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NMR Relaxation Studies in Solutions of Transition Metal Complexes. X. The Stepwise Equilibria in the Iron(III)–Thiocyanate System Studied by NMR Relaxation

I. KORONDÁN and I. NAGYPÁL

Institute of Inorganic and Analytical Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary

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The T_2 NMR relaxation times of water protons have been measured to study the stepwise complex formation equilibria in the iron(III)–thiocyanate system in aqueous solution in a wide total iron(III) (0.0025–0.3 M*) and total thiocyanate (0–3.0* M*) concentration range, in 3* M *Na(ClO$_4$, SCN), at 25 °C.*

The measured relaxation rates are interpreted as a linear combination of the concentration of the different complexes. With this assumption, the following stepwise formation constants are given: $\log K_1 = 2.53$, $\log K_2 = 1.35$, $\log K_3 = 1.31$, $\log K_4 = 1.33$, $\log K_5 = -0.32$. The ratio of the stepwise equilibrium constants and the molar relaxation coefficients are interpreted by assuming octahedral–tetrahedral configuration equilibria in case of the bis, tris and tetrakis complexes.

Introduction

The iron(III)–thiocyanate is one of the most thoroughly studied stepwise equilibrium systems. In spite of this, the results of the different studies agree with each other only in the case of the mono- and bis-thiocyanato complexes, mainly because of the experimental difficulties in the determination of the formation constants for the further complexes. This is illustrated in Table I, where the results of those studies which were carried out to determine all of the formation constants are collected [1–7].

Beside these, there are a number of studies in which the formation constants for the first or for the first and second step were determined [8–13].

As seen from Table I, spectrophotometry and extraction are the most widely used experimental methods to study the system. There are, however, unavoidable difficulties in both methods. It is known from the work of Momoki *et al.* [14] that the value of the formation constant to be determined by spectrophotometry and the total concentration of the metal ion are strictly inter-related, even if only 1:1 complexes are formed. The weaker the complex, the higher the total concentration of the metal ion should be used to get reliable data. Evidently, the same relation is true if the stepwise processes are studied spectrophotometrically; the total metal ion concentration should be varied within as wide a range as possible. In this system, however, the wide iron(III) concentration range which would be necessary for the determination of the formation constants of the higher complexes cannot be studied because of the extremely high molar absorbancies. In the case of

TABLE I. Reported Values for the Formation Constants of the Complexes Formed in the Iron(III)–Thiocyanate System.

Method		Medium,	temp.	[H$^+$]	log K$_1$	log K$_2$	log K$_3$	log K$_4$	log K$_5$	log K$_6$	Reference
phot.		?	room	?	2.3	1.94	1.40	0.80	0.02		1
extr.	1.8 *M*	NaClO$_4$,	18 °C	0.18	2.09	1.75	−0.74	1.80	−0.70	−1.03	2
extr.	1.8 *M*	KNO$_3$,	18 °C	0.18	1.95	2.02	−0.41	−1.14	−1.57	−1.51	2
paper ionoph.	1.4 *M*	HClO$_4$,	18 °C	1.4	2.35	1.55	1.31	0.66	0.21		3
phot.	4.0 *M*	NaNO$_3$,	22 °C	0.2	2.1	1.3	0.5	0.0	−0.1	−0.1	4
extr.	3.0 *M*	LiClO$_4$,	25 °C	0.2	2.18	1.42	1.40	1.30	−0.07	−0.09	5
phot.	3.0 *M*	LiClO$_4$,	25 °C	0.2	2.19	1.48			0.0	−0.35	6
extr.	2.0 *M*	NaClO$_4$,	20 °C	0.2	(2.09)	1.48	1.00	0.67	0.18	−0.6	7[a]

[a] $K_i/K_{i+1} = i(n-i)/(n-i+1)(i+1)k$ relation and $\log K_1 = 2.09$ were supposed. The calculated parameter was k only, beside the partition coefficient.

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extraction studies, the ion-pairs may also be extracted beside the neutral complex, so that the evaluation is extremely complicated.

It is well known, that the paramagnetic iron(III) ion decreases enormously the spin–spin relaxation time of the protons in aqueous solutions. The stepwise complex formation gradually decreases the number of water molecules remaining in the first coordination sphere, so that the complex formation is accompanied with an increase of the relaxation time. In this case the reciprocal relaxation time may be given as a linear combination of the concentration of the species formed:

$$T_{2P}^{-1} = T_{2M}^{-1} - T_{2O}^{-1} = \sum_{i=0}^{6} r_i[\mathrm{Fe(SCN)}_i] \qquad (1)$$

where: T_{2P} = the paramagnetic contribution to the relaxation time

T_{2M} = the measured relaxation time

T_{2O} = the relaxation time in the absence of the paramagnetic species

r_i = the molar relaxation coefficient of the i-th complex.

The mathematical form of eqn. (1) is exactly the same, which describes the spectrophotometric measurements, but the molar absorbancies are replaced by the molar relaxation coefficients. There are, however, two features of the NMR relaxation which makes it much more suitable for the study of this system than photometry:

1. The conveniently measurable range of the T_2 spin–spin relaxation time is about 6 orders of magnitude, much higher than that of the absorbancy measurements.
2. The r_i values are decreasing with increasing number of ligands, while the molar absorbancies—in this system—are increasing. Thus, in the case of relaxation measurements, it is possible to increase the total iron(III) concentration at the higher thiocyanate concentration range.

As a result of these two features, the total iron(III) concentration may be varied between 0.0025–0.3 Mdm^{-3}, which is an appropriate range to study 5–6 consecutive complex formation steps, even if the complexes are relatively weak.

The result of the relaxation studies for the determination of the stepwise formation constants in the iron(III)–thiocyanate system in aqueous solution is reported in the present paper.

Experimental

Fluka $Fe(ClO_4)_3 \cdot 9H_2O$, Merck NaSCN, Reachim $NaClO_4$ and VEB-Apolda $HClO_4$ were used to prepare the stock solutions.

The T_2 NMR relaxation times were determined from the line-width of water protons measured at 25 ± 1 °C, with a Bruker WP 200 SY instrument. The ionic strength was kept constant, 3 *M* ($NaClO_4$ + NaSCN + $HClO_4$). The ClO_4^- concentration coming from the iron(III) perchlorate was not taken into account even in the $T_{Fe^{3+}} \sim 0.2\text{–}0.3\,M$ solutions, because these solutions were studied only at high thiocyanate concentration, where mainly the second to fifth complex formation steps took place. The coordination of the thiocyanate thus roughly compensates for the increase of the ClO_4^- concentration. Solution-pairs with the same iron(III), but different thiocyanate concentrations were prepared, the samples for NMR measurements were made from these by appropriate mixing.

The solutions contained 0.1 *M* $HClO_4$ below $T_{Fe^{3+}} = 0.1\,M$; the perchloric acid and iron(III) perchlorate concentrations were the same in solutions where $T_{Fe^{3+}} > 0.1\,M$. In this way the hydrolysis of Fe^{3+} and the complexes could be avoided.

Results and Discussion

The experimental results and the back-calculated curves are seen on Figs. 1–3. It is seen in Fig. 1 that the data above $T_{SCN^-} \sim 0.2$ are practically independent on the total thiocyanate concentration, thus the total iron(III) concentration range of 0.0025–0.03 is enough to calculate the formation constants of the complexes formed up to 0.2 Mdm^{-3} thiocyanate. Figures 2 and 3, however, clearly show, that the relaxation rate normalized for the total iron(III) concentration depends on the total iron(III) concentration even at $T_{SCN^-} \sim 2\,M$, but a rather high total iron(III) concentration is necessary to get a measurable deviation between the normalized curves. The measurable difference means that the species formed,

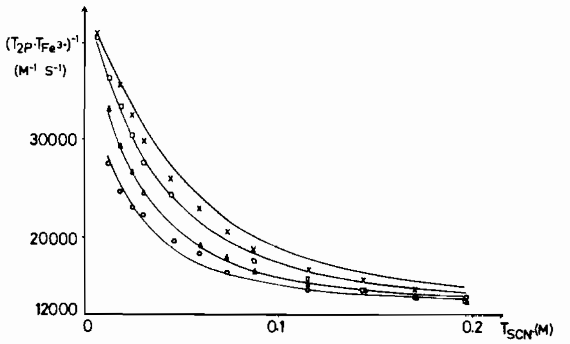

Fig. 1. The normalized relaxation rate as a function of the total thiocyanate concentration.

Notations: —○—○— $T_{Fe^{3+}} = 0.00248\,M$

—△—△— $T_{Fe^{3+}} = 0.00992\,M$

—□—□— $T_{Fe^{3+}} = 0.01984\,M$

—×—×— $T_{Fe^{3+}} = 0.02976\,M$

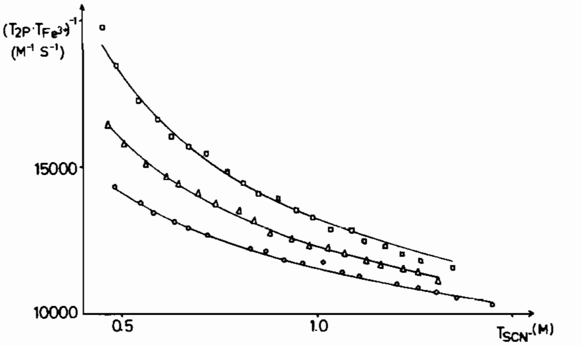

Fig. 2. The normalized relaxation rate as a function of the total thiocyanate concentration.
Notations: —○—○— $T_{Fe^{3+}} = 0.0997\,M$
—△—△— $T_{Fe^{3+}} = 0.1495\,M$
—□—□— $T_{Fe^{3+}} = 0.1993\,M$

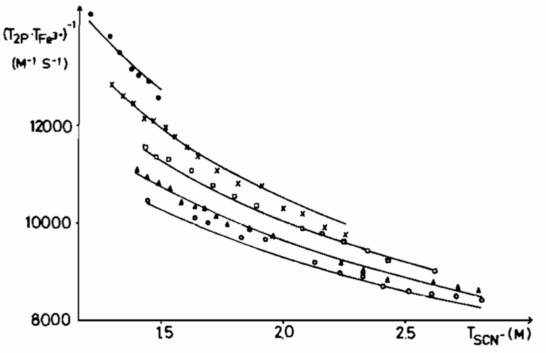

Fig. 3. The normalized relaxation rate as a function of the total thiocyanate concentration.
Notations: —○—○— $T_{Fe^{3+}} = 0.0997\,M$
—△—△— $T_{Fe^{3+}} = 0.1495\,M$
—□—□— $T_{Fe^{3+}} = 0.1993\,M$
—×—×— $T_{Fe^{3+}} = 0.2492\,M$
—●—●— $T_{Fe^{3+}} = 0.2990\,M$

even between 2–3 *M* thiocyanate concentration, can be identified and their formation constants calculated.

The experimental data were evaluated by using the program PSEQUAD [15], minimizing the percentage average difference of the measured and calculated line-widths. No acceptable value could be calculated for the formation constants of $Fe(SCN)_6^{3-}$, thus the formation of this complex was not assumed in the final evaluation.

The average deviation of all of the five constants is about ~0.1 log unit. The stepwise formation constants and the molar relaxation coefficients are collected in Table II.

The concentration distribution of the complexes is illustrated in Fig. 4, together with the $-\log T_{Fe^{3+}} = f(-\log[SCN])$ functions at different total ligand-total metal concentration ratios [16].

Two specific features of the system are seen from the data collected in Table II.

- The r_2 molar relaxation coefficient is surprisingly low.

TABLE II. Stepwise Formation Constants and Molar Relaxation Coefficients of the Complexes Formed in the Iron(III)–Thiocyanate System.

i	$\log K_i$	r_i
0		44200[a]
1	2.53	28070
2	1.35	9130
3	1.31	18685
4	1.33	13061
5	−0.32	3878

[a] Determined separately in absence of thiocyanate.

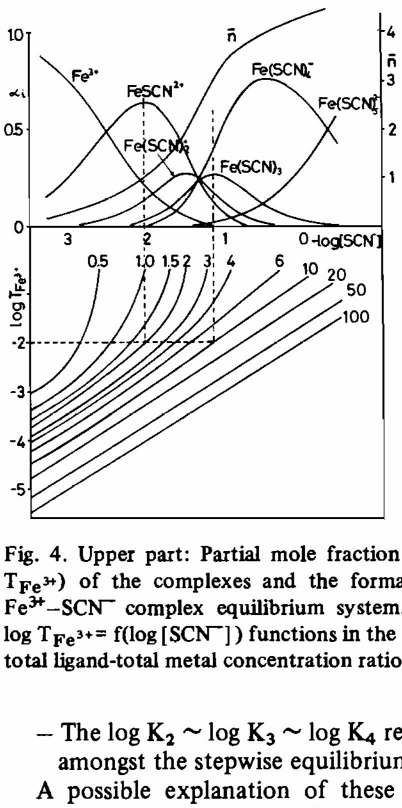

Fig. 4. Upper part: Partial mole fraction ($\alpha_i = [Fe(SCN)_i]/T_{Fe^{3+}}$) of the complexes and the formation curve in the Fe^{3+}–SCN^- complex equilibrium system. Lower part: The $\log T_{Fe^{3+}} = f(\log[SCN^-])$ functions in the system at different total ligand-total metal concentration ratios [16].

- The $\log K_2 \sim \log K_3 \sim \log K_4$ relation is unusual amongst the stepwise equilibrium systems.

A possible explanation of these two features is that a partial configuration change around the central iron(III) takes place when the second ligand is coordinated.

The bis complex may have octahedral and tetrahedral configuration, with an equilibrium between them shifted to the tetrahedral. The uptake of the further ligands (tris and tetrakis complexes) is accompanied by the shift of the equilibrium toward the octahedral configuration. The shift of the configuration-equilibrium to the octahedral form is completed when the fifth complex is formed.

This assumption completely explains the unusual relations found in the r_i and $\log K_i$, values, but further work is necessary before more definite conclusions can be drawn.

The only indication of the possibility of the octahedral–tetrahedral equilibria in the Fe^{3+}–SCN^- system is found in the work of Antipova-Karataeva *et al.* [17], who found similar wavelength shifts in the visible spectra of the Co^{2+}–SCN^- and Fe^{3+}–SCN^- systems at higher thiocyanate concentrations. The tetrahedral configuration of $Co(SCN)_4^{2-}$ is known; thus these workers concluded that the iron(III)–thiocyanate complexes formed at higher thiocyanate concentrations are also tetrahedral.

The concentration distribution in Fig. 4 shows that only the first step of the complex formation can be studied separately; the second, third and fourth steps are completely overlapping. The lower part of the Figure shows the $\log T_{Fe^{3+}} = f(\log[SCN^-])$ function at different $q = T_{SCN^-}/T_{Fe^{3+}}$ concentration ranges. This part of the Figure is useful from the analytical point of view, when the concentration distributions at different total concentrations are necessary. It can be read directly from the Figure (dotted line) that at $T_{Fe^{3+}} = 0.01\,M$ and $T_{SCN^-} = 0.02\,M$ total concentrations ($q = 2$) mainly the mono complex is formed, and that the partial mole fraction of bis complex is only about 0.15. The tris complex reaches its maximum concentration at $T_{SCN^-} = 0.1\ M$ ($q = 10$), but the concentration of $Fe(SCN)_4^-$ is considerably higher than that of the $Fe(SCN)_3$.

Comparing the data collected in Table I and Table II it is seen that our results are in acceptable agreement with the data of Mironov and Rutkovsky [5], but that the other values are completely different.

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