Studies on Metal Complexes in Aqueous Solution by Infrared Spectrophotometry

II. An Investigation on Some First-Row Transition Metal Thiocyanato Complexes

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The frequency and intensity of the C—N vibration have been measured for the SCN⁻ ion and the first thiocyanato complex of some divalent first-row transition metals. The stability constants of these complexes have been determined. The data are reported in Table 5. Moreover, it has been found that for the complexes investigated the integrated absorption is constant and equal to that of the free ligand.

It has also been found that a linear relation exists between $\log \beta_1$ and the frequency shift.

A detailed investigation has been made on the nickel system. The results are in good agreement with earlier determinations on the complex formation. There are some indications that part of the complexity of this system is due to outer-sphere coordination. ($\beta_{1\text{ in}} = 12 \pm 2$ M⁻¹; $\beta_{1\text{ out}} = 3 \pm 2$ M⁻¹)

The thiocyanate ion, like the cyanide ion, exhibits a strong infrared absorption due to the stretching vibration of the carbon-nitrogen bond. It has been pointed out by Jones [1] that this fact might make possible examinations of thiocyanato complexes in aqueous solution analogous to the investigations on cyanide systems made by Jones and Penneman [2,3]. As many thiocyanate systems have been investigated in detail by conventional methods [4,5], such an undertaking could be rewarding.

We have accordingly performed infrared absorption measurements on some thiocyanate systems of the first-row transition metals. Our aim has been to verify the assignment of the absorption peaks to certain complexes by using the data for making a calculation of the stability constants of the complexes postulated.

EXPERIMENTAL

The spectrophotometer used was a Perkin-Elmer PE 221 with a grating monochromator. Cells with windows of calcium fluoride and with spacers of equally thick platinum foil were used in both the sample and the reference beam. The solution in the reference cell had a composition equal to that in the sample cell except for a certain amount of sodium perchlorate exchanged for sodium thiocyanate in the latter. In this way an almost complete compensation of the water absorption was obtained in the spectral region under investigation, 1900 − 2300 cm⁻¹.

The instrument was operated with the "automatic gain control" characteristic of the model. The setting of the resolution knob was "940" corresponding to a mechanical slit opening of 307 − 283 μ. The time for making a scan within the limits given above was about 10 min. As the "speed suppression" of the instrument was set at its maximum value, the greater part of this time was spent in the recording of the absorption peaks. With these arrangements absolute extinction coefficients could be obtained (*vide infra*).

The wave-number readings were checked by measuring the spectra of carbon monoxide in a 10 cm gas cell.

Chemicals used. Sodium thiocyanate of reagent quality was used to make a 3.00 M solution, the concentration of which was checked by Volhard-titration. Most of the metal salts were perchlorates, obtained by treating the corresponding carbonate or chloride with an excess of perchloric acid and recrystallizing the salt from water. From the perchlorates stock solutions were made by weighing; the concentrations were checked by colorimetric methods.

MEASUREMENTS

A. The free thiocyanate ion. In order to verify Beer's law and to test the performance of the apparatus measurements were made of the absorption of the free SCN⁻ ion in solutions of the composition C_A M NaSCN + (3.00−C_A) M NaClO₄. The reference cell then contained 3.00 M NaClO₄ (*vide supra*). Two different sets of platinum spacers were used, the thicknesses of which were given by the manufacturer to be 8.8 μ and 20 μ, respectively.

The optical densities obtained are given graphically in Fig. 1. It is seen that straight lines are obtained. Furthermore, if extinction coefficients are calculated from the slopes of the lines using the thicknesses of the spacers given above we obtain the values 535 M⁻¹cm⁻¹ (8.8 μ) and 538 M⁻¹cm⁻¹ (20 μ). *Throughout this paper the mean value 537 M⁻¹cm⁻¹ will be used for the extinction coefficient of the free thiocyanate ion.*

It must be stressed that the good agreement of the two sets of measurements are in striking disagreement with the proposal of Jones and Penneman [2] that the real cell thickness should be considered to be greater than the thickness of the spacer. We noted that with solutions of very strong total absorption (NaSCN with 34 μ spacers) a curvature of the Beer-law plots was obtained, probably because too little energy was reaching the detector. The deviation from straight line appearance was such as to yield too small values of the extinction coefficient. It is also of interest that using the thinnest spacer and with no compensation in the reference beam a few years ago we obtained the value $\varepsilon = 540$ M⁻¹cm⁻¹ with a Hilger H 800 Spectrophotometer fitted with a sodium chloride prism and operated at its extreme capacity. Thus we can state that absolute extinction coefficients can be obtained with fair accuracy and that the slit width when properly set is not of critical importance for a good result. That this is so is quite obvious from the rules given by Ramsay [6].
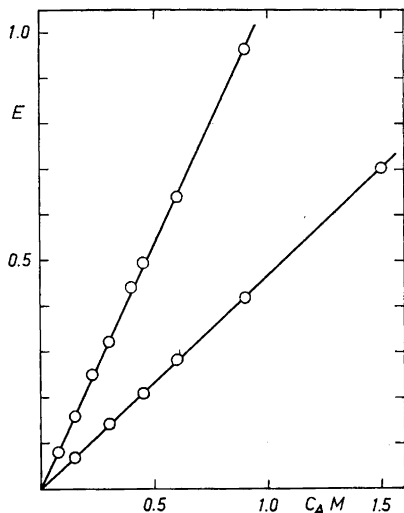
Fig. 1. Optical densities of solutions of NaSCN with a total salt concentration = 3 M. Upper line corresponds to 20.0 μ spacer, lower line to 8.8 μ spacer.
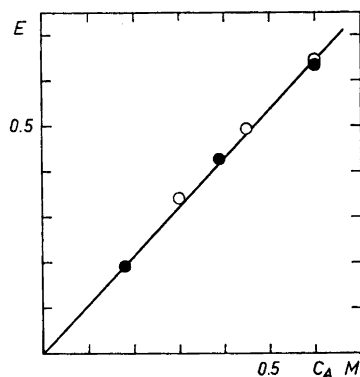
Fig. 2. Optical densities of solutions of NaSCN without extra salt addition (open dots) and with total salt concentration = 6 M (filled dots). Spacer: 20.0 μ. The line is the one drawn in Fig. 1.

The half-width of the absorption peak under discussion was found to be 37 $\pm$ 1 cm^{-1}.

The frequency of the SCN$^-$-absorption was found to be 2066 cm^{-1} in good agreement with previously reported infrared [1,7] and Raman [8] data. Within the experimental error no change in the frequency was found as the thiocyanate concentration increased. In order to test the invariance of intensity and frequency of absorption with changing total electrolyte concentration some measurements were made on 6 M salt solutions and on solutions containing only NaSCN. The optical densities are given in Fig. 2 and show no systematic deviation; the frequency of the 6 M salt solutions was shifted to 2069 cm^{-1} whereas the other solutions showed the normal value 2066 cm^{-1}.

B. *The metal-thiocyanate systems.* In Figs. 3—4 are given representative examples of the spectra obtained.

Common to all the systems there is a new absorption peak at a frequency higher than that of the free thiocyanate ion. The most reasonable explanation is to assume that this peak corresponds to the metal complexes formed in solutions of indicated composition. That this is so will be evident from the following calculations.

In the case of the iron(II)-system some irregularities were observed. At high iron concentrations a decrease of the intensity of the 2099 cm^{-1} peak was observed relative to the peaks at moderate iron concentration. We suggest that in this case more than one iron-containing complex was formed, probably some polynuclear hydrolytic complex. This fact rendered a detailed analysis of the system impossible.
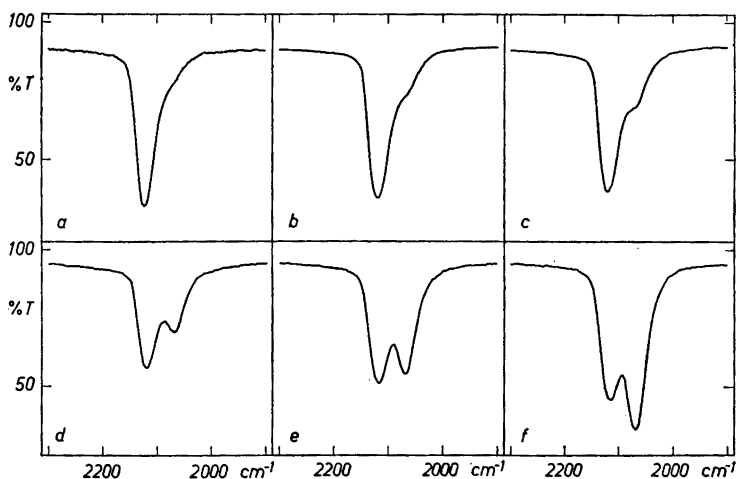
Fig. 3. The Ni²⁺ —SCN- system. Spacer: a.—c. 20.0 μ; d.—f. 8.8 μ.

a. C_M = 1.32 M; C_A = 0.36 M   d. C_M = 0.30 M; C_A = 0.60 M
b. C_M = 0.66 M; C_A = 0.36 M   e. C_M = 0.30 M; C_A = 0.98 M
c. C_M = 0.44 M; C_A = 0.36 M   f. C_M = 0.30 M; C_A = 1.50 M

A QUANTITATIVE TREATMENT OF SOME OF THE SYSTEMS

For the Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}-systems it was possible to undertake a quantitative analysis of the data, resulting in the determination of the extinction coefficient and the stability constant of the first complex. The calculation method will be presented below.
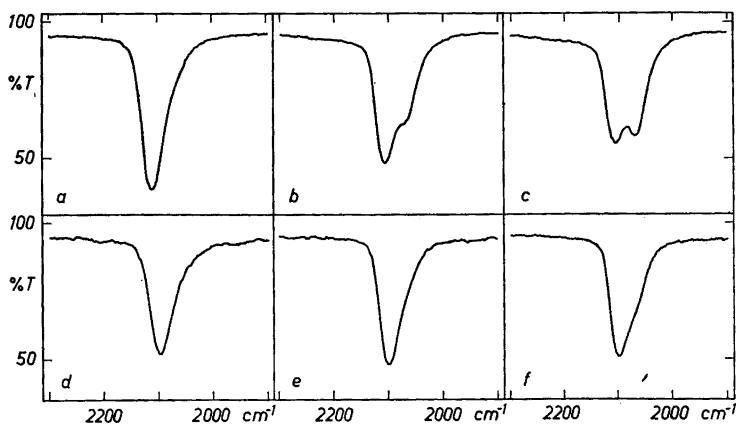

Fig. 4. a.—c. The Zn^{2+}—SCN- system.   d.—f. The Fe^{2+}—SCN- system.

a. C_M = 2.89 M; C_A = 0.30 M   d. C_M = 1.8 M; C_A = 0.30 M
b. C_M = 0.49 M; C_A = 0.30 M   e. C_M = 0.90 M; C_A = 0.30 M
c. C_M = 0.25 M; C_A = 0.30 M   f. C_M = 0.45 M; C_A = 0.30 M

C_A = total concentration of ligand
C_M = » » » metal
[A] = free » » ligand
[M] = » » » metal
[MA] = concentration of the first complex
ε_1 = extinction coefficient of the first complex at the maximum of the peak
E = observed optical density at the maximum of the "complex peak"
E_0 = the same quantity for $C_M \to \infty$
d = the cell thickness
β_1 = stability constant of the first complex

In the experiments under discussion C_A was kept constant and C_M was varied.

As C_M was always greater than C_A we can assume as an approximation that the first complex MA prevails in regard to the higher complexes MA_2, MA_3 etc.

This approximation gives us the following relations:

$$C_A = [A] + [MA] \tag{1}$$

$$C_M = [M] + [MA] \tag{2}$$

$$E = \varepsilon_1[MA]d \tag{3}$$

Furthermore, by definition:

$$\beta_1 = \frac{[MA]}{[M][A]} \tag{4}$$

Also it must hold:

$$E_0 = \varepsilon_1 . C_A . d \tag{5}$$

From eqns. (3) and (5) we obtain:

$$[MA] = \frac{E}{E_0} . C_A \tag{6}$$

and from eqns. (3) and (1):

$$E = \varepsilon_1 d(C_A - [A]) \tag{7}$$

Eqn. (4) is inserted in eqn. (7):

$$E = \varepsilon_1 d\left(C_A - \frac{[MA]}{\beta_1[M]}\right) \tag{8}$$

Now eqns. (2), (5) and (6) are inserted in eqn. (8) and we finally obtain:

$$E = E_0\left(1 - \frac{E/E_0}{\beta_1(C_M - \frac{E}{E_0}C_A)}\right) \tag{9}$$

Table 1. The Mn^{2+} — SCN^- system. Composition of the solutions: C_M M $Mn(ClO_4)_2$ + 0.300 M NaSCN.

C_M M	E_{2093}	$\dfrac{1}{C_M - C_A}$ M^{-1}	$\dfrac{E/E_0^1}{C_M - E/E_0^1 \cdot C_A}(M^{-1})$	$\Delta \nu_{1/2}$ cm^{-1}
1.63	0.332	0.75	0.65	34
1.31	0.327	0.99	0.84	34
1.09	0.308	1.27	0.98	30
0.95	0.292	1.53	1.08	30
0.82	0.280	1.93	1.26	32
0.54	0.233	4.1	1.73	28
0.41	0.205	9.3	2.24	28

$E_0^1 = 0.375$; $E_0 = 0.393$
$\varepsilon = 655$ $M^{-1}cm^{-1}$; $\beta_1 = 4.4$ M^{-1} 31 ± 2

Table 2. The Co^{2+} — SCN^- system. Composition of the solutions: C_M M $Co(ClO_4)_2$ + 0.300 M NaSCN.

C_M M	E_{2112}	$\dfrac{1}{C_M - C_A}$ M^{-1}	$\dfrac{E/E_0^1}{C_M - E/E_0^1 \cdot C_A}(M^{-1})$	$\Delta \nu_{1/2}$ cm^{-1}
1.35	0.377	0.95	0.87	31
1.08	0.366	1.28	1.12	28
0.90	0.356	1.67	1.38	30
0.79	0.340	2.05	1.57	26
0.68	0.328	2.67	1.88	31
0.45	0.301	6.7	3.27	30
0.34	0.267	26.3	4.71	30

$E_0^1 = 0.405$; $E_0 = 0.417$
$\varepsilon = 696$ $M^{-1}cm^{-1}$; $\beta_1 = 8.9$ M^{-1} 29 ± 1

Thus if the approximation involving the neglection of higher complexes holds true, E plotted against $\dfrac{E/E_0}{C_M - E/E_0 \cdot C_A}$ should yield a straight line with the slope $k = E_0/\beta_1$ and an intercept on the ordinate axis equal to E_0. From these quantities ε_1 and β_1 can be obtained.

The calculation procedure was to make a first plot of E against $1/(C_M - C_A)$ and extrapolate to $1/(C_M - C_A) = 0$. This gave an approximate value of $E_0 = E_0^1$. Thereafter $\dfrac{E/E_0^1}{C_M - E/E_0^1 \cdot C_A}$ could be calculated and E was plotted against this quantity. This gave a new value of $E_0 = E_0''$ and from the limiting slope β_1 could be calculated. Renewed plotting using E_0'' gave no perceptible change in the parameters.

Table 3. The $Ni^{2+}-SCN^-$ system. Composition of the solutions: C_M M $Ni(ClO_4)_2 + 0.360$ M NaSCN $+ (2.64-2 \, C_M)$ M $NaClO_4$.

C_M M	E_{2119}	$\dfrac{1}{C_M-C_A}$ M^{-1}	$\dfrac{E/E_o^1}{C_M-E/E_o^1\cdot C_A}(M^{-1})$	$\varDelta\nu_{1/2}$ cm^{-1}
1.32	0.433	1.04	0.95	32
1.10	0.417	1.35	1.16	32
0.99	0.419	1.59	1.36	34
0.88	0.418	1.92	1.63	32
0.77	0.406	2.44	1.93	30
0.66	0.395	3.33	2.42	32
0.61	0.396	3.98	2.82	32
0.54	0.384	5.62	3.47	32
0.49	0.378	7.75	4.18	32
0.44	0.369	12.50	5.21	34

$E_o^1 = 0.463;$ $E_o = 0.461$
$\varepsilon = 640$ M^{-1} $cm^{-1};$ $\beta_1 = 15.0$ M^{-1} $\qquad 31 \pm 2$

Table 4. The $Zn^{2+}-SCN^-$ system. Composition of the solutions: C_M M $Zn(NO_3)_2 + 0.300$ M NaSCN.

C_M M	E_{2109}	$\dfrac{1}{C_M-C_A}$ M^{-1}	$\dfrac{E/E_o^1}{C_M-E/E_o^1\cdot C_A}(M^{-1})$	$\varDelta\nu_{1/2}$ cm^{-1}
2.89	0.389	0.39	0.37	38
2.47	0.392	0.46	0.44	34
1.65	0.383	0.74	0.69	34
0.83	0.333	1.90	1.41	32
0.49	0.287	5.15	2.50	32
0.25	0.224		6.75	32

$E_o^1 = 0.407;$ $E_o = 0.411$
$\varepsilon_1 = 685$ M^{-1} $cm^{-1};$ $\beta_1 = 8.2$ M^{-1} $\qquad 34 \pm 2$

With this technique the Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} could be successfully treated. The results are given in Tables 1—4 and Figs. 5 and 6.

The stability constants thus obtained seem to be rather independent of the total salt concentration within the range used in the investigations. Not all systems were investigated under exactly comparable conditions but as no certain rules are known for the variation of the activity coefficients in such highly concentrated solutions, we did not consider it worth while to maintain a rigorously controlled salt medium. The cobalt system was investigated with and without adding sodium perchlorate to constant salt concentration (in equivalents per liter). The results agreed well within experimental error, as seen from Fig. 5.
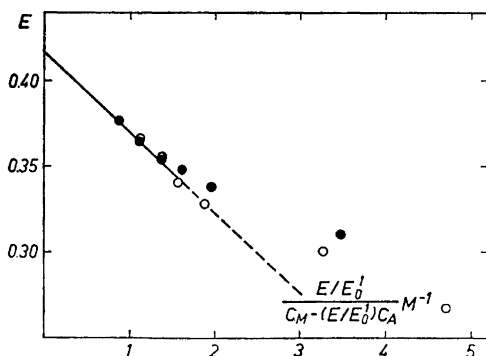
Fig. 5. The Co²⁺ —SCN⁻ system. Filled dost correspond to measurements in a medium of constant salt concentration = 3 M. The open dots represent the measurements reported in Table 2.
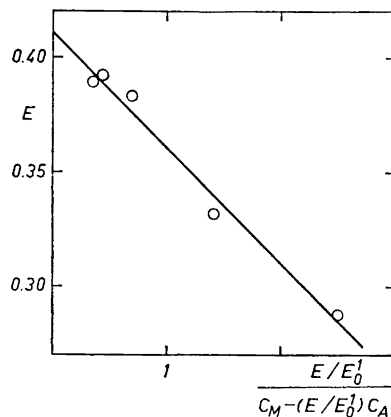
Fig. 6. The Zn²⁺ —SCN⁻ system. The data are those reported in Table 4.

DISCUSSION

A. General relations between the constants obtained

In Table 5 we report the values obtained for the stability constant and the spectral parameters of the first complex of the metals investigated.

One striking observation emerges from an inspection of the data, namely the constancy of the integrated absorption, for which quantity we have used the approximation $\varepsilon_1 \cdot \Delta v_{1/2}$, where $\Delta v_{1/2}$ means the half-width of the peak. This fact will be commented upon in a forthcoming paper.

The stability constants reported show the trend expected from the Williams-Irving rule [9]. It is also the trend reported by Yatzimirskii and Korableva [5] at low ionic strength. Especially the perfect agreement between the value of β_1 for the nickel system found here (15 M⁻¹) and that reported earlier (15 M⁻¹) by one of us [10] should be noted. As that work was done at the ionic strength

Table 5. Spectral parameters and stability constants of the investigated complexes.

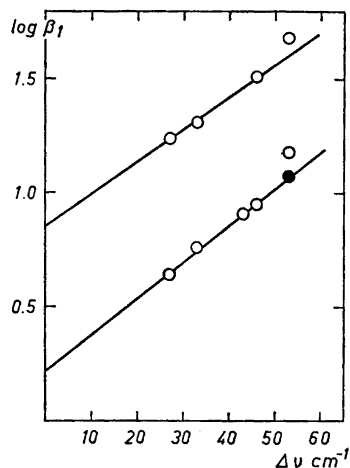|	v cm⁻¹	ε M⁻¹cm⁻¹	$\Delta v_{1/2}$ cm⁻¹	$\varepsilon \cdot \Delta v_{1/2}$ × 10⁻⁴	β_1 M⁻¹ This work	Ref.[5]
SCN⁻	2066	537	37	1.99		
Mn²⁺ — SCN⁻	2093	655	31	2.03	4.4	17.(3)
Fe²⁺ — SCN⁻	2099					20.(4)
Co²⁺ — SCN⁻	2112	696	29	2.02	8.9	32.(3)
Ni²⁺ — SCN⁻	2119	640	32	2.05	15.0	47.(6)
Zn²⁺ — SCN⁻	2109	685	34	2.32	8.2	15.(4)

Fig. 7. The logarithm of β_1 as a function of the frequency shift ($\Delta\nu$) of the investigated systems of the first-row transition metals. Upper set: the stability constant reported by Yatzimirskii and Korableva [6]. Lower set: the stability constants obtained in the present investigation (β_1 Fe computed by analogy from the data of Ref.[5]). ●: β_1 Ni corrected for outer-sphere complexity.

1 M, the good agreement gives support to our somewhat sanguine treatment of the problem of the salt medium of the solutions investigated.

Above all, the agreement between the two determinations of β_1 for the nickel system confirms our working hypothesis that the new peak, observed in the spectra of metal solutions, corresponds really to mononuclear metal-thiocyanato complexes.

A further correlation between the data obtained has been found. If log β_1 for the metals investigated is plotted against the frequency shift a straight line is obtained (Fig. 7). As we could not determine β_1 for the ferrous system because of the disturbing effects caused by the large metal concentration, we have made an estimate founded on the parallellism between our data and those of Yatzimirskii and Korableva [5] for the Mn^{2+}, Ni^{2+} and Co^{2+}-systems.

If it is assumed, as we have done in an earlier paper [11], that the frequency shift of the ligand vibration following upon coordination is proportional to the enthalpy of coordination, and if it is further assumed that the entropy term is almost constant for a sequence of similar metals, then we should expect a linear relation between log β_1 and the frequency shift. Furthermore the line should not go through the origin. Such a relation is actually found here (Fig. 7).

B. The nickel system

As the nickel system exhibited the greatest frequency difference between the complex peak and that of the free ligand, and thus allowed easy absorption determinations, it was selected for a more detailed investigation.

The measurements at a constant value of C_A have already been mentioned. Measurements were also made at a constant value of C_M' (*cf.* Fig. 3). The absorption was determined both for the complex peak, E_{2119}, and the free ligand peak, E_{2066}. The absorption was actually measured at the position of the maximum of the peak in question. This position varied a little, to the

Table 6. Determination of $\bar{n}$ of the nickel system. Composition of the solutions: 0.30 M Ni(ClO₄)₂ + C_A M NaSCN + (2.40 − C_A) M NaClO₄.

C_A M	E_{2066}/d			E_{2119}/d			$\Delta\nu_{1/2}$ cm⁻¹	[A] from E_{2066} mM	$\bar{n}$ eqn. (10)	$\bar{n}$ eqn. (15)	[A] eqn. (10) mM	$\bar{n}$ eqn. (17)	[A] eqn. (10) mM	β_1 out M⁻¹
	$d=8.8\ \mu$	$d=20\ \mu$	MEAN	$d=8.8\ \mu$	$d=20\ \mu$	MEAN								
0.075	18.2	12.4	15.3	40.2	40.0	40.1		28.5	0.16	0.208	12.6			4.6
0.200	33.6	34.8	34.2	92	100	96	31	63.7	0.46	0.50	50			1.4
0.225	43.9	40.3	42.1	109	116	113	32	78.4	0.49	0.59	49			3.6
0.300	59.7	54.7	57.2	139	144	142	30	106.5	0.53	0.74	79			5.8
0.450	89.5	94.8	92.1	181	197	189	32	171.5	0.93	0.99	154			1.3
0.600	138.6	140.2	139.4	245	240	242	33	259.6	1.13	1.26	222			3±2
0.750	183.5	190.8	187.2	260	271	266	35	349	1.34	1.38	335	1.51	300	
0.975	268.1	273.9	271.0	299	306	302	38	505	1.57	1.58	500	1.87	415	
1.200	361	359	360	325	333	329	40	670	1.77	1.71	690	2.14	560	
1.500	492	462	477	361	364	362	40	888	2.04	1.89	930	2.36	790	

effect that at very high C_A-values the two peaks came a little closer together. As the peaks are not very acuminate, any error thereby introduced is certainly within the random errors. The designations E_{2119} and E_{2066} are thus more of a classificatory type than a descriptive one. Both 8.8 μ and 20 μ spacers were used; the values obtained are reported in Table 6.

It was our aim when performing these measurements to calculate the mean ligand number $\bar{n}$ and compare this quantity with the values obtained from the stability constants reported by Fronæus [10].

By definition

$$\bar{n} = \frac{C_A - [A]}{C_M} \tag{10}$$

One obvious way to calculate $\bar{n}$ is then to use the E_{2066} values and the already determined value of ε_A to determine [A] and thus $\bar{n}$ from eqn. (10). Such a calculation is reported in Table 6.

We will now consider an alternative method for the calculation of $\bar{n}$. It must hold that

$$E_{2119} = d([MA]\varepsilon_1 + [MA_2]\varepsilon_2 + [MA_3]\varepsilon_3 + - - -) \tag{11}$$

It is reasonable as a first approximation to put

$$\varepsilon_2 = 2\,\varepsilon_1, \qquad \varepsilon_3 = 3\,\varepsilon_1 - - - \tag{12}$$

Then we have

$$\frac{E_{2119}}{d \cdot \varepsilon_1} = [MA] + 2[MA_2] + 3[MA_3] + - - - \tag{13}$$

or

$$\frac{E_{2119}}{d\,\varepsilon_1} = C_A - [A] \tag{14}$$

It then follows that

$$\frac{E_{2119}}{d \cdot \varepsilon_1 \cdot C_M} = \bar{n} \tag{15}$$

This approximation can be expected to work well when [A] is rather low so that the first complex MA dominates in the solution. For higher [A] the approximation of eqns. (12) will eventually introduce a systematic error.

However, having established the invariance of the product $\varepsilon_1 \cdot \Delta\nu_{1/2}$ with coordination, we can obtain a successive correction of ε_1 by measuring $\Delta\nu_{1/2}$ for the 2119-peak.

Then we obtain

$$\varepsilon_{1corr} = \frac{(\Delta\nu_{1/2})_1}{\Delta\nu_{1/2}} \cdot \varepsilon_1 \tag{16}$$

and consequently, if ε_1 in eqn. (21) is exchanged for ε_{1corr}

$$\bar{n} = \frac{E_{2119}}{d \cdot C_M \cdot \varepsilon_1} \cdot \frac{\Delta\nu_{1/2}}{(\Delta\nu_{1/2})_1} \tag{17}$$
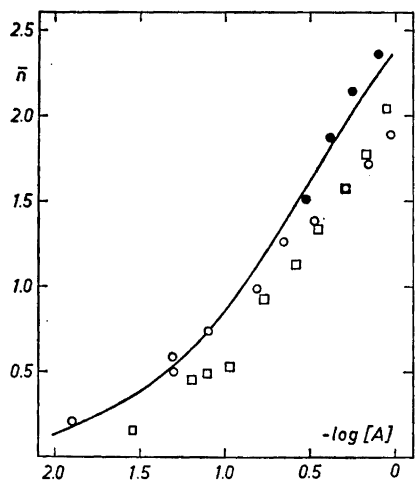
Fig. 8. The complex formation curve of the Ni^{2+}—SCN^- system. Fulldrawn line: $\bar{n}$ according to Fronæus [10]. The dots and squares represent data obtained in the present investigation.
$\bar{n}$ calculated from eqn. (15): ○
$\bar{n}$ »   » eqn. (17): ●
$\bar{n}$ »   » eqn. (10): □

where ε_{1corr} means an average value in which the deviation from eqns. (12) is implied, and $(\Delta \nu_{1/2})_1$ means the half-width of the 2119-peak determined under such conditions (Table 3) where only the first complex is present in great amount.

The appropriate data for such a calculation and the values of $\bar{n}$ obtained are also included in Table 6.

A comparison between the data reported by Fronæus [10] and our $\bar{n}$-values is found in Fig. 8. It is seen that the values obtained with our second method agree almost completely with Fronæus' $\bar{n}$-curve, whereas those of the first method lie systematically below that curve.

Although the difference is not very great we believe it to be significant and suggest that the cause may be traced to a so called outer-sphere coordination of the thiocyanate ion to the hydrated nickel ion. If we denote such a species as $(M\ aq_6)A_n$ and the inner sphere complex as (MA_n), we obtain for the total concentration of the first complex [MA]:

$$[MA] = [(MA)] + [(M\ aq_6)A] \tag{18}$$

and for the stability constant

$$\beta_1 = \frac{[MA]}{[M][A]} = \frac{[(MA)]}{[M][A]} + \frac{[(M\ aq_6)A]}{[M][A]} \tag{19}$$

or

$$\beta_1 = \beta_{1\ in} + \beta_{1\ out} \tag{20}$$

It is now assumed that the absorption frequency of the thiocyanate ion in the outer-sphere complexes $(M\ aq_6)A_n$ is equal or almost equal to that of the free ligand. The formal quantity calculated from the optical density E_{2066} should then correspond to $[A] + \sum_n [(M\ aq_6)A_n]$, *i.e.* too large a value giving

in its turn too small a value of $\bar{n}$. This is the trend of the discrepancy under discussion.

From this starting-point we have tried a quantitative treatment of the data to obtain $\beta_{1\ \text{out}}$.

$$\bar{n}_{\text{eqn. (15)}} = \frac{C_A - [A]}{C_M} \tag{21}$$

$$\bar{n}_{\text{eqn. (10)}} = \frac{C_A - [A] - \underset{n}{\Sigma}[(M\ aq_6)A_n]}{C_M} \tag{22}$$

We define a quantity $\Delta\bar{n}$ as

$$\Delta\bar{n} = \bar{n}_{\text{eqn. (15)}} - \bar{n}_{\text{eqn. (10)}} \tag{23}$$

For small values of [A] where only the first complex is formed in appreciable amounts, we then obtain

$$\Delta\bar{n} = \frac{[(M\ aq_6)A]}{C_M} \tag{24}$$

This expression is easily transformed to

$$\Delta\bar{n} = \frac{\beta_{1\ \text{out}}\ [A]}{1 + \beta_1[A]} \tag{25}$$

Thus we obtain

$$\beta_{1\ \text{out}} = \frac{\Delta\bar{n}}{[A]}\ (1 + \beta_1[A]) \tag{26}$$

In the last column of Table 6 we report $\beta_{1\ \text{out}}$ calculated according to eqn. (26) from corresponding values of [A] and $\Delta\bar{n}$, obtained from columns 10, 11 and 12. From eqn. (20) we can then obtain $\beta_{1\ \text{in}} = 12\ M^{-1}$. It may be well worth remarking that if we use this value in the log $\beta_1 - \Delta\nu$ plot in Fig. 7, we obtain a much better fit to the linear relationship found for the other systems.

As we have not performed any determination of the degree of outer-sphere complex formation for these other systems we are not in a position to judge whether this better fit is significant or not.

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