NaSCN solutions were carried out. The emf experiments were performed as potentiometric titrations. All the solutions studied were made to contain a constant ionic concentration $[ClO_4^-] = 1$ M or, for $X>0$, $[ClO_4^-]+X = 1$ M. The solutions contained also 0.05 M $HClO_4$ to repress hydrolytic equilibria of Hg^{2+} ion.

In the following the activity coefficients of the reacting species will be considered to remain constant for qualitative changes in the ionic medium. Thus activities will be replaced by concentrations in the formulas expressing chemical equilibrium.

As in our previous work[12] on the complex formation between Hg^{2+} and Cl^- ions, we attempted to determine the constants for all the Hg^{2+} –SCN^- species by measuring, in the range $-B \leqslant X \leqslant 0.1$ M, the emf of the cell

$$-\text{Ref/solution } S_1,\ Hg^{2+},\ Hg_2^{2+},\ Hg_2(SCN)_2(s)/Pt+ \qquad (A)$$

where

$$\text{Ref} = Ag,\ AgCl/0.01\text{ M } Cl^-,\ 0.99\text{ M } ClO_4^-,\ 1\text{ M } Na^+/1\text{ M } NaClO_4$$

and solution

$$S_1 = B\text{ M } Hg(ClO_4)_2,\ M\text{ M } Hg_2(ClO_4)_2,\ A\text{ M NaSCN}$$
$$0.05\text{ M } HClO_4,\ (0.95-2M-2B)\text{ M } NaClO_4$$
$$(\text{or, for } X>0,\ (0.95-A)\text{ M } NaClO_4)$$

(12) L. Ciavatta and M. Grimaldi, *J. Inorg. Nucl. Chem.*, 30, 197 (1968).

It has been shown previously[12] that from data measured in solutions where $X>0$ one can calculate K_3 and K_4. Once these constants are assessed, one can compute the values of K_1 and K_2 from data obtained in the range $X<0$.

For SCN^- this method proved impracticable. Emf-s values of so poor reproducibility were measured in solutions where $X>0$ to warrant the accurate determination of the constants. Thus the equilibria were studied by a different approach.

The results of measurements with cell(A) in the range $X<0$ were combined with the solubility product of $Hg_2(SCN)_2$, K_{So}. From these data the constants K_1 and K_2 could be obtained. For the calculations it proved necessary to known the value of K. This was assessed by inserting in cell (A) solutions S_1 with so little Hg_2^{2+} to prevent precipitation of $Hg_2(SCN)_2$.

The solubility product of $Hg_2(SCN)_2$ was calculated from titrations of Hg_2^{2+} with SCN^- using the cell

$$-\text{Ref/solution } S_2,\ Hg_2^{2+}/Hg+ \qquad (B)$$

Solutions S_2 were prepared by adding to a solution $S_2'(=B'\text{M } Hg(ClO_4)_2$, 0.05 M $HClO_4$, $(0.95\text{-}2B')$M $NaClO_4$ equilibrated with Hg metal until equilibrium

$$Hg+Hg^{2+} \rightleftharpoons Hg_2^{2+} \qquad (1)$$

was attained) equal volumes of $S_2''(=2B'\text{M } Hg(ClO_4)_2$, 0.1 M $HClO_4$, $(0.9\text{-}4B')$M $NaClO_4$, presaturated with Hg as S_2') and $S_2'''(=A'\text{M NaSCN}$, 1 M $NaClO_4$). For $X>0$ S_2''' was replaced by: A'M NaSCN, $(1-A'+4B')$M $NaClO_4$.

The equilibria involving the formation of higher complexes were studied with the cell

$$-Hg/Hg^{2+},\ \text{solution } S_3/\text{Ref}+ \qquad (C)$$

Solutions $S_3(=B$ M $Hg(ClO_4)_2$, A M NaSCN, 0.05 M $HClO_4$, $(0.95-A)$M $NaClO_4$) were made to contain a high ratio $A\ B^{-1}$ in order to avoid formation of $Hg_2(SCN)_{2(s)}$ as a consequence of equilibrium (1). A special titration was performed with solutions where the acidity was 0.1 M instead of 0.05 M; this to see whether appreciable uncertainty is introduced in the calculations by neglecting association between H^+ and SCN^-.

By assuming the activity coefficients remain constant the emf–s of cell (A), (B) and (C) can be written at 25°C

$$E_A = E_A^\circ + 29.58 \log q \qquad (2)$$

$$E_B = E_B^\circ + 29.58 \log m = E_B^\circ + 29.58 \log K_{So} - 59.15 \log a \qquad (3)$$

$$E_C = E_C^\circ - 29.58 \log b \qquad (4)$$

where E_A°, E_B°, and E_C° are constants in each run and include the liquid junction potential between test solutions and 1 M $NaClO_4$. According to Biedermann and Sillén[13] the latter quantity depends mainly on the H^+ concentration of the test solution; since the

(13) G. Biedermann and L. G. Sillén, *Arkiv Kemi*, 5, 425 (1953).

acidity was kept constant in each titration, it may be considered constant.

The value of E_A° was assessed before each run by measurements with cell (A) in the absence of thiocyanate ions, thus putting $q = B^2M^{-1}$ in equation (2). To obtain E_B° and/or E_C° solutions S_2' were inserted in cell (B), and E_B was measured as a function of B'. By assuming equilibrium (1) we computed $m = B'(1+K_o^{-1})^{-1}$ which introduced in equation (3) gave E_B°. In the calculations we employed $K_o = 170.4 \pm 2$ which was determined by following the method proposed by Hietanen and Sillén.[14] These authors under experimental conditions identical to ours found for K_o a value of 168.4. Once E_B° was assessed, E_C° could be calculated by means of the relationship $E_C^\circ = E_B^\circ + 29.58 \log K_o$ which is easily derived by taking into account equilibrium (1).

When applying the potentiometric approach the assumption was made that no appreciable amounts of soluble Hg_2^{2+} $-SCN^-$ complexes are present in solution. In order to verify the correctness of the potentiometric results the equilibria involving the formation of higher complexes were also studied by solubility determinations of $Hg(SCN)_2$ in NaSCN solutions.

Experimental Section

Reagents and analysis.

Sodium perchlorate, perchloric acid, mercury(II) and mercury(I) perchlorates were prepared and analysed as described previously.[12,15]

Sodium thiocyanate stock solutions were prepared by a NaSCN C. Erba p.a. product which was crystallized twice from water. The total $[SCN^-]$ in the stock solutions was determined iodometrically by following the method proposed by Schulek,[16] as well as argentometrically by Volhard's method. The results of analyses coincided within 0.1 per cent or better.

Mercury(II) thiocyanate was prepared by mixing NaSCN and $Hg(ClO_4)_2$ dilute solutions. The crystals which formed were carefully washed with water and dried in a vacuum desiccator over conc. H_2SO_4. The final preparation was analysed for Hg, as HgS or electrogravimetrically, as well as for SCN^- by Schulek's method. The solid had the following composition: 63.52 per cent Hg(calculated 63.33) and 36.48 per cent SCN^-.

Apparatus and experimental details. The emf measurements were performed with the apparatus described previously.[15]

Attainment of equilibrium in experiments with cell (A) and (B) was rather slow, most probably for aging of the $Hg_2(SCN)_2$ precipitated. The potentials attained a constant value after 2-4 hours waiting; after these intervals they remained constant for 12 hours or more. In some instances the value of E_B for a point was followed during a period of three days. The $E_B - E_B^\circ$ values showed no systematic trend and was constant to within ± 0.3 mV. Data $E_C - E_C^\circ$ obtained in parallel series could be reproduced to within ± 0.2 mV. All the test solutions were carefully freed from O_2 by passing in them a vigorous stream of nitrogen purified on activated copper. The removal of last traces of oxygen from solutions where $X > 0$ is the prerequisite for accurate measurements since Hg metal and Hg^I are readily and rapidly oxidized in these conditions.

Equilibration between solid $Hg(SCN)_2$ and NaSCN solutions was effected by running the aqueous phase through a glass tube, packed with a column of solid, kept in a water bath at 25.00 ± 0.05°C. In the saturated solution both Hg^{II} and SCN^- were determined as described above for $Hg(SCN)_2$.

Since acid solutions of SCN^- deteriorate with time, as indicated by a smell of H_2S after some days from their preparation, only freshly mixed solutions were employed for the experiments. That no significant decomposition of SCN^- took place during the measurements is indicated by the constancy and reproducibility of the potential values within 12 hours or more. Furthermore it is corroborated by the coincidence, within the limits of experimental error, of points obtained in forward titrations with those of back titrations.

Data and Calculations

The experimental data, which form the basis of the following calculations, are collected in Tables I, II, III, IV, and V. The calculations will be presented in such an order to avoid as long as possible the use of constants derived at a later stage. It will be assumed that no appreciable association between H^+ and SCN^- occurs in the concentration range studied. The validity of this hypothesis is demonstrated in the next section.

Determination of β_3 and β_4. The experimental data $\log B\,b^{-1}$ (A), obtained from titrations with cell (C) and summarized in Table I, form the basis for the calculation of β_n of higher complexes. In our solutions, where a high AB^{-1} ratio had to be used to prevent precipitation of $Hg_2(SCN)_2$ on the Hg electrode, the main species are $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$. Then

$$Bb^{-1} = \beta_3 a^3 + \beta_4 a^4 \quad (5)$$

$$A = a + 3\beta_3 b a^3 + 4\beta_4 b a^4 = a + \bar{n}B \quad (6)$$

and the constants can be calculated from the plot of

$$Bb^{-1}a^{-3} = \beta_3 + \beta_4 a \quad (7)$$

as a function of a.

For each experimental point a, thus $Bb^{-1}a^{-3}$, was estimated by means of $a = A - 4B$. This may be regarded as a good approximation since the points of the plot $\log B/b$ against $\log A$ seemed to fit a curve of slope ranging from 3.8, at the lowest A, to 4.0 as A ap-

(14) S. Hietanen and L. G. Sillén, *ibid.*, *10*, 103 (1956).
(15) L. Ciavatta and M. Grimaldi, *J. Inorg. Nucl. Chem.*, *30*, 563 (1968).
(16) E. Schulek, *Z. analyt. Chem.*, *62*, 337 (1923).

Table I. Survey of measurements for β_3 and β_4

$B = 5\times10^{-3}$ M		$B = 2\times10^{-3}$ M Back titration		$B = 5\times10^{-4}$ M		$B = 2\times10^{-3}$ M 0.1 M $HClO_4$	
$\log B/b$	A M	$\log B/b$	A M	$\log B/b$	A M	$\log B/b$	A M
20.481	0.5219	17.769	0.1113	18.915	0.2029	19.650	0.3174
20.165	0.4379	18.405	0.1577	18.602	0.1693	19.516	0.2945
19.892	0.3758	19.104	0.2331	18.335	0.1454	19.378	0.2721
19.543	0.3098	19.717	0.3298	18.195	0.1342	19.142	0.2386
19.007	0.2316	19.991	0.3840	17.983	0.1188	18.949	0.2147
18.580	0.1854	20.299	0.4595	17.728	0.1024	18.683	0.1825
				17.418	0.0856_3	18.137	0.1369
				17.044	0.0689_4		
				16.649	0.0548_3		
				16.192	0.0421_3		

Table II. Determination of K

$B = 2\times10^{-3}$ M			$B = 2\times10^{-3}$ M			$B = 5.1\times10^{-3}$ M		
$\log B/b$	$A\times10^3$ M	$K\pm\Delta K$	$\log B/b$	$A\times10^3$ M	$K\pm\Delta K$	$\log B/b$	$A\times10^3$ M	$K\pm\Delta K$
0.614	1.672	24.3±0.8	0.308	1.052	33±12	0.708	4.646	23.1±0.7
1.062	2.318	21.2±0.3	0.560	1.594	22.4± 0.9	0.882	5.299	21.8±0.4
1.574	2.888	20.6±0.2	0.988	2.240	19.8± 0.2	1.147	6.181	20.6±0.2
2.118	3.330	20.4±0.2	1.348	2.658	20.1± 0.2	1.412	6.946	20.2±0.2
*0.698	1.818	21.6±0.5	1.897	3.180	20.5± 0.2	1.686	7.625	20.4±0.2

* Back titrated

Table III. Titration for K_{so}

$E_B^\circ = 426.70\pm0.05$ mV, $X\times10^3$ M	E_B mV	$B' = 5\times10^{-3}$ M $E_B^\circ+29.58\log K_{so}$ mV
0.141_3	93.32	−135.02
0.642_5	54.62	−134.87
1.124	40.06	−135.13
2.438	20.75	−134.67
2.878	16.03	−135.16
3.578	10.52	−135.16
$-\log K_{so} = 18.989\pm0.013$		

Table IV. Titrations for K_1 and K_2

$B\times10^3$ M	$-\log q$	$-X\times10^3$ M	$B\times10^3$ M	$-\log q$	$-X\times10^3$ M
3.206	4.521	11.39	2.949	4.570	13.66
3.098	4.545	9.32_1	2.844	4.572	11.39
2.997	4.581	7.39_4	2.748	4.607	9.32_1
2.857	4.681	4.70_9	2.659	4.653	7.39_5
2.792	4.774	3.45_6	2.575	4.710	5.58_1
2.729	4.946	2.25_8	2.495	4.796	3.86_8
			2.458	4.876	3.05_1

Table V. Solubility of $Hg(SCN)_2$ in NaSCN solutions (A total SCN^- in the aqueous phase at equilibrium, R defined by equation (24))

$s\times10^3$	1.99_0	2.63_8	3.30_9	4.64	7.27	12.60	28.50
$A\times10^3$	3.98_0	6.44_7	9.01_9	14.10	24.26	45.11	107.5
R		0.263	0.262	0.262	0.260	0.258	0.256

proaches 0.5 M, indicating that $\bar{n}$ is very nearly 4.0. The results of calculations are illustrated in Figure 1 where $Bb^{-1}a^{-3}$ is given as a function of a. The points are seen to fit well the hypothesis that $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ only are formed. The most probable values of β_3 and β_4, listed in Table VI, were obtained as intercept and slope of the best line passing through the points, estimated by the least squares method. The uncertainties of the constants represent maximum deviations from mean values.

It is worth noting that data of Table I include a special titration performed at an acidity of 0.1 M $HClO_4$ instead of 0.05 M. The coincidence, within the limits of experimental error, of points (Figure 1) measured at different acidities affords some evidence for the correctness of the hypothesis that no appreciable association occurs between H^+ and SCN^- in our solutions.

Determination of K. The equilibrium constant for $Hg^{2+} + Hg(SCN)_2 \rightleftharpoons 2HgSCN^+$

$$K = [HgSCN^+]^2 b^{-1} [Hg(SCN)_2]^{-1} \quad (8)$$

is calculated from data $\log B/b$, A given in Table II, which were measured with cell (A) in solutions containing $A < 2B$ and so little Hg_2^{2+} that no $Hg_2(SCN)_2$ (s) formed, thus $m = M$ and $b^2 = qM^{-1}$. In these solutions a is negligibly small compared to A and the only species occuring are Hg^{2+}, $HgSCN^+$ and $Hg(SCN)_2$, thus we may write

$$B = b + [HgSCN^+] + [Hg(SCN)_2] \qquad (9)$$

$$A = [HgSCN^+] + 2[Hg(SCN)_2] \qquad (10)$$

Combining equations (8), (9), and (10) the expression for K is obtained

$$K = (2(B-b)-A)^2 b^{-1} (A+b-B)^{-1} \qquad (11)$$

Table VI. Survey of equilibrium constants

From potentiometric data	
$Hg^{2+} + Hg(SCN)_2 \rightleftharpoons 2HgSCN^+$	$\log K = 1.31_2 \pm 0.005$
$Hg_2(SCN)_2(s) \rightleftharpoons Hg_2^{2+} + 2SCN^-$	$\log K_{So} = -18.99_6 \pm 0.013$
$Hg^{2+} + SCN^- \rightleftharpoons HgSCN^+$	$\log K_1 = 9.08 \pm 0.03$
$Hg^{2+} + 2SCN^- \rightleftharpoons Hg(SCN)_2$	$\log K_1K_2 = 16.86 \pm 0.05$
$Hg^{2+} + 3SCN^- \rightleftharpoons Hg(SCN)_3^-$	$\log \beta_3 = 19.7 \pm 0.1$
$Hg^{2+} + 4SCN^- \rightleftharpoons Hg(SCN)_4^{2-}$	$\log \beta_4 = 21.67 \pm 0.03$
From solubility data	
$Hg(SCN)_2(s) \rightleftharpoons Hg(SCN)_2$	$\log s_o = -2.70_1 \pm 0.005$
$Hg(SCN)_2 + SCN^- \rightleftharpoons Hg(SCN)_3^-$	$\log K_3 = 2.80 \pm 0.03$
$Hg(SCN)_2 + 2SCN^- \rightleftharpoons Hg(SCN)_4^{2-}$	$\log K_3K_4 = 4.8 \pm 0.1$

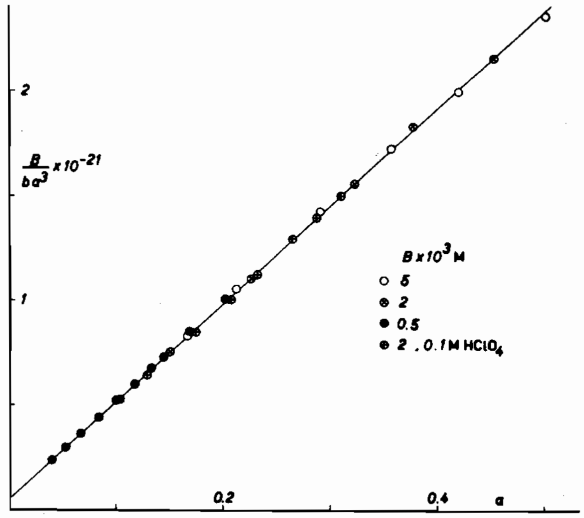

Figure 1. Determination of β_3 and β_4. $Bb^{-1}a^{-3}$, equation (7), as a function of a. The line represents the equation $Bb^{-1}a^{-3} = 5 \times 10^{19} + 4.68 \times 10^{21} a$.

For each experimental point K was computed by inserting data of Table II in equation (11). In order to examine the influence on K of experimental error, the calculations were also made with higher and lower limits of b estimated taking a value of ± 0.2 mV for the uncertainty of the potential of cell (A). The results are given in Table II. The most probable value of K was calculated by using the standard least squares method. This yielded, assuming for each K a weight of $(\Delta K)^{-2}$, the value listed in Table VI. The limits of the constant represent three times the standard deviation.

Titrations for K_{So}. Table III gives in detail a titration performed with cell (B). Because of equilibrium (1), in these solutions where $X > 0$ also the species $Hg(SCN)_2$, $Hg(SCN)_3^-$, and $Hg(SCN)_4^{2-}$ must be considered. We have then

$$B' = [Hg_2(SCN)_2]_{solid} + [Hg(SCN)_2] + [Hg(SCN)_3^-] + [Hg(SCN)_4^{2-}] \qquad (12)$$

$$A = a + 2[Hg_2(SCN_2]_{solid} + 2[Hg(SCN)_2] + 3[Hg(SCN)_3^-] + 4[Hg(SCN)_4^{2-}] \qquad (13)$$

and

$$X = a + [Hg(SCN)_3^-] + 2[Hg(SCN)_4^{2-}] = a + K_{So}\beta_3 K_o^{-1} a + 2K_{So}\beta_4 K_o^{-1} a^2 \qquad (14)$$

Since K_o, β_3 and β_4 are known, the solubility product can be calculated from $E_B(X)_{E_B^\circ}$ data by combining equations (3) and (14). First an approximate value of K_{So} is estimated by inserting $a = X$ in equation (3). Then better values of a are computed from equation (14), and the couple (K_{So}, a) refined by successive approximations.

The results of calculations are given in Table III. As average value of three determinations we have estimated for K_{So} the value given in Table VI.

The solubility product of $Hg_2(SCN)_2$ has been determined at 25°C by Sherill and Skowronski[1] and by Grossmann[2] who estimated $-\log K_{So} = 19.74$ and 19.84 respectively. From Immerwahr's[17] data Brodsky[18] has computed 19.52. It should be noted that Grossmann's value, since it was derived from measurements in 1 M $K^+(NO_3^-)$ ionic medium, should not differ so much from ours. The apparent disagreement can be explained as follows. Grossmann measured at 25°C the solubility of $Hg_2(SCN)_2$ in KSCN solutions and calculated for the equilibrium $Hg_2(SCN)_2\ (s) + 2SCN^- \rightleftharpoons Hg(l) + Hg(SCN)_4^{2-}$ the constant $\varkappa = [Hg(SCN)_4^{2-}]\ [SCN^-]^{-2} = 3$. With this value, $K_o = 120$ and $\beta_4 = 10^{22.4}$, which was derived from experiments at 18°C, he estimated $K_{So} = K_o \varkappa \beta_4^{-1}$. From our results we find $K_o = 170.4$ and $\varkappa = 2.75$, thus the difference in the K_{So} values rests on the assumption tacitly introduced by Grossmann that β_4 does nct change appreciably from 18°C to 25°C. The findings of several authors[4,11] indicate however that the temperature has a remarkable influence on the equilibrium $Hg^{2+} + 4SCN^- \rightleftharpoons Hg(SCN)_4^{2-}$.

Determination of K_1 *and* K_2. The primary data B, X, q measured with cell (A) are summarized in Table IV. The values of K_1 and K_2 are estimated by recalculating the data in the form B, b, a, and by constructing the plot

$$(Bb^{-1} - 1)a^{-1} = K_1 + K_1K_2 a \qquad (15)$$

as a function of a.

(17) C. Immerwahr, *Z. Elektrochem.*, *7*, 477 (1901).
(18) A. E. Brodsky, *Z. Elektrochem.*, 35, 833 (1929).

In order to compute b, thus a through

$$m = b^2q^{-1} \tag{16}$$

and $K_{So} = ma^2$, we started with the equations

$$B = b + [HgSCN^+] + [Hg(SCN)_2] \tag{17}$$

$$M = m + [Hg_2(SCN)_2]_{solid} \tag{18}$$

$$A = [HgSCN^+] + 2[Hg(SCN)_2] + 2[Hg_2(SCN)_2]_{solid} \tag{19}$$

thus

$$X = 2m + 2b + [HgSCN^+] \tag{20}$$

By inserting (16) in (20) an expression between $[HgSCN^+]$ and b through known quantities was obtained, $[HgSCN^+] = f(b)_{X,q}$. Introduction of this expression in (17) gave $[Hg(SCN)_2] = \varphi(b)_{B,X,q}$. By putting these expressions of $[HgSCN^+]$ and $[Hg(SCN)_2]$ in equation (8) a polynomial $P(b)=0$ of fourth degree, with known coefficients, was obtained. From this b was computed by successive approximations. A preliminary value was estimated graphically, then it was refined by numerical interpolation.

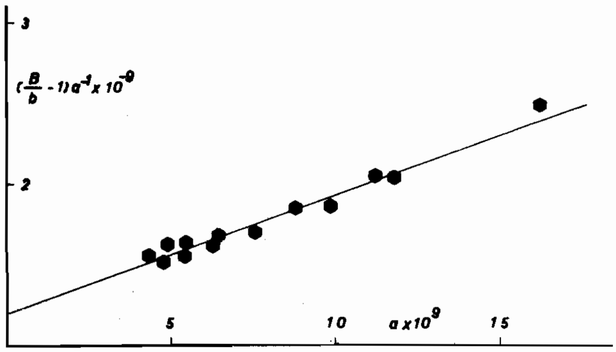

Figure 2. Determination of K_1 and K_2. $(Bb^{-1}-1)a^{-1}$, equation (15), as a function of a. The line represents the equation $(Bb^{-1}-1)a^{-1} = 1.2\times10^9+7.25\times10^{16}a$.

The results of calculations are shown in Figure 2 where $(Bb^{-1}-1)a^{-1}$ is plotted against a. From the slope and intercept of the best line passing through the points, estimated by the least squares method, we have calculated the values of K_1 and K_1K_2 given in Table VI. The uncertainties of the constants represent maximum deviations from the most probable values.

Solubility measurements. The solubility data are collected in Table V. If only mononuclear complexes are assumed to exist in solutions of Hg^{II}, the solubility, s, and the total thiocyanate concentration in the aqueous phase at equilibrium with solid $Hg(SCN)_2$ can be written for $X>0$ as

$$s = [Hg(SCN)_2] + K_3[Hg(SCN)_2]a + K_3K_4[Hg(SCN)_2]a^2 \tag{21}$$

$$A = a + 2[Hg(SCN)_2] + 3K_3[Hg(SCN)_2]a + 4K_3K_4[Hg(SCN)_2]a^2 \tag{22}$$

In solutions at equilibrium with solid $Hg(SCN)_2$, $[Hg(SCN)_2]$ is constant and equal with good approximation to the solubility, s_o of $Hg(SCN)_2$ in 1 M $NaClO_4$, and the values of K_3 and K_3K_4 can be calculated from the plot of

$$(\frac{s}{s_o}-1)a^{-1} = K_3+K_3K_4a \tag{23}$$

as a function of a.

In order to obtain a from the experimental data we calculated first the function

$$R = \frac{s-s_o}{A-2s_o} = \frac{K_3s_o+K_3K_4s_oa}{1+3K_3s_o+4K_3K_4s_oa} \tag{24}$$

which extrapolated to $A-2s_o \to 0$ gave K_3s_o. Then using this K_3s_o value a was estimated by means of the relationship $4s-A-2s_o = (K_3s_o-1)a$.

The results of calculations are given in Table V and Figure 3. It is seen in Table V that R approaches to 0.263 as $A-2s_o \to 0$. From this estimate we found the K_3 value given in Table VI. The best slope of the line passing through points of Figure 3 gave for K_3K_4 the value of Table VI.

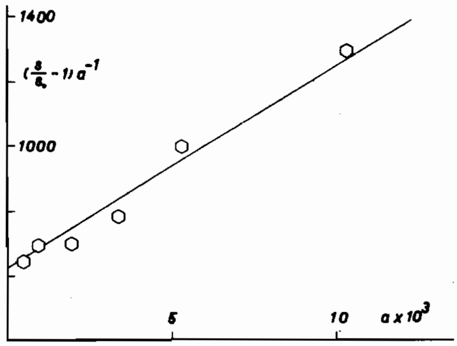

Figure 3. Solubility measurements. $(s\,s_o^{-1}-1)a^{-1}$ as a function of a. The line represents the equation $(s\,s_o^{-1}-1)a^{-1} = 630+6.3\times10^4a$.

It should be added that quantities as R are to be avoided when values near 0.250 should be considered because in such a case R is independent of A and the calculation of a is very sensitive to small experimental error. In the present case R is near to 0.250 however the data seem of sufficient accuracy to allow the determination of log K_3K_4 with an uncertainty not exceeding ±0.1.

Discussion

The main conclusion of this work is that in the $Hg^{II}-SCN^-$ system a series of mononuclear complexes, *viz.* $HgSCN^+$, $Hg(SCN)_2$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$, is formed in solutions where $10^{-9} \leqslant a \leqslant 0.5$ M and $B \leqslant 5\times10^{-3}$ M. A number of equilibrium constants, derived from potentiometric and solubility data, are listed in Table VI. We estimate from the potentiometric results log $K_3 = 2.8_4 \pm 0.15$ and log $K_3K_4 = 4.8 \pm 0.1$ which are in good agreement with the values derived from solubility measurements. The coincidence of the constants within the limits of estimated uncertainty affords evidence for the validity of the hypothesis that no detectable amounts of Hg_2^{2+}–SCN^- complexes are formed in our solutions.

Our equilibrium constants β_2, K_3 and K_4 can be compared with those determined polarographically by Nymann and Alberts[9] who used experimental conditions identical to ours, namely 25°C and 1 M $NaClO_4$ ionic medium. The K_3 and K_4 values ($10^{2.88}$ and $10^{1.99}$) are in good agreement with ours, however their β_2 value, $10^{16.07}$, is much lower. Exact comparison of our equilibrium constants with those of other previous workers is difficult because of the different experimental conditions under which the measurements were carried out.

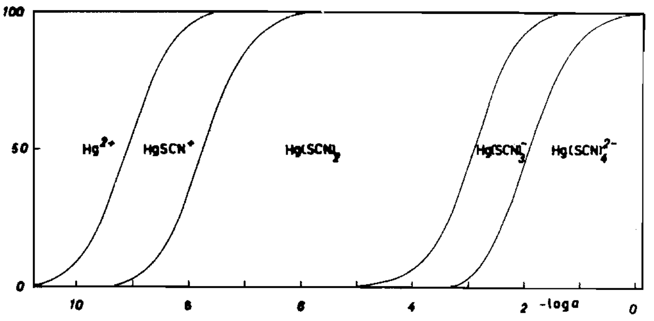

Figure 4. Distribution of Hg^{II} (in percent) over Hg^{2+}, $HgSCN^+$, $Hg(SCN)_2$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ as a function of log *a*.

The equilibria involving the species Hg^{2+}, $HgSCN^+$, $Hg(SCN)_2$, $Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$ are visualized in Figure 4, where the distribution of Hg^{II} over different complexes is given as a function of log *a*. As it is seen there is a large log *a* range where almost only $Hg(SCN)_2$ is present. The broad range of existence of the second complex is a characteristic feature of the complex formation between Hg^{2+} and monodentate ligands as Hg^{2+}–halides[19], Hg^{2+}–NH_3[20], Hg^{2+}–CN^-[21]. The range of existence of $HgSCN^+$ and $Hg(SCN)_3^-$ seems however much broader than that found for corresponding species in the Hg^{II}–Cl^- and Hg^{II}–NH_3 systems.

Added in Proof. Recently E. A. Gyunner and N. D. Belyck, Ukrain Khim. Zhur. *32*, 1270 (1966), have studied at 20°C the solubility, *s*, of $Hg(SCN)_2$ in solutions of various total Hg^{II} concentrations by measuring the volume of a standardized KSCN solution to be added to a given volume of $Hg(NO_3)_2$ until the appearance of permanent turbidity. The Hg^{II} concentration ranged from 0.065 to 0.724 M, and the ionic strength was adjusted to 4.6 M by adding HNO_3, KNO_3 and $Ca(NO_3)_2$. By extrapolating the *s* data to $C_{Hg(NO_3)_2} \rightarrow 0$ they estimate a value of 0.0147 M for s_o, the solubility of $Hg(SCN)_2$ in the medium, then from the slope (=1) of the plot $\log(s-s_o)$ against log $C_{Hg(NO_3)_2}$ conclude that $Hg_2(SCN)_2^{2+}$ is formed according to

$$Hg(SCN)_2(s) + Hg^{2+} \rightleftharpoons Hg_2(SCN)_2^{2+},$$

$$[Hg_2(SCN)_2^{2+}][Hg^{2+}]^{-1} = K_{22} = 0.201 \pm 0.005$$

The conclusions of these authors are mainly based on the hypothesis that linear extrapolation of the *s* data to $C_{Hg(NO_3)_2} \rightarrow 0$ gives s_o. Since, however, their data extend into a range of high $C_{Hg(NO_3)_2}$ where $[Hg^{2+}]$ prevails over s_o, the extrapolation is uncertain and accuracy is gained only if the law of dependence of *s* on the Hg^{II} concentration is known. This point is illustrated by testing a few reaction mechanisms.

By assuming the formation of $Hg_2(SCN)_2^{2+}$ we estimate $s_o = 0.0176$ M and $K_{22} = 0.26 \pm 0.02$; the difference between these estimates and the values given by Gyunner and Belyck is accounted by the erroneous way of writing mass balance equations by these authors. On the other hand the hypothesis that $HgSCN^+$ is formed according to

$$Hg(SCN)_2(s) + Hg^{2+} \rightleftharpoons 2HgSCN^+,$$

$$[HgSCN^+]^2[Hg^{2+}]^{-1} = K_{11}$$

gives s_o nearly zero and $K_{11} = 0.13 \pm 0.04$. For Hg^{II} concentrations higher than 0.5 M a small systematic trend is observed in the K_{11} values, but this seems not sufficient to strengthen the formation of $Hg_2(SCN)_2^{2+}$. In fact we are not able to estimate to what extent oversaturation as well as precipitation by local excess of reagent affect the accuracy of the solubility data.

We may thus conclude that their solubility data can be explained by assuming the formation of either $Hg_2(SCN)_2^{2+}$ or $HgSCN^+$. However on the basis of the s_o value, 2×10^{-3} M, obtained from our direct determination, it seems that the formation of $Hg_2(SCN)_2^{2+}$ must be excluded at least from data of present accuracy.

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