

The Iron(III)–Thiocyanate System. The Stepwise Equilibria studied by Measurements of the Distribution of Tris(thiocyanato)Iron(III) between Octan-2-ol and Aqueous Thiocyanate Solutions

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The equilibria in the iron(III)–thiocyanate system have been studied by measurement of the partition coefficient for the distribution between octan-2-ol and aqueous iron(III)thiocyanate solutions using spectrophotometry. It was shown that $\text{Fe}(\text{NCS})_3$ is the only species which is extracted from the aqueous solutions. The six consecutive formation constants were obtained from measurements in 1 M $\text{K}(\text{Cl}, \text{SCN})$, 1 M $\text{Na}(\text{CF}_3\text{SO}_3, \text{SCN})$ and in potassium thiocyanate solutions with KSCN concentrations ranging from 1 to 10 M (saturated solution). The measurements in the chloride-containing medium were strongly influenced by chloride complex formation. The main result of the work is that by introducing an activity correction and a correction for the salting-out influence of the medium in the concentrated KSCN solutions, it has been possible to obtain trustworthy values for the three last very small formation constants K_4 , K_5 and K_6 in the system.

The iron(III)–thiocyanate system is one of the most extensively studied stepwise equilibrium systems.^{1,2} However, reasonable agreement between the values of formation constants obtained in the different studies is found only in the case of the mono- and bis-thiocyanato complexes, mainly due to the experimental difficulties encountered in determining the much smaller formation constants for the subsequent complexes up to the hexakis complex. This is illustrated in Table 1, in which the results of those studies carried out with the aim of determining all the formation constants are collected^{3–13} and compared with the results of the present work.

The stability constants determined in this work were obtained from measurements of the partition coefficients K_D for distribution of the complex species between octanol and the various aqueous thiocyanate solutions:

$$K_D = \frac{C_{\text{Fe(III)}(\text{oct})}}{C_{\text{Fe(III)}(\text{aq})}} \quad (1)$$

The two liquid phases were analysed spectrophotometrically and it was shown that tris(thiocyanato)iron(III) was the only species extracted from the aqueous solutions.

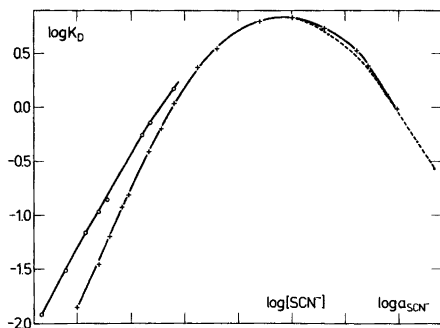


Fig. 1. Iron(III)-thiocyanate distribution curves. Variation of experimental values of $\log K_D$ in 1 M Na(CF₃SO₃,SCN) versus $\log[\text{SCN}^-]$ (O), in 1 M K(Cl,SCN) and for $C_{\text{KSCN}} \geq 1$ M versus $\log[\text{SCN}^-]$ (+). The dashed curve for $C_{\text{KSCN}} \geq 1$ M is corrected for salting-out effects and plotted versus $\log a_{\text{SCN}^-}$.

Measurements were made with solutions of iron(III) in 1 M K(Cl,SCN), in 1 M Na(F₃CSO₃,SCN) media and in KSCN solutions with a concentration varying from 1 M up to saturation. The experimental data are summarised in Fig. 1, in which $\log K_D$ is plotted versus $\log [\text{SCN}^-]$.

The first four consecutive constants were determined from the partition coefficients for octanol and 1 M K(Cl,SCN). As a result of appreciable chloride complex formation, the values of K_1 in particular and K_2 are considerably smaller than the literature values obtained for perchlorate- and nitrate solutions. For this reason some measurements were also made in 1 M Na(F₃CSO₃,SCN), in which chloride is replaced by the poorly coordinating trifluormethansulfonate anion. From these data values for K_1 and K_2 were estimated, which were in more reasonable agreement with the literature values for these constants (*cf.* Table 1).

The main result of the work described here is that more reliable values for K_3 , K_4 , K_5 and K_6 , the four last consecutive constants in the system, have been obtained. In order to determine these constants activity corrections for the thiocyanate ion in solutions with $C_{\text{KSCN}} > 1$ M was introduced, and the partition coefficients were corrected for the salting-out effect of the medium. The activity coefficient of the thiocyanate ion in strong KSCN solutions was approximated from measurements of the Hg/Hg(SCN)₄²⁻ potential in these solutions under simplifying assumptions (see Table 7) as well as by using literature values for the activity coefficient of KSCN. The salting-out of tris(thiocyanato)iron(III) from aqueous solutions with nearly maximum content of Fe(NCS)₃ into octanol was determined for different salts (KCl and KBr), and the salting-out effect of the latter salts compared with that of KSCN was determined in separate distribution experiments with tris(acetylacetonato)cobalt(III) (Tables 5 and 6).

For several reasons,¹⁵ it is not possible to determine formation constants which have values smaller than $\leq 1 \text{ l mol}^{-1}$ with a sufficiently high degree of precision. However, the six stepwise constants determined in this work (shown in the three lowest rows of Table 1) are certainly of the correct order of magnitude.

EXPERIMENTAL

Reagents and solutions. The reagents were of analytical grade or of good commercial quality. Octan-2-ol with $d_4^{20} = 0.820$ was obtained from Merck-Schuchardt. The iron(III)-content in the KSCN, NaSCN and NH₄SCN reagents employed was so low that their saturated solutions were practically colourless. They were analysed by Volhard titration and used

Table 1. Reported values for the formation constants of the complexes formed in the iron(III)thiocyanato system.

Method	Temp.	Medium	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	Ref.
sp, emf	25	var.	2.29	1.58	-0.22	-	-	-	37 M ³
sp	rt	var.	2.3	-	-	-	-	-	46 Ba ⁴
hyp	-	-	-	(1.94)	(1.4)	(0.8)	(0.2)	-	46 Ba ⁵
dis	18	1.8 M (NaClO ₄)	2.09	1.75	< -0.74	> 1.80	-0.70	-1.03	51 Ma ⁶
dis	18	1.8 M (KNO ₃)	1.96	2.02	< -0.41	> -0.14	-1.57	-1.51	51 Ma ⁶
chroma	rt	1.4 M (NaClO ₄)	2.35	1.55	1.31	0.66	0.21	-	64 J ⁷
sp	22-23	4 M (NaNO ₃)	2.1	1.3	0.5	0	-0.1	-0.1	64 V ⁸
sp	25	1.1 M (LiNO ₃)	1.91	1.08	-	-	-	-	66 V ⁹
dis	25	3 M (LiClO ₄)	2.18	1.42	1.40	1.30	-0.07	-	65 Mi ¹⁰
sp	25	3 M (LiClO ₄)	2.19	1.48	-	-	0.00	-0.035	65 Mi ¹¹
dis	20	2 M (NaClO ₄)	2.09 ^a	1.48	1.00	0.67	0.18	-0.6	73 M ¹²
dis	25	3 M Na(ClO ₄ ,SCN)	2.53	1.35	1.31	1.33	-0.32	-	83 K ¹³
nmr	rt	0.655 M (NaCl)	1.0	-	-	-	-	-	69 Ma ¹⁴
dis	24	1 M K(Cl,SCN)	1.55±0.03	0.95±0.03	0.6±0.05	-0.4±0.1	-	-	85 B _j
dis	24	1 M Na(CF ₃ SO ₃ ,SCN)	2.30±0.05	1.69±0.05	0.4±0.1	-	-	-	85 B _j
dis	24	1-10 M KSCN corr ^b	-	-	-	-0.30±0.05	-1.0±0.05	-1.7±0.1	85 B _j
dis	24	1-4 M KSCN corr ^c	-	-	-	-0.25±0.05	-0.8±0.1	-1.3±0.2	85 B _j

^a $\log K_1$ was determined as 2.09 and $K_2/K_{n+1} = \{n(6-n)/(6-n+1)\}k$ with k assumed to be 1.65. ^b Corrected to 1 M KSCN from measurements of the $\text{Hg}/\text{Hg}(\text{SCN})_4^{2-}$ potential under simplifying assumptions. ^c Corrected to 1 M KSCN with literature values for the activity coefficients of KSCN.

without further purification. A stock solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.1 M HClO_4 was analysed by Zimmermann-Reinhardt permanganate titration^{1b} as well as by Volhard titration. An oxygen-free solution of Mohr's salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was also employed in some cases. The various solutions were prepared in volumetric flasks by weighing or pipetting from stock solutions.

Partition coefficients. Octan-2-ol has a low vapour pressure and is practically insoluble in water, and for these reasons it was chosen for the distribution experiments. Unfortunately, the use of such an alcohol does not permit the use of a strong perchlorate medium because of the risk of explosion. Equal volumes of octanol and the aqueous solution were normally employed in the experiments, and the distribution equilibrium was established within a few minutes when the mixture was shaken in a separating funnel at 24 °C. The two liquid phases separated easily, and only in a few cases was it necessary to filter the solution due to emulsion formation.

The solutions were analysed spectrophotometrically: denoting the absorbance of the freshly prepared iron(III)-thiocyanate solutions A_{aq}^0 and that of the aqueous solution after shaking with octanol A_{aq} , the partition coefficient K_D is given by the expression

$$K_D = \frac{A_{\text{aq}}^0 - A_{\text{aq}}}{A_{\text{aq}}} \times \frac{V_{\text{aq}}}{V_{\text{oct}}} \quad (2)$$

where V_{aq} is the volume of the aqueous- and V_{oct} of the alcohol layer. The calculations were usually made with absorbances measured directly on the spectrophotometer at three wavelengths (520, 500 and 480 nm) close to the absorption maximum of the band. Denoting the iron(III)-concentration in the initial iron(III)-thiocyanate solution $C_{\text{Fe(III)}}^0$, then the iron(III)-concentration in the octanol phase in cases where there are equal volumes of the two liquid phases is given by $C_{\text{Fe(III)}}^0(A_{\text{aq}}^0 - A_{\text{aq}})/A_{\text{aq}}^0$, so that the molar absorbances of the complex in the octanol layer could also be determined.

Conversely, a knowledge of this spectrum made it possible to determine the iron(III) concentration also in those cases where only a few per cent of the iron is extracted. In these cases the average values of $\log \epsilon$ for the tris(thiocyanato) complex in octanol tabulated in Table 2 were used to calculate K_D . Very small partition coefficients (~ 0.01) could therefore also be measured even when the quantity $A_{\text{aq}}^0 - A_{\text{aq}}$, and thus the expression (2) became too small to determine accurately. The iron(III) concentration was so small in all cases that no correction for the thiocyanate extracted with the iron was necessary.

Aqueous iron(III)thiocyanate solutions decompose slowly,³ and for this reason the time elapsed since the preparation of the test solution was measured, and a small correction to the final absorbance readings was made.

Table 2. Determinations of molar absorbances of tris(thiocyanato)iron(III) in octan-2-ol solutions obtained by extraction from aqueous phases with a large range of thiocyanate concentrations. The numbers refer to the solutions in Tables 3 and 4.

No.	C_{KCl}	C_{HCl}	C_{KSCN}	$\log \epsilon_{520}$	$\log \epsilon_{500}$	$\log \epsilon_{480}$
8	0.870	0.052	0.01303	4.086	4.130	4.127
9	0.800	0.002	0.2004	4.094	4.149	4.147
10	0.500	0.002	0.501	4.084	4.139	4.138
11	0	0.002	1.002	4.074	4.130	4.129
12	0	0.002	2.004	4.086	4.141	4.136
13	0	0.002	4.008	4.083	4.135	4.128
14	0	0.002	5.150	4.094	4.147	4.140
14a	0	0.020	5.150	4.093	4.151	4.146
14b	0	0.100	5.150	4.091	4.149	4.143
Av.				4.09	4.14	4.135

The iron(III) complex in the octanol phase was more stable than the complex in the aqueous solutions. The latter could be stabilized by addition of an equimolar concentration of iron(II) as shown by Möller.³ However, it was found that some oxidation of iron(II) took place during the shaking with octanol. For this reason iron(II) could not be added when the partition coefficients were to be determined, but it could be employed with advantage when the complete spectra of the aqueous iron(III) solutions were to be recorded.

Spectrophotometric measurements were made on a Cary 118 spectrophotometer at 23–24 °C. Owing to the high absorbance of the iron(III)–thiocyanate solutions most of the measurements were made in 0.1 cm silica cells.

Emf measurements with cells containing a mercury(II)–thiocyanate solution and a mercury electrode were performed using a thermostated jacketed vessel with liquid junction to a saturated KCl-calomel electrode. A melted-in platinum wire provided contact to the mercury pool situated in a cavity in the bottom of the cell.

DISCUSSION OF SPECTRA

In the lower part of Fig. 2 is shown a series of ϵ, λ -absorption curves for aqueous iron(III)–thiocyanate solutions. The molar absorbance increases with the thiocyanate concentration from 7000 at 0.06 M up to $\epsilon_{\max} = 16\,800$ at 8–9 M, *i.e.* nearly saturated KSCN, with only a very slight shift of the maximum towards lower wavelength. The virtual constancy of the molar absorbance at $C_{\text{KSCN}} \geq 8$ M is also seen from Fig. 3, in which the absorbance A at three wavelengths is plotted *versus* the thiocyanate concentration for KSCN and NH_4SCN . Superficially, this would seem to indicate that formation of the hexacoordinated complex is complete in saturated solutions of these alkali metal thiocyanates. However, this cannot be the case since it can be concluded from the formation curve shown in Fig. 4 that the ligand number \bar{n} is only between four and five in this concentration range. It is therefore reasonable to conclude that the apparent constancy of the absorbance actually corresponds to a flat maximum and that the penta- and hexa-complexes have a lower absorbance than the tetra complex as *e.g.* is the case in the nickel(II)ammine system.¹⁷

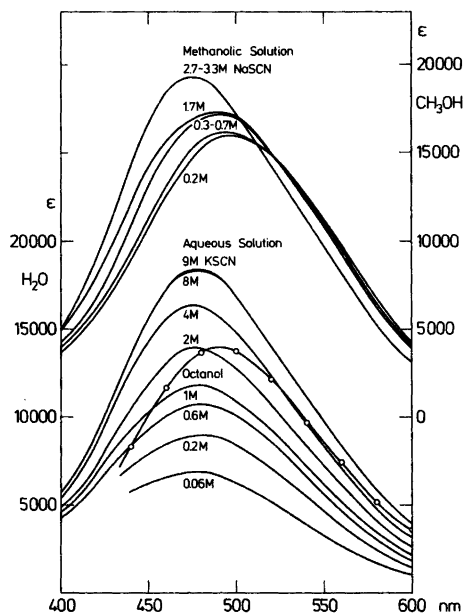


Fig. 2. ϵ, λ -spectra of iron(III)–thiocyanate solutions. *Lower part.* Spectra in aqueous KSCN-solutions with $C_{\text{Fe(III)}} = 0.000542$ M, $C_{\text{Fe(II)}} = 0.00038$ M, $C_{\text{H}^+} = 0.004$ M, and C_{KSCN} varying from 0.06 to ~ 9 M. Spectrum of $\text{Fe}(\text{NCS})_3$ in octanol (\circ). *Upper part.* Spectra in 98 % (v/v) methanol with $C_{\text{Fe(III)}} = 0.000542$ M, $C_{\text{H}^+} = 0.002$ M, and C_{NaSCN} varying from 0.20 to 3.32 M.

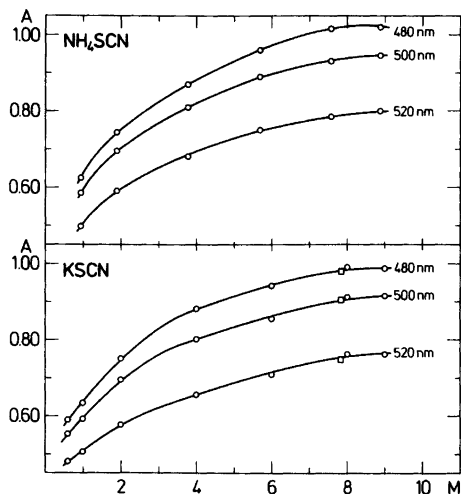


Fig. 3. Absorbance curves at three wavelengths for iron–thiocyanate solutions with $C_{\text{Fe(III)}}=0.000542$ M, $C_{\text{Fe(II)}}=0.00380$ M and $C_{\text{H}^+}=0.0040$ M as a function of the thiocyanate concentration for different thiocyanate salts. *Upper figure.* The absorbance A in 0.1 cm cells for NH_4SCN -solutions with $C_{\text{NH}_4\text{SCN}}$ varying from 0.9 M to 8.9 M. *Lower figure.* The absorbance A in 0.1 cm cells for KSCN -solutions with C_{KSCN} varying from 0.6 M to 9 M. A single point (\square) for 7.8 M NaSCN is also shown.

In his pioneering work Max Möller³ studied the iron(III)–iron(II) redox potential in aqueous thiocyanate solutions and showed that the iron(III) complexes contain only one iron atom. Mitchell and Macdonald¹⁸ used ebullioscopic measurements to determine the molecular weight of $\text{Fe}(\text{NCS})_3$ in diethyl ether and found that it is monomeric in contrast to the earlier result of Schlesinger and Walkenburgh.¹⁹ Mironov and Rutkowski^{10,11} incorrectly assume, on the other hand, that $\text{HFe}(\text{NCS})_4$ rather than $\text{Fe}(\text{NCS})_3$ is preferentially extracted from aqueous solutions by diethyl ether. This is inconsistent with the results of the present work in which it is shown that the distribution of the iron(III)-complex between octanol and aqueous thiocyanate solutions is independent of the hydrogen ion concentration between 0.002 and 0.1 M also in the range of thiocyanate concentrations where anionic complexes are dominant. This is seen from Table 2, in which the molar absorbances of $\text{Fe}(\text{NCS})_3$ in the octanol phase at three wavelengths are shown for some of the solutions examined (see especially Nos. 14, 14a and 14b). The numbers in Table 2 refer to those in Tables 3 and 4, in which all the measured partition coefficients are collected.

The absorption curve for the tris(thiocyanato)iron(III) complex in octanol is shown in the lower part of Fig. 2, whilst the absorption spectra for some iron(III)-thiocyanate solutions in methanol are shown in the upper part of the figure. The spectra in methanol are practically unchanged from 2.7–3.3 M (saturated NaSCN). The absorption band in this

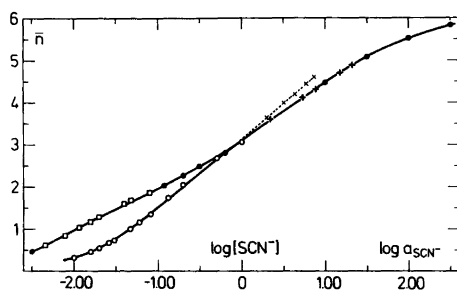


Fig. 4. Iron(III)–thiocyanate formation curves. Calculated values of \bar{n} , $\log[\text{SCN}^-]$ for 1 M $\text{Na}(\text{CF}_3\text{SO}_3, \text{SCN})$ (\square) and for 1 M $\text{K}(\text{Cl}, \text{SCN})$ (\circ) taken from the data in Table 3, and \bar{n} , $\log a_{\text{SCN}^-}$ values ($+$) for $C_{\text{KSCN}} > 1$ M taken from the data in Table 4. Further points (\bullet) extending the curves were calculated utilizing the derived stability constants. The incomplete dashed curve through the points (\times) are calculated under the assumption that the thiocyanate activity can be equated with the activity of potassium thiocyanate.

Table 3. Results for the distribution of tris(thiocyanato)iron(III) between aqueous iron(III)thiocyanate solutions in 1 M salt medium and octan-2-ol at 24 °C.

$C_{\text{Fe(III)}}^{\circ}=0.000542 \text{ M}, K_{\text{D}}=C_{\text{oct}}/C_{\text{aq}}$							
No.	C_{KCl}	C_{HCl}	C_{KSCN}	$\log C_{\text{KSCN}}$	$\log K_{\text{D}}(\text{exp})$	$\log K_{\text{D}}^{\text{a}}(\text{calc})$	$\bar{n}_{\text{calc}}^{\text{a}}$
1	0.984	0.102	0.01602	-1.795	-1.467	-1.439	0.45
2	0.980	0.052	0.02004	-1.698	-1.201	-1.215	0.53
3	0.974	0.052	0.02605	-1.584	-0.928	-0.943	0.66
4	0.970	0.052	0.03006	-1.522	-0.812	-0.801	0.73
5	0.954	0.052	0.04609	-1.336	-0.410	-0.401	0.98
6	0.940	0.052	0.06012	-1.221	-0.199	-0.178	1.15
7	0.920	0.052	0.08016	-1.096	+0.035	+0.039	1.36
8	0.870	0.052	0.1303	-0.885	+0.372	+0.346	1.74
9	0.800	0.002	0.2004	-0.698	+0.540	+0.550	2.07
10	0.500	0.002	0.501	-0.300	+0.794	+0.793	2.68
11	0.000	0.002	1.002	+0.001	+0.835	+0.835	3.03
	$C_{\text{CF}_3\text{SO}_3\text{Na}}$	$C_{\text{CF}_3\text{SO}_3\text{H}}$	C_{NaSCN}	$\log C_{\text{NaSCN}}$	$\log K_{\text{D}}(\text{exp})$	$\log K_{\text{D}}^{\text{b}}(\text{calc})$	$\bar{n}_{\text{calc}}^{\text{b}}$
17	0.895	0.100	0.00471	-2.327	-1.928	-2.007	0.61
18	0.895	0.100	0.00786	-2.105	-1.517	-1.502	0.84
19	0.884	0.100	0.01178	-1.929	-1.158	-1.138	1.04
20	0.884	0.100	0.01571	-1.804	-0.964	-0.902	1.18
21	0.930	0.050	0.01964	-1.707	-0.824	-0.730	1.29
22	0.910	0.050	0.0393	-1.406	-0.257	-0.263	1.60
23	0.903	0.050	0.0471	-1.327	-0.145	-0.156	1.68
24	0.879	0.050	0.0786	-1.105	+0.174	+0.114	1.88

^a $\beta_1=10^{1.55}$, $\beta_2=10^{2.50}$, $\beta_3=10^{3.09}$, $\beta_4=10^{2.66}$, $K_{\text{D}}^{\text{a}}=10^{1.05}$. ^b $\beta_1=10^{2.30}$, $\beta_2=10^{3.90}$, $\beta_3=10^{4.25}$, $K_{\text{D}}^{\text{b}}=10^{1.05}$.

Table 4. Results for the distribution of tris(thiocyanato)iron(III) between octanol and iron(III)thiocyanate solutions with $C_{\text{KSCN}} \cong 1 \text{ M}$. $C_{\text{Fe(III)}}^{\circ}=0.000542 \text{ M}$; $C_{\text{H}^+} \sim 0.002 \text{ M}$.

$\log K_{\text{D}}(\text{corr})=\log K_{\text{D}}(\text{exp})-0.064 (C_{\text{KSCN}}-1)$						
No.	C_{KSCN}	$\log a_{\text{SCN}^-}$	$\log K_{\text{D}}(\text{exp})$	$\log K_{\text{D}}(\text{corr})$	$\log K_{\text{D}}(\text{calc})^{\text{a}}$	$\bar{n}_{\text{calc}}^{\text{a}}$
11	1.002	0.001	+0.835	+0.835	+0.835	3.03
12	2.004	0.338	+0.736	+0.672	+0.654	3.61
13	4.008	0.721	+0.529	+0.337	+0.327	4.11
14	5.150	0.880	+0.387	+0.121	+0.134	4.32
15	7.83	1.169	+0.121	-0.316	-0.297	4.69
16	9.59	1.325	-0.014	-0.564	-0.577	4.88

^a $K_3=10^{0.6}$, $K_4=10^{-0.3}$, $K_5=10^{-1.0}$, $K_6=10^{-1.7}$, $K_{\text{D}}^{\text{a}}=10^{1.05}$.

concentration range is very closely similar to that in 8–9 M aqueous KSCN: The absorption maximum is situated at the same wavelengths (475 nm) and the intensity of the band is only slightly higher than that in aqueous solution. Formation of the hexakis(thiocyanato)complex is therefore not necessarily complete in methanol saturated with NaSCN. Moreover, it can be seen that the spectra in 0.3–0.7 M methanolic NaSCN exhibit an absorption maximum at the same wavelength (490 nm) as iron(III)-thiocyanate in octanol, and must therefore correspond to the predominant formation of the methanol solvated tris(thiocyanato)-iron(III) complex.

CALCULATION OF STABILITY CONSTANTS

Since $\text{Fe}(\text{NCS})_3$ is the only species extracted from the aqueous solutions, the relationship between the fraction of this complex $\alpha_3 = [\text{Fe}(\text{NCS})_3]/C_{\text{Fe(III)}}$, the partition coefficient K_D and the stability constants β_n is given by the expression:

$$\alpha_3 = K_D/K_D^0 = \beta_3 l^3 / (1 + \sum_1^6 \beta_n l^n) \quad (3)$$

K_D^0 is the partition constant and $l = [\text{SCN}^-]$, the free ligand concentration. In 1 M $\text{K}(\text{Cl}, \text{SCN})$ the fractions of $\text{Fe}(\text{NCS})_2^-$ and $\text{Fe}(\text{NCS})_6^{3-}$ are negligible, and for this reason our measurements in this medium can only be used to determine the first four constants β_1 to β_4 . Introducing this in (3) and rearranging the equation we obtain:

$$1 + l\beta_1 + l^2\beta_2 + l^3\beta_3 + l^4\beta_4 = (l^3/K_D) K_D^0\beta_3 \quad (4)$$

Dividing (4) by $K_D^0\beta_3$ and introducing as new constants:

$$X_0 = 1/K_D^0\beta_3, \quad X_1 = \beta_1/K_D^0\beta_3, \quad X_2 = \beta_2/K_D^0\beta_3, \quad X_3 = 1/K_D^0\beta_3, \quad X_4 = \beta_4/K_D^0\beta_3$$

the equation can be written:

$$X_0 + lX_1 + l^2X_2 + l^3X_3 + l^4X_4 = l^3/K_D \quad (5)$$

Equation (5) was used to determine the five X_n -values for the 1 M $\text{K}(\text{Cl}, \text{SCN})$ medium using a computer program for solving linear equations. Eleven equations of this kind with inserted values for K_D and $l = C_{\text{KSCN}}$ (Nos. 1–11 in Table 3) were used in these calculations, and the following values were obtained:

$$\begin{aligned} X_0 &= (7.16 \pm 0.70) \cdot 10^{-5} \\ X_1 &= (2.56 \pm 0.20) \cdot 10^{-3} \\ X_2 &= (2.28 \pm 0.15) \cdot 10^{-2} \\ X_3 &= (8.83 \pm 0.60) \cdot 10^{-2} \\ X_4 &= (3.24 \pm 0.30) \cdot 10^{-2} \end{aligned}$$

from which in turn were calculated $\log \beta_1 = 1.55$, $\log \beta_2 = 2.50$, $\log \beta_3 = 3.09$, $\log \beta_4 = 2.66$, and $\log K_D^0 = 1.05$, the uncertainty in all cases being 0.03. Determination of the constants by graphical methods give a somewhat higher uncertainty. The value of the first constant in the iron(III)–chloride system at ionic strength ~ 1 M is of the order $\log \beta_1 \sim 0.6$,^{20,21} so that the derived constants for the 1 M $\text{K}(\text{Cl}, \text{SCN})$ medium, in particular β_1 and β_2 , must necessarily be strongly influenced by chloro complex formation and are much too small.

In order to correct for chloride complex formation, supplementary measurements were made in an otherwise similar medium in which Cl^- is replaced by the poorly coordinating anion CF_3SO_3^- (Nos. 17–24 in Table 3). For thiocyanate concentrations up to $C_{\text{SCN}^-} \sim 0.1$ M, β_3 is without influence, and making the tacit assumption that K_D^0 has the same value as in the $\text{K}(\text{Cl}, \text{SCN})$ medium the following values for the three first stability constants can be calculated: $\log \beta_1 = 2.30$, $\log \beta_2 = 3.90$, $\log \beta_3 = 4.25$, all these values having a somewhat higher uncertainty than for the chloride medium. For this medium the quantity $\alpha_3 = K_D/K_D^0$ has its maximum value $6.8/11.2 = 0.607$ for $\bar{n} = 3$ at $\log[\text{SCN}^-] = 0.00$.

Table 5. The salting-out influence of KCl and KBr on the distribution coefficient (close to $K_D(\text{max})$).

$$K_D = C_{\text{Ox}}/C_{\text{aq}}; C_{\text{Fe(III)}}^{\circ} = 0.000542, C_{\text{H}^+} = 0.002 \text{ M.}$$

C_{KSCN}	C_{KCl}	C_{salt}	$\log K_D$	$\frac{\Delta \log K_D}{\Delta (C_{\text{salt}} - 1)}$
0.660	0.340	1.00	0.825	
0.660	1.340	2.00	0.952	0.127
0.660	2.340	3.00	1.080	0.127
0.660	3.28 ^a	3.94	1.229	0.137

C_{KSCN}	C_{KBr}	C_{salt}	$\log K_D$	$\frac{\Delta \log K_D}{\Delta (C_{\text{salt}} - 1)}$
0.660	0.34	1.00	0.830	
0.660	2.34	3.00	1.185	0.177
0.660	3.34	4.00	1.313	0.161

^a Saturated solution.

Av 0.15

With the derived β_n -constants for the $\text{Na}(\text{CF}_3\text{SO}_3, \text{SCN})$ medium combined with $\log K_4 = -0.4$ for the chloride-containing medium, α_3 (max) is estimated to be 0.548 at $\log[\text{SCN}^-] = 0.05$. According to these calculations, $\log K_D^{\circ}$ should be ~ 0.04 logarithmic units greater for 1 M $\text{Na}(\text{CF}_3\text{SO}_3, \text{SCN})$ than for 1 M $\text{K}(\text{Cl}, \text{SCN})$ and $\log \beta_3$ should be correspondingly smaller. In Table 3 the β_n -constants for the two media have been used to recalculate the partition coefficients K_D as well as the ligand number \bar{n} . The agreement between the experimental and calculated values of K_D is seen to be reasonably good. The values of the consecutive constants with estimated uncertainties are tabulated in Table 1.

The stability constants for $C_{\text{KSCN}} \geq 1 \text{ M}$. Some measurements of the partition coefficients for concentrated KSCN-solutions with $C_{\text{KSCN}} \geq 1 \text{ M}$ is shown in Table 4, and $\log K_D$ is plotted versus $\log[\text{SCN}^-]$ in Fig. 1. In order to use these data for a calculation of the stability constants β_4 , β_5 and β_6 it is necessary, as mentioned in the introduction, to make activity corrections and to take account of the salting-out influence of the salt medium.

Some data for the salting-out effect of the addition of increasing concentrations of KCl and KBr to a solution of initially 1 M $\text{K}(\text{Cl}, \text{SCN})$ are shown in Table 5. A solution with $C_{\text{KSCN}} = 0.66 \text{ M}$ having a nearly maximum content of the tris complex was selected for the experiments. The table shows that the increase in $\log K_D$ caused by the salts is somewhat greater for KBr than for KCl, but in both cases the increase is approximately proportional to the increase in salt concentration ($C_{\text{salt}} - 1$) as is usually the case for the activity factor of a neutral species.

Addition of thiocyanate ions strongly affects the complex equilibrium. The salting-out influence of KSCN can therefore only be obtained indirectly. This was done by comparing the salting-out effect of KSCN, KCl and KBr on an inert non-electrolyte. The initial experiments were made with Erdmann's salt $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$, but this complex proved to be insufficiently stable in aqueous solutions, and the final distribution experiments were made with tris(acetylacetonato)cobalt(III).

Apart from a flat maximum in the visible spectrum ($\epsilon_{\text{max}} \sim 108$ at 590 nm), this complex also showed strong UV-absorption which was also utilized in the experiments. A selection of the determined partition coefficients is given in Table 6. The following salting-out law was assumed to be valid:

Table 6. Results for the distribution of tris(acetylacetonato)cobalt(III) between octan-2-ol and aqueous salt solutions at 24 °C.

		$C_{\text{Co(acac)}_3}^0 \cong 0.02 \text{ M}, K_D = C_{\text{oct}}/C_{\text{aq}}$			
		$K_D(\text{av})$	$\log K_D$	$\log K_D - 0.28$	k_s
KCl	1.80 M	14.0	1.15	0.87	0.483
KBr	2.00 M	12.2	1.09	0.81	0.405
KSCN	1.00 M	2.9	0.46	0.18	0.18
KSCN	2.00 M	4.5	0.65	0.37	0.185
KSCN	3.00 M	6.6	0.82	0.54	0.18
KSCN	5.00 M ^a	20.9	1.32	1.04	0.21
No salt		1.9	0.28		

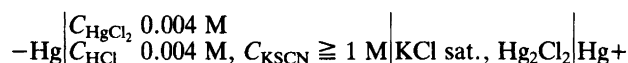
^a Supersaturated with respect to Co(acac)_3 .

$$\log K_D = \log k_o + k_s \times C_{\text{salt}},$$

where k_o is the partition coefficient for Co(acac)_3 between pure water and octanol and k_s is the salting-out coefficient for the salt in question. The values of k_s determined for KSCN are much smaller than for the halide salts, but as can be seen from Table 6 there is reasonable proportionality of $(\log K_D - 0.28)$ with the potassium thiocyanate concentrations. Potassium chloride has a somewhat stronger salting-out effect than potassium bromide, but as Table 5 shows, this is the opposite of the behaviour found for the iron(III)-thiocyanate solutions.

For this reason, the average k_s values found for the halide salts have been used in order to obtain a reasonable estimate of the salting-out effect of KSCN in iron (III)-thiocyanate solutions. Thus the ratio of k_s for KSCN (0.19) to the average value for the two halide salts (0.444) has been assumed to be equal to the ratio of $\Delta \log K_D / \Delta C_{\text{KSCN}} - 1$ for KSCN to the average value of $\Delta \log K_D / \Delta (C_{\text{salt}} - 1)$ for the two halide salts (0.15). In this way $\Delta \log K_D / \Delta (C_{\text{KSCN}} - 1)$ is calculated to be $0.19 / 0.444 \times 0.15 = 0.064$, and this value has been used to correct the experimental partition coefficients at high thiocyanate concentrations in Table 4 to 1 M KSCN.

As mentioned in the introduction, a measure of the activity of the thiocyanate ion was approximated by measuring the $\text{Hg}/\text{Hg}(\text{SCN})_4^{2-}$ potential in potassium thiocyanate solutions with $C_{\text{KSCN}} > 1 \text{ M}$. Measurements were made with the following cell:



In 1 M KSCN HgCl_2 is completely converted to $\text{Hg}(\text{SCN})_4^{2-}$, and the variation of the diffusion potential of the cell with C_{KSCN} is relatively small. Max Möller³ using Henderson's formula in the same way as Bjerrum and Unmack³⁵ calculates the diffusion potential of the combination



to be ~5 mV, which should be compared with the total change of 85 mV of the potential of the above cell for C_{KSCN} 1 and 4 M. If diffusion potentials can be ignored the electrode reaction is given by the expression:

$$E = E^{\circ} + 0.0295 \log \frac{a_{\text{Hg}(\text{SCN})_4^{2-}}}{a_{\text{SCN}^-}^4}$$

In this formula, a_{SCN^-} appears in a fourth and $a_{\text{Hg}(\text{SCN})_4^{2-}}$ only in a first power, the activity of SCN^- relative to 1 M KSCN can then as a rough estimate be expressed by the relationship:

$$\log a_{\text{SCN}^-} = \frac{(-E - E^{\circ})}{4 \times 0.0295}$$

with $E^{\circ} = 0.1135$ Volt. The experimental data are presented in Table 7. In Fig. 1 the corrected partition coefficients are plotted *versus* $\log a_{\text{SCN}^-}$ with the values tabulated in Table 4. Inserting these corrected partition coefficients in the relationship:

$$1 + K_3 l + K_3 K_4 l^2 + K_3 K_4 K_5 l^3 + K_3 K_4 K_5 K_6 l^4 = \frac{l}{K_{\text{D}}(\text{corr})} \times K_3 K_{\text{D}}^{\circ}$$

with $l = a_{\text{SCN}^-}$, and using the known values for K_3 ($=10^{0.6}$) and K_{D}° ($=10^{1.05}$) in 1 M $\text{K}(\text{Cl}, \text{SCN})$, the following values for the three last consecutive constants can be calculated:

$$K_4 = 10^{-0.3}, K_5 = 10^{-1.0}, K_6 = 10^{-1.7}.$$

Table 4 shows how well $\log K_{\text{D}}$ calculated using these constants agrees with the corrected experimental values.

Another approach would be to equate the activity of the thiocyanate ion with that of potassium thiocyanate.

The activity coefficients γ_{m} for KSCN solutions of up to 5 molal at 25 °C have been determined by Robinson and Stokes.²⁵ From these data $\gamma_{\text{c}}(\text{rel})$ relative to that in 1 M KSCN is calculated to have the following values:

C_{KSCN}	1.00	1.813	2.591	3.289	3.925 M
$\gamma_{\text{c}}(\text{rel})$	1	0.978	0.994	1.026	1.065

Assuming the activity of the thiocyanate ion to be equal to $\gamma_{\text{c}}(\text{rel}) \times C_{\text{KSCN}}$ and extrapolating with considerable uncertainty up to 6 M KSCN, the following values for the

Table 7. Estimate of the thiocyanate activity relative to that in 1 M KSCN defined as unity. Calculated from measurements on the cell:



C_{KSCN}	E	$\log C_{\text{KSCN}}$	$\log a_{\text{SCN}^-}$	$\log f_{\text{SCN}^-}$
1.005	-0.1135	0.002	0.002	0.000
2.010	-0.1533	0.301	0.337	0.036
4.020	-0.1985	0.602	0.720	0.118
8.040	-0.2539	0.903	1.190	0.287
9.850	-0.2719	0.991	1.342	0.351

consecutive constants have been estimated with the partition coefficients in this concentration range (compare Table 4):

$$K_4=10^{-0.25}, K_5=10^{-0.8}, K_6\sim 10^{-1.3}.$$

The \bar{n} , $\log a_{\text{SCN}^-}$ -values calculated from the two sets of constants are plotted in Fig. 4.

DISCUSSION OF RESULTS

The formation curves in Fig. 4 give a survey of the results obtained. Determination of partition coefficients has made it possible to determine all of the six stability constants in the system, although this method is not the best in the case of the first stability constant; it cannot compete with methods in which the first complex is stabilized by having a much higher concentration of iron(III) than of SCN^- . The best values in the literature²⁶⁻²⁸ according to this method (at about ionic strength 1 M) are of the order $\log K_1$ 2.10–2.15 to be compared with the value in this work $\log K_1\sim 2.30$ (see Table 1). The part of the formation curve determined in 1 M $\text{Na}(\text{CF}_3\text{SO}_3, \text{SCN})$ is rather incomplete, but a comparison with that for 1 M (Cl, SCN) shows directly the considerable influence of chloride complex formation. The last part of the formation curve at high concentrations of KSCN is dependent on the activity scale^{23,24} used for the ligand ion. The full-drawn curve for $C_{\text{KSCN}} > 1$ M is calculated with the constants derived using the emf measurements in Table 7, and the dashed part with those derived by use of $\gamma_c \times C_{\text{KSCN}}$ for the thiocyanate activity. The solid curve follows the curve section for 1 M $\text{Na}(\text{CH}_3\text{SO}_3, \text{SCN})$ better than the incomplete dashed section, but this does not necessarily mean that it is the best approach to the problem.

The six stability constants in the iron(III)–thiocyanate system estimated in this work are collected in Table 8. The ratio of the consecutive constants are compared in the table with the statistical effect.¹⁷ The data shows that the system behaves rather normally with an even distribution of the consecutive constants, and that as much as one third of the ratios between the constants are accounted for by the statistical effect. Babko,⁵ and Maddock and Mederios¹² assumed hypothetically that the system should behave in such a way (with too small a spread of the constants; see Table 1), but it is first in the present paper that this has been shown to be correct. Using the measured stability constants it can be calculated that

Table 8. Stability constants obtained in this work for the iron(III)thiocyanate system, and the statistical effect. β_n and K_n for $n=4,5$ and 6 are estimated under different assumptions – see footnotes *b* and *c* in Table 1.

<i>n</i>	$S_{n,n+1} = \log\{(6-n+1)(n+1)/(6-n)n\}$					
	1	2	3	4	5	6
$\log \beta_n$	2.3	3.9	4.5	4.2	3.2	1.5 ^b
$\log K_n$	2.3	1.6	0.6	4.25	3.45	2.15 ^c
$\log (K_n/K_{n+1})$	0.7	1.0	0.9	−0.3	−1.0	−1.7 ^b
			0.85	−0.25	−0.8	(−1.3) ^c
$S_{n,n+1}$	0.38	0.27	0.25	0.7	0.7	0.5
				0.55	0.5	0.38
				0.27	0.38	

saturated 10 M thiocyanate solutions contain about 10 % of the hexakisthiocyanato complex. It is therefore understandable that the alkali metal salts, as well as the ammonium salt of the hexakisthiocyanato complex can be prepared by evaporation of aqueous iron(III) thiocyanate solutions.²⁹

The slow auto-reduction which takes place in aqueous iron(III)thiocyanate solutions to give Fe(II) and (SCN)₂ was first studied by Möller,³ who in order to explain the rather complicated reaction found it necessary to assume the existence of "secondary" iron(II) complexes such as Fe(SCN)₂²⁺ and Fe[(SCN)₂](SCN)₂. Betts and Dainton²⁸ have subsequently confirmed that the ionradical (SCN)₂⁻ plays an important rôle in the mechanism.

The proposal that the thiocyanate ligands in the iron(III) complexes are coordinated by the nitrogen atom was first made by Haim and Sutin.³⁰ Po, Wong and Chen³¹ later found that FeNCS²⁺ in 10 M HClO₄ is converted to the protonated sulfur-bound species FeSCNH³⁺, with an attendant large shift of the absorption maximum towards the red end of the spectrum. The sulfur-bonded complex FeSCN²⁺ in dilute aqueous solution is converted relatively slowly to the nitrogen-bonded species, in contrast to the much faster formation of the N-bonded complex from metal ion and ligand.³²⁻³⁴

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