A Potentiometric Investigation of the Silver-Thiocyanato Complex System in Pyridine Solution

ATIS MIEZIS and RAGNAR LARSSON

Divison of Inorganic Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

The thiocyanato complexes of silver in pyridine solution have been studied by means of potentiometric measurements using an Ag/Ag$^+$ electrode. The investigation has been performed at a temperature of 25°C in a medium with a constant ionic strength of 1.5 M using pyridinium perchlorate as the supporting electrolyte and also in varying ionic strength in which no supporting "inert" electrolyte was added.

From the data the stability constants given in Table 7 were determined and compared with those obtained from the infrared spectroscopic investigation reported previously.[1] A rather good agreement has been obtained when using similar conditions.

The aim of this investigation was primarily to determine the stability constants of the silver-thiocyanate system in pyridine solution and to compare the results with those obtained in an earlier investigation [1] in which spectroscopic techniques were used. The degree of complex formation between the silver ions and the thiocyanate ions was followed by a potentiometric determination of the concentration of free silver ions using an Ag/Ag$^+$ electrode. This method enabled us to keep the ionic strength constant, thus diminishing the variation of activity coefficients when the concentration of thiocyanate was successively increased. The "inert" electrolyte used for this purpose was pyridinium perchlorate.

In view of the fact that the infrared spectroscopic investigation had to be performed without any inert electrolyte present, comparative measurements have been made with and without the use of such an electrolyte.

PRINCIPLE OF THE INVESTIGATION

Notations

C_M = total concentration of metal
C_L = » » » ligand
[M] = free » » » metal
[L] = » » » ligand

$$\bar{n} = \frac{C_L - [L]}{C_M} = \text{the mean ligand number}$$

$[M_m L_n]$ = concentration of the complex $M_m L_n$.

$$\beta_{n,m} = \frac{[M_m L_n]}{[M]^m [L]^n} = \text{the stability constant of the complex } M_m L_n.$$

$$\beta_{0,1} = \beta_{1,0} = 1$$
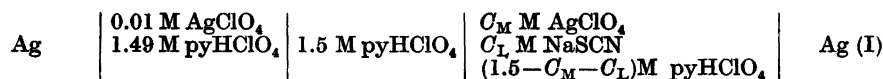
$$X = \sum_{n=0}^{N} \beta_{n,1} \cdot [L]^n \qquad\qquad Y = \sum_{m=0}^{M} \beta_{1,m} \cdot [M]^m$$

$$X_n = \frac{X_{n-1} - \beta_{n-1,1}}{[L]} \qquad\qquad Y_m = \frac{Y_{m-1} - \beta_{1,m-1}}{[M]}$$

Derivation of the stability constants

The emf E of the following type of cell has been measured:

$$\text{Ag} \left| \begin{array}{l} 0.01 \text{ M AgClO}_4 \\ 1.49 \text{ M pyHClO}_4 \end{array} \right| 1.5 \text{ M pyHClO}_4 \left| \begin{array}{l} C_M \text{ M AgClO}_4 \\ C_L \text{ M NaSCN} \\ (1.5 - C_M - C_L)\text{M pyHClO}_4 \end{array} \right| \text{Ag (I)}$$

The experiments were performed by titrating sodium thiocyanate against silver perchlorate keeping the total silver ion concentration constant.

The emf of the cell can be written:

$$E = E^\circ + \frac{RT}{F} \ln a_{Ag^+} - E_{ref} + E_j \tag{1}$$

where E_{ref} stands for the potential of the left hand halfcell as written above, and E_j is the liquid junction potential. The difference denoted E_M between the emf value of the initial solution, i.e. before any sodium thiocyanate has been added, and the emf value of the solution of composition (C_M, C_L) may be expressed by the following equation assuming that the activity coefficients and the liquid junction potentials remain constant

$$E_M = \frac{RT}{F} \ln \frac{C_M}{[M]} \tag{2}$$

Several such titrations were made at different values of the parameter C_M. Adopting the procedure developed by Fronæus,[2] C_L was plotted against E_M,

giving one curve for each value of C_M. These curves were cut at a number of constant E_M values and from the points of intersections, the values obtained for C_L were plotted against C_M for every constant E_M chosen. If only mononuclear complexes exist it holds that

$$C_M/[M] = X \tag{3}$$

and consequently

$$E_M = (RT/F) \ln X \tag{4}$$

When E_M, and thus X are constant, [L] and $\bar{n}$ are also constant and C_L must be a linear function of C_M with the equation

$$C_L = [L]_j + \bar{n}_j C_M \tag{4}$$

By extrapolating these lines to $C_M=0$ one obtains for every constant E_M (or X) the corresponding [L] value. In this way a set of data X([L]),[L] was determined and the stability constants could then be calculated using an appropriate method, *e.g.* graphically.

If polynuclear complexes are also present a fixed value of E_M does not correspond to constant values of X and [L]. But when C_M and thus [M] $\rightarrow$ 0 the effects due to polynuclear complexes and also other C_M-depending disturbances vanish and the relation $E_M = (RT/F) \ln X$ is still valid. As $C_L \rightarrow$ [L] when $C_M \rightarrow 0$ the necessary X,[L] data are obtained by extrapolating the $C_L - C_M$ curves to $C_M = 0$.

In order to determine the stability constants of the polynuclear complexes that may exist, a series of emf measurements were made using the same cell (I) as before, with the exception that the total thiocyanate ion concentration was kept constant and the silver ion concentration was varied. If in the system the thiocyanate ion is regarded as the central ion and the silver ions as the ligands the methods of calculation implying measurement of the ligand concentration can be used (*cf.* the formulae in the infrared spectroscopic investigation[1]). This concentration can be obtained from measurements of the emf of the cell (I) which is written as

$$E = \frac{RT}{F} \ln \frac{[Ag^+]}{[Ag^+]_{ref}} = 59.2 \times \log \frac{[Ag^+]}{0.01} \tag{6}$$

provided that the activity coefficients and the liquid junction potentials are constant in the two halfcells.

The mean ligand number is now expressed by

$$\bar{n}' = \frac{C_M - [M]}{C_L} \tag{7}$$

and one can calculate corresponding values of [M] and $Y([M])$ by graphical integration of the equation

$$\ln Y([M]_j) = \int_0^{[M]_j} \frac{\bar{n}'}{[M]} d[M] \tag{8}$$

If $\bar{n}'$ depends on C_{L} the limiting value of $\bar{n}'/[\mathrm{M}]$ when $C_{\mathrm{L}} \to 0$ is used in the integral above. From the $Y,[\mathrm{M}]$ data the stability constants can be determined graphically in the usual way.

EXPERIMENTAL CONDITIONS

All the measurements have been performed at 25.0°C. Pyridine solutions are very poor conductors of electricity and as a consequence of the large resistance in the cell an oil thermostat was used as recommended by Gupta[3] at temperatures above 18°C.

The emf was measured with a Radiometer pH Meter 4 C, with which it was possible to make readings with an accuracy of 0.1 mV. The electrodes were silver-plated platinum electrodes and were made by precipitating silver onto a platinum cathode from a solution of potassium cyanoargentate(I) in water. Mixing was brought about by a stream of nitrogen passing through both the halfcells all the time except during the readings. In this way any moisture in the air was also prevented from coming in contact with the solutions.

As a result of the tendency of pyridine to absorb moisture from the air all the solutions had to be kept well isolated, and it was preferred to make small amounts of the stock solutions immediately before the mixings instead of keeping large amounts for a long time. It was equally important to keep the moisture away from the solutions during the titrations. In a separate experiment when water was deliberately added to the cell it was observed that *ca.* 0.3 volume % water in a 0.1 M solution of silver perchlorate in pyridine caused an increase in emf of 1.5 mV. By bubbling well dried nitrogen through both the halfcells, however, it was possible to keep the emf practically constant for 4—5 h, *i.e.* the time for every titration run. As a further control every titration was repeated in the reverse direction in order to prove that the emf readings at the end were not influenced by moisture.

Another factor of importance was the age of the silver plated electrodes. For the measurements two different electrodes were used simultaneously in both halfcells. The four combinations of electrodes gave at the start of every titration approximately the same emf, at the end they differed a little from each other and from fresh ones in the same solution. In the same way electrodes immersed in pyridine during the night gave different values compared to those immersed in water. Therefore in order to obtain reproducible emf values it was necessary to renew the silver surface of the electrodes prior to every titration run.

In order to get the highest possible ionic strength pyridinium perchlorate was used as ionic medium, to give the total equivalent concentration of 1.5 M in all solutions. The solubility of pyridinium perchlorate in pyridine was found experimentally to be ca. 2 M. Other conceivable salts which are normally used as supporting electrolytes are less soluble in pyridine, for example sodium perchlorate is only soluble to an extent of ca. 0.5 M.

Chemicals used. All chemicals were of analytical grade and used without further purification. Silver perchlorate was prepared from silver oxide and perchloric acid and pyridinium perchlorate from equivalent amounts of pyridine and perchloric acid. Both preparations were dried at 120°C. (Caution!) Stock solutions were then prepared and the concentration of the silver perchlorate was determined by electrolysis.

RESULTS

A. Measurements at constant ionic strength. Before starting the titrations it was necessary to verify that a Ag/Ag$^+$ electrode obeyed Nernst's law in solutions of silver perchlorate in pyridine and that the activity coefficients could be regarded as constant within the actual range of concentration and for the ionic medium used. The deviation from the theoretically calculated values of emf, $E = 59.2 \log (C_{\mathrm{Ag}^+}/C_{\mathrm{Ag}^+(\mathrm{ref})})$ was found to be < 0.3 mV and

Table 1. Experimental data of C_L and E_M in section A at five different values of C_M.

$C_M = 0.010$ M		$C_M = 0.025$ M		$C_M = 0.050$ M		$C_M = 0.075$ M		$C_M = 0.100$ M	
C_L (M)	E_M (mV)	C_L (M)	E_M (mV)	C_L (M)	E_M (mV)	C_L (M)	E_M (mV)	C_L (M)	E_M (mV)
0.0097	19.1	0.0129	13.1	0.0097	5.6	0.0226	9.4	0.0258	9.0
0.0188	34.7	0.0194	21.1	0.0194	11.7	0.0438	19.9	0.0375	12.8
0.0273	47.7	0.0250	26.8	0.0273	17.0	0.0636	30.8	0.0500	18.0
0.0353	58.2	0.0364	40.8	0.0353	22.6	0.0824	42.2	0.0545	19.7
0.0429	66.3	0.0375	42.1	0.0429	28.2	0.1000	53.1	0.0706	26.5
0.0500	73.3	0.0471	52.3	0.0545	37.7	0.1167	63.2	0.0727	27.7
0.0568	79.3	0.0545	60.2	0.0632	44.3	0.1324	72.2	0.0857	33.7
0.0706	91.0	0.0571	62.2	0.0706	50.6	0.1375	74.2	0.0941	37.7
0.0857	100.5	0.0667	70.8	0.0805	57.7	0.1500	80.9	0.1000	40.2
0.1000	108.3	0.0757	78.1	0.1000	72.2	0.1650	88.4	0.1143	48.0
0.1135	115.0	0.0842	84.4	0.1135	81.0	0.1833	97.3	0.1263	53.7
0.1263	120.5	0.0923	89.9	0.1263	88.4	0.2063	106.9	0.1333	57.5
0.1385	125.3	0.1000	94.6	0.1385	94.8	0.2200	112.4	0.1500	65.6
0.1500	129.6	0.1073	98.9	0.1500	100.5	0.2357	118.2	0.1714	75.8
0.1610	133.3	0.1143	102.8	0.1610	105.7	0.2538	124.4	0.2000	88.9
0.1714	136.7	0.1209	106.2	0.1714	110.0	0.2750	131.0	0.2250	98.9
0.1814	139.8	0.1273	109.2	0.1814	114.2	0.2946	136.7	0.2400	104.9
0.1909	142.4	0.1391	114.7	0.1909	118.0	0.3113	141.2	0.2571	111.1
0.2000	145.1	0.1500	119.2	0.2087	124.6	0.3300	145.9	0.2800	118.9
0.2087	147.3	0.1600	123.3	0.2250	130.2	0.3511	150.9	0.3000	125.2
0.2250	151.6	0.1692	126.6	0.2400	135.0	0.3667	154.3	0.3214	131.6
0.2400	155.2	0.1800	130.5	0.2538	139.2	0.3837	158.0	0.3462	138.4
0.2538	158.3	0.1857	132.3	0.2786	146.0	0.4024	161.7	0.3600	142.0
0.2786	163.5	0.2000	136.7	0.3000	150.9	0.4231	165.9	0.3750	145.7
0.3000	167.8	0.2125	140.5	0.3191	155.3	0.4459	170.0	0.3913	149.4
0.3158	170.6	0.2286	145.0	0.3333	158.2	0.4714	174.4	0.4000	151.4
0.3333	173.8	0.2500	150.4	0.3488	161.4	0.4853	176.7	0.4186	155.3
0.3529	177.0	0.2800	157.2	0.3659	164.9	0.5000	179.1	0.4390	159.7
0.3636	178.7	0.3000	161.4	0.3846	168.4	0.5156	181.6	0.4500	161.7
0.3750	180.6	0.3200	165.4	0.4054	172.0	0.5323	183.9	0.4737	166.2
0.3871	182.3	0.3333	167.9	0.4286	176.1	0.5500	186.4	0.5000	170.9
0.4000	184.1	0.3529	171.3	0.4545	180.3			0.5143	173.2
		0.3636	173.5	0.4688	182.5			0.5294	175.7
		0.3750	175.5	0.4839	184.7			0.5455	178.2
		0.3871	177.6	0.5000	187.0			0.5625	180.8
		0.4000	180.0					0.5806	183.5
		0.4091	181.6					0.6000	186.2
		0.4219	183.4						
		0.4355	185.7						
		0.4500	187.5						

no marked trend in the deviation was obvious after the necessary steps had been taken to prevent moisture from coming in contact with the solutions.

The emf titrations were made at five different values of $C_M = 0.010$, 0.025, 0.050, 0.075, 0.100 M, and in Table 1 the corresponding C_L and E_M for the different series are collected. In Fig. 1, C_L are plotted against E_M for the five C_M values, and Fig. 2 gives examples of C_L as a function of C_M at
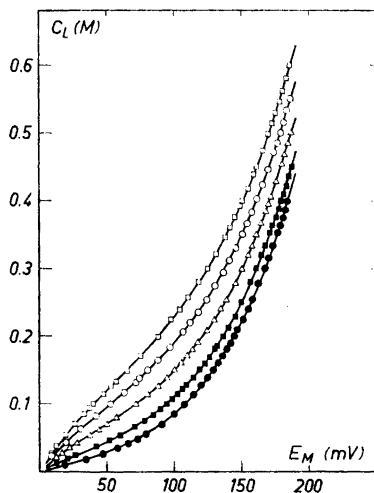
Fig. 1. C_L as a function of E_M at five different values of C_M. $C_M=0.100$ M ($\square$), $C_M=0.075$ M ($\bigcirc$), $C_M=0.050$ M ($\triangle$), $C_M=0.025$ M ($\blacksquare$), and $C_M=0.010$ M ($\bullet$).
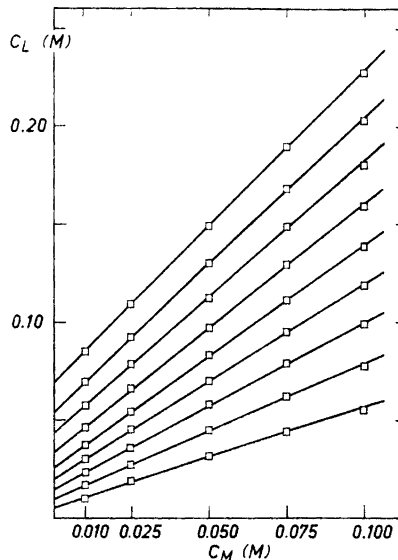
Fig. 2. C_L as a function of C_M at some different values of $E_M=20, 30, 40, 50, 60, 70, 80, 90,$ and 100 mV as beginning at the bottom of the figure.

some different E_M. As seen these functions are very good straight lines and by extrapolating the lines to $C_M=0$ [L] for each corresponding E_M or X is obtained. The stability constants are then determined graphically. Fig. 3 shows the X_1 *versus* [L] curve giving $\beta_{1,1}$ when extrapolated to [L]=0, Fig. 4 shows the X_2 *versus* [L] curve giving $\beta_{2,1}$ when extrapolated to [L]=0 and $\beta_{3,1}$ from the slope of the approximately straight line. All the experimental data of this determination are collected in Table 2.
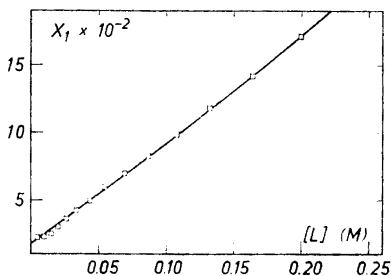

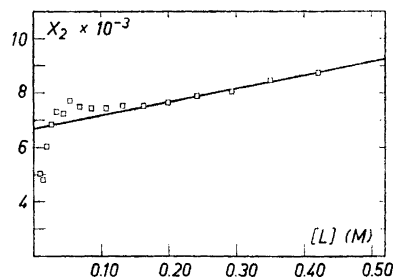
Fig. 3. The function X_1 plotted against [L].

Fig. 4. The function X_2 plotted against [L].

Table 2. Experimental values of [L], X, X_1, X_2, and $\bar{n}$ in section A ($\bar{n}_s$ is the mean ligand number obtained from the slope of the C_L *versus* C_M lines in Fig. 2 and $\bar{n}_c$ is the one calculated from the stability constants).

E_M (mV)	[L] (M)	$\bar{n}_s$	X	$X_1 \times 10^{-2}$	$X_2 \times 10^{-3}$	$\bar{n}_c$
20	0.0053	0.52	2.178	2.223	7.981	0.62
30	0.0097	0.69	3.215	2.284	4.990	0.89
40	0.0149	0.84	4.744	2.513	4.785	1.10
50	0.0200	0.99	7.004	3.002	6.010	1.24
60	0.0261	1.13	10.34	3.579	6.816	1.36
70	0.0335	1.27	15.26	4.257	7.334	1.47
80	0.0435	1.39	22.51	4.945	7.230	1.57
90	0.0541	1.51	33.23	5.957	7.684	1.65
100	0.0690	1.60	49.03	6.961	7.480	1.73
110	0.0867	1.69	72.39	8.234	7.421	1.79
120	0.1078	1.76	106.8	9.814	7.434	1.85
130	0.1327	1.85	157.6	11.80	7.536	1.91
140	0.1639	1.89	232.7	14.14	7.529	1.96
150	0.2000	1.96	343.4	17.12	7.660	2.00
160	0.2421	2.02	506.7	20.89	7.885	2.05
170	0.2939	2.03	748.0	25.42	8.037	2.09
180	0.3500	2.06	1104	31.51	8.489	2.13
190	0.4210	2.08	1629	38.67	8.758	2.18

The constants determined with this method were:

$$\beta_{1,1} = 180\pm 10 \ (M^{-1})$$
$$\beta_{2,1} = 6700\pm200 \ (M^{-2})$$
$$\beta_{3,1} = 4900\pm300 \ (M^{-3})$$

A comparison between the mean ligand number $\bar{n}$ when calculated from the stability constants above and those obtained from the slope of the C_L *versus* C_M lines (in Table 2 denoted as $\bar{n}_c$ and $\bar{n}_s$) shows that the first ones in all cases were larger.

B. Measurements without supporting "inert" electrolyte. The measurements were made exactly as in the case of constant ionic strength but with no pyridinium perchlorate present in the both halfcells. As known the emf of the cell (I) is a function of the activity of the silver ions. Earlier, when we had a constant ionic strength, we could assume rather safely the activity coefficients and the liquid junction potentials to remain constant throughout the experimental range of concentration. In the present case, *i.e.* without constant ionic medium, the question arises how the activity coefficients change when the ionic strength increases and when other ions are present. The emf of the cell can now be written

$$E = 59.2 \log \frac{[\mathrm{Ag^+}]}{0.01} + E_j{}'$$

where $E_j{}' = 59.2 \log \dfrac{f_{\mathrm{Ag^+}}}{f_{\mathrm{Ag^+}}(0.01)} + E_j$

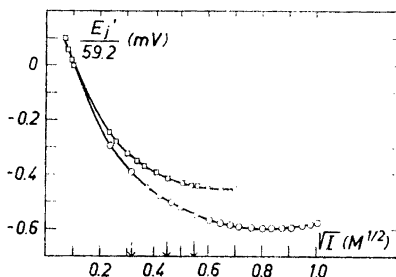*Fig. 5.* The variation of E_j' with the ionic strength:

1) when $I=[Ag^+]$ ($\square$),
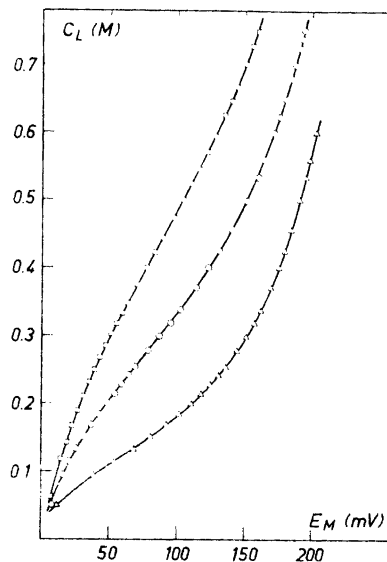2) when $I=[Ag^+]+[pyH^+]$, $[Ag^+]=0.01$ M ($\bigcirc$). The arrows indicate $I=0.1$, $I=0.2$, and $I=0.3$ M.

Fig. 6. C_L as a function of E_M at three different values of C_M. $C_M=0.3$ M ($\square$). $C_M=0.2$ M ($\bigcirc$), and $C_M=0.1$ M ($\triangle$). The points represent the experimental data after the corrections discussed in section B have been made.

Here E_j is the liquid junction potential and f_{Ag^+} the activity coefficient of the silver ions.

Fig. 5 visualizes the variation of E_j' with the ionic strength I, on the one hand when $I=[Ag^+]$, *i.e.* emf of varying silver perchlorate solutions is measured, and on the other when $[Ag^+]=0.01$ M (constant) and $I=[Ag^+]+[pyH^+]$, the negative ion being ClO_4^-.

E_j' decreases strongly when I increases but gradually becomes more constant at larger I. There is also a rather great difference between the two curves. Obviously the variation of E_j' is dependent on the other ions present in the solution besides Ag^+. In the silver-thiocyanate system there are besides Ag^+ and ClO_4^- also Na^+, SCN^-, and varying Ag—SCN complexes. Since one does not know the exact amounts of these, E_j' cannot be determined. However, when working with solutions containing high concentrations of metal and ligand, it can perhaps be supposed that E_j' is rather constant.

In this investigation three emf titrations with $C_M=0.1$, 0.2, 0.3 M were made and C_L was varied up to 0.75 M. However the E_M used in the calculations is a difference $E_M=E_0-E$ where E_0 stands for the emf before any ligand has been added, that is

$$E_M=59.2(\log C_{Ag}-\log [Ag^+])+E_j'(C_{Ag})-E_j'(I)$$

Supposing that E_j' is approximately constant for $I \gtrsim 0.3$ then

$$E_j'(0.3) \approx E_j'(I); \quad I \gtrsim 0.3$$

and $E_M = 59.2 \log \dfrac{0.3}{[\mathrm{Ag^+}]}$

When $C_{\mathrm{Ag}} = 0.1$ or 0.2 M

$$E_M = 59.2 \log \frac{C_{\mathrm{Ag}}}{[\mathrm{Ag^+}]} + E_j'(C_{\mathrm{Ag}}) - E_j'(0.3)$$

or $E_M^{\mathrm{corr}} = E_M - (E_j'(C_{\mathrm{Ag}}) - E_j'(0.3)) = 59.2 \log \dfrac{C_{\mathrm{Ag}}}{[\mathrm{Ag^+}]}$

Table 3. Experimental data of C_L and E_M^{corr} in section B at three different values of C_M.

$C_M = 0.100$ M		$C_M = 0.200$ M		$C_M = 0.300$ M	
C_L (M)	E_M^{corr} (mV)	C_L (M)	E_M^{corr} (mV)	C_L (M)	E_M (mV)
0.0500	11.5	0.0500	6.9	0.0625	7.2
0.0941	38.7	0.0941	16.3	0.1176	14.9
0.1143	53.9	0.1143	20.8	0.1429	18.9
0.1333	68.3	0.1333	26.1	0.1667	22.7
0.1514	80.9	0.1514	31.6	0.1892	26.7
0.1684	92.3	0.1684	37.2	0.2105	30.9
0.1846	101.9	0.1846	42.7	0.2308	35.1
0.2000	110.9	0.2000	48.6	0.2500	39.3
0.2146	118.4	0.2146	54.1	0.2683	43.5
0.2286	124.9	0.2286	59.3	0.2857	47.5
0.2419	130.8	0.2419	64.4	0.3023	51.5
0.2545	136.1	0.2545	69.4	0.3182	55.6
0.2783	144.3	0.2783	78.5	0.3333	59.4
0.3000	151.6	0.3000	86.8	0.3478	63.2
0.3200	157.5	0.3200	94.8	0.3750	70.5
0.3385	162.3	0.3385	101.6	0.4000	77.2
0.3714	170.0	0.3714	113.4	0.4231	83.4
0.4000	176.0	0.4000	122.5	0.4444	89.0
0.4250	180.2	0.4250	130.8	0.4737	96.9
0.4571	185.4	0.4571	139.7	0.5000	103.9
0.5000	191.5	0.5000	150.8	0.5238	110.1
0.5333	195.8	0.5333	158.4	0.5455	115.5
0.5600	198.9	0.5600	164.0	0.5714	122.0
0.6000	203.4	0.6000	171.6	0.5946	127.7
		0.6235	175.8	0.6250	134.6
		0.6500	180.2	0.6471	139.5
		0.6800	184.8	0.6667	143.6
		0.7000	187.7	0.7000	150.2
		0.7250	191.0	0.7273	155.3
		0.7400	192.7	0.7500	159.4
		0.7516	194.2		

The correction terms would be determined from Fig. 5

$$E_j'(0.1)-E_j'(0.3)=6.4 \text{ mV}$$
$$E_j'(0.2)-E_j'(0.3)=1.8 \text{ mV}$$

The corrected E_M values are valid for $I > 0.3$ M under the premise that E_j' is constant, and thus all the experimental data could in this way be transferred to that state. However, the lowest E_M values in the titration runs for $C_M = 0.1$ and 0.2 M where $I < 0.3$ are very uncertain.

In Table 3 the experimental material is gathered and Fig. 6 shows the C_L versus E_M curves. Thereafter C_L is plotted versus C_M with E_M as a param-

Table 4. Experimental values of [L], X, and X_1 in section B.

E_M (mV)	X	[L] (M)	X_1
160	506.7	0.1140	4425
150	343.4	0.0920	3733
140	232.7	0.0720	3233
130	157.6	0.0580	2718
120	106.8	0.0440	2428
110	72.39	0.0340	2100
100	49.03	0.0290	1656
90	33.23	0.0240	1343
80	22.51	0.0200	1076
70	15.26	0.0160	891
60	10.34	0.0120	778
50	7.00	0.0100	600
40	4.74	0.0090	416
30	3.22	0.0075	295
20	2.18	0.0060	196

eter and the curves extrapolated to $C_M = 0$. From the points of intersection the [L] values could be obtained. They are given in Table 4 together with the corresponding E_M, X, and X_1. From the graphical determination (Fig. 7) two mononuclear stability constants could be established with some certainty.

$$\beta_{1,1} = \quad 350\pm \quad 150 \quad (\text{M}^{-1})$$
$$\beta_{2,1} = 40\ 000\pm5\ 000 \quad (\text{M}^{-2})$$

C. Measurements at constant ionic strength. Ag^+ as ligand. The Ag^+ concentration was measured and $\bar{n}'$ calculated at five different values of $C_{SCN^-} = 0.05$, 0.10, 0.20, 0.30, and 0.40 M (Table 5). From the $\bar{n}'/[Ag^+]$ versus [Ag$^+$] curves, it can be seen that $\bar{n}'$ is dependent on C_{SCN^-}, therefore the limit value of $\bar{n}'/[Ag^+]$ when $C_{SCN^-} \to 0$ must be determined. Some examples of this procedure are shown in Fig. 8. Note the negative slopes of the $\bar{n}'/[Ag^+]$ against C_{SCN^-} plots (*cf.* Fronæus [2]). This behavior could perhaps be ascribed to small amounts of water being present in the solutions.

Table 5. Experimental data of C_M, E, [M], $\bar{n}'$, and $\bar{n}'/$[M] in section C at five different values of C_L.

$C_L = 0.050$ M

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/$[M] (M^{-1})
0.0161	− 52.1	0.0013	0.296	227.7
0.0313	− 18.2	0.0049	0.528	107.8
0.0455	3.0	0.0112	0.686	61.3
0.0588	17.2	0.0195	0.786	40.31
0.0714	27.0	0.0286	0.856	29.93
0.0833	34.5	0.0383	0.900	23.50
0.1053	44.9	0.0574	0.958	16.67
0.1250	52.0	0.0757	0.986	13.03
0.1429	56.7	0.0909	1.040	11.44
0.1591	60.9	0.1070	1.051	9.82
0.1739	64.4	0.1227	1.067	8.70
0.1875	67.1	0.1363	1.077	7.90
0.2000	69.5	0.1496	1.082	7.23
0.2222	73.3	0.1735	1.102	6.35
0.2414	76.3	0.1950	1.106	5.67
0.2581	78.8	0.2149	1.107	5.15
0.2857	82.5	0.2481	1.079	4.35
0.3077	85.2	0.2757	1.070	3.88
0.3256	87.2	0.2979	1.049	3.52
0.3333	88.0	0.3074	1.039	3.38

$C_L = 0.100$ M

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/$[M] (M^{-1})
0.0226	− 74.3	0.0006	0.226	377
0.0438	− 38.0	0.0023	0.415	180
0.0636	− 12.3	0.0062	0.574	92.6
0.0824	6.2	0.0127	0.697	54.88
0.1000	19.6	0.0214	0.786	36.73
0.1167	29.5	0.0315	0.852	27.05
0.1324	37.0	0.0422	0.902	21.37
0.1615	48.0	0.0648	0.967	14.92
0.1878	55.2	0.0857	1.021	11.91
0.2116	61.4	0.1092	1.029	9.42
0.2333	65.9	0.1300	1.050	8.08
0.2532	69.6	0.1502	1.060	7.06
0.2714	72.7	0.1694	1.076	6.35
0.2962	76.5	0.1964	1.088	·5.54
0.3250	80.4	0.2287	1.066	4.66
0.3500	83.6	0.2590	1.049	4.05
0.3818	87.3	0.2991	1.020	3.41
0.4000	89.2	0.3220	0.998	3.10

$C_L = 0.200$ M

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/$[M] (M^{-1})
0.0258	−110.7	0.0001	0.129	1290
0.0500	− 78.0	0.0005	0.248	495
0.0727	− 52.9	0.0013	0.357	275
0.0941	− 32.6	0.0028	0.457	163
0.1143	− 16.1	0.0053	0.545	103
0.1313	− 2.1	0.0092	0.611	66.4

Table 5. Continued.

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/[M]$ (M^{-1})
0.1514	9.1	0.0143	0.686	47.94
0.1684	18.1	0.0202	0.741	36.68
0.1846	25.7	0.0272	0.787	28.93
0.2000	32.0	0.0348	0.826	23.74
0.2286	41.9	0.0511	0.888	17.37
0.2545	49.4	0.0684	0.931	13.60
0.2783	55.1	0.0854	0.965	11.29
0.3000	60.0	0.1034	0.983	9.51
0.3200	63.9	0.1203	0.999	8.30
0.3556	69.9	0.1520	1.018	6.70
0.3862	74.0	0.1783	1.040	5.83
0.4129	77.7	0.2058	1.036	5.03
0.4571	83.1	0.2540	1.016	4.00
0.4923	87.0	0.2956	0.984	3.33
0.5209	90.0	0.3323	0.943	2.84
0.5600	93.7	0.3837	0.882	2.30
0.6000	97.2	0.4397	0.802	1.82

$C_L = 0.300$ M

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/[M]$ (M^{-1})
0.0323	−125.5	0.0001	0.107	1070
0.0625	− 95.7	0.0002	0.208	1040
0.0909	− 71.3	0.0006	0.301	502
0.1176	− 50.3	0.0014	0.387	277
0.1429	− 32.1	0.0029	0.467	161
0.1667	− 16.6	0.0052	0.538	104
0.1892	− 3.6	0.0087	0.602	69.2
0.2105	7.1	0.0132	0.658	49.83
0.2308	16.3	0.0189	0.706	37.37
0.2500	24.0	0.0255	0.748	29.35
0.2683	30.1	0.0323	0.787	24.36
0.3023	40.7	0.0488	0.845	17.32
0.3333	48.8	0.0668	0.888	13.30
0.3617	55.0	0.0851	0.922	10.83
0.3878	60.3	0.1046	0.944	9.03
0.4231	66.6	0.1336	0.965	7.22
0.4643	72.4	0.1674	0.990	5.91
0.5000	77.8	0.2066	0.978	4.73
0.5455	83.3	0.2560	0.965	3.77
0.5946	88.3	0.3110	0.945	3.04
0.6341	92.5	0.3662	0.893	2.44
0.6667	95.4	0.4099	0.856	2.09
0.7273	100.4	0.4981	0.764	1.53
0.7500	102.3	0.5362	0.713	1.33

$C_L = 0.400$ M

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/[M]$ (M^{-1})
0.0625	−117.0	0.0001	0.156	1560
0.0909	− 95.7	0.0002	0.227	1130
0.1176	− 77.9	0.0005	0.293	586
0.1429	− 61.1	0.0009	0.355	394
0.1667	− 46.0	0.0017	0.413	243
0.1892	− 32.3	0.0028	0.466	166
0.2105	− 20.0	0.0046	0.515	112

Table 5. Continued.

C_M (M)	E (mV)	[M] (M)	$\bar{n}'$	$\bar{n}'/[M]$ (M^{-1})
0.2308	− 9.8	0.0068	0.560	82.4
0.2500	− 0.5	0.0098	0.601	61.3
0.2683	7.0	0.0131	0.638	48.70
0.2857	13.8	0.0171	0.672	39.27
0.3023	19.8	0.0216	0.702	32.49
0.3182	25.1	0.0266	0.729	27.41
0.3333	29.8	0.0319	0.754	23.62
0.3617	37.8	0.0436	0.795	18.24
0.3878	44.5	0.0565	0.828	14.66
0.4231	52.1	0.0760	0.868	11.42
0.4643	60.1	0.1038	0.901	8.68
0.5000	66.2	0.1316	0.921	7.00
0.5455	72.8	0.1701	0.939	5.52
0.5946	79.4	0.2200	0.937	4.26
0.6341	84.0	0.2630	0.928	3.53
0.6667	87.5	0.3014	0.913	3.03
0.7273	93.2	0.3763	0.878	2.33
0.7500	95.3	0.4083	0.854	2.09

The lim $\bar{n}'/[Ag^+](C_{SCN^-} \rightarrow 0)$ *versus* $[Ag^+]$ was then integrated graphically and the results are given in Table 6. From Y, [M] data two stability constants were found (Fig. 9).

$$\beta_{1,1} = 170 \pm 5 \quad (M^{-1})$$
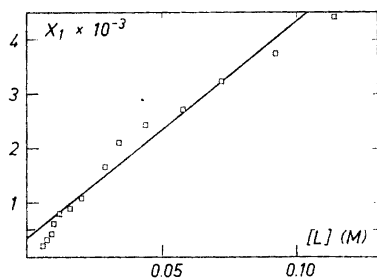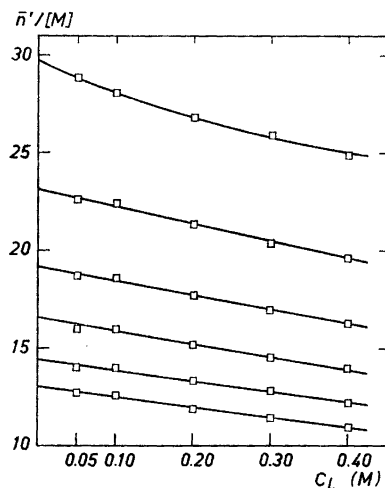$$\beta_{1,2} = 220 \pm 20 \quad (M^{-2})$$

Fig. 7. The function X_1 plotted against [L].

Fig. 8. $\bar{n}'/[M]$ as a function of C_L at some different values of [M]=80, 70, 60, 50, 40, and 30 mM as beginning at the bottom of the figure.

Table 6. Experimental values of [M] Y, and Y_1 in section C.

[M] (M)	Y	Y_1 (M^{-1})
0.030	6.250	175.0
0.040	8.106	177.7
0.050	10.01	180.2
0.060	11.98	183.0
0.070	13.98	185.4
0.080	16.04	188.0
0.090	18.15	190.6
0.100	20.30	193.0
0.110	22.48	195.3
0.120	24.71	197.6
0.130	26.95	199.6
0.140	29.24	201.7
0.150	31.56	203.7
0.160	33.89	205.6
0.170	36.27	207.5
0.180	38.69	209.4
0.190	41.14	211.3
0.200	43.62	213.1
0.210	46.13	214.9
0.220	48.64	216.5
0.230	51.14	218.0
0.240	53.65	219.4
0.250	56.16	220.6
0.260	58.64	221.7

DISCUSSION

The stability constants obtained in this work are collected in Table 7 together with those found for the same system in the infrared spectroscopic

Table 7. Summary of the stability constants. The corresponding constants from the infrared spectroscopic investigation reported previously [1] are included in the table.

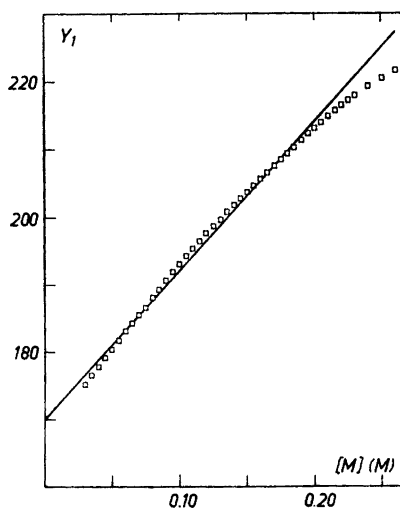|	Potentiometric investigation			IR-investigation
	A Const. $I = 1.5$ M	B Varying I	C Const. $I = 1.5$ M Ag$^+$ as ligand	Varying I
$\beta_{1,1}$ (M^{-1})	180 $\pm$ 10	350 $\pm$ 150	170 $\pm$ 5	355 $\pm$ 20
$\beta_{2,1}$ (M^{-2})	6700 $\pm$ 200	40 000 $\pm$ 5000		27 500 $\pm$ 2500
$\beta_{3,1}$ (M^{-3})	4900 $\pm$ 300			31 000 $\pm$ 1000
$\beta_{1,2}$ (M^{-2})			220 $\pm$ 20	

Fig. 9. The function Y_1 plotted against [M].

investigation.[1] As seen there is a fairly good agreement between the IR-results and those of section B, *i.e.* with no supporting inert salt, at least for the first complex. The constants of section A, where the ionic strength is constant, are much smaller. This behaviour can be explained qualitatively if the ionic medium is not quite inert, *i.e.* assuming that the positive pyridinium ions can bind the negative thiocyanate ions to some extent, thus necessitating a higher concentration of "free" thiocyanate ions to reach the same degree of complex formation compared to the situation with no pyridinium ions present.

It is also interesting to compare the stability constant of the first dinuclear complex $\beta_{1,2}=220$ (M^{-2}) with the k_1 value found by the IR-measurements. k_1 was defined as $k_1=[M_2L]/[ML]\cdot[M]$ or by $\beta_{1,1}$ and $\beta_{1,2}$ inserted, $k_1=\beta_{1,2}/\beta_{1,1}$. From section C $\beta_{1,1}=170$ (M^{-1}) and $\beta_{1,2}=220$ (M^{-2}) and thus $k_1=220/170=1.29$ (M^{-1}) while the IR-investigation gave $k_1=(1.36\pm0.20)$ (M^{-1}). These are almost identical values in spite of the fact that the IR-investigation was made without any supporting electrolyte and therefore in a medium of varying ionic strength. This agreement can be related to the discussion above since k_1 is not dependent on [L] and therefore not influenced by the pyridinium perchlorate.

In the previous paper[1] on the same system attention was drawn to the great differences between the silver-thiocyanato complexes in pyridine and in aqueous solutions.[4] The present potentiometric investigation confirms the observations reported previously with respect to the stability of the complexes but it cannot tell anything further about their structure.

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