Magnetic and Spectrophotometric Studies on the Decoloration of Thiocyanatoiron(III) Complexes in Solutions. II. Effect of Acids

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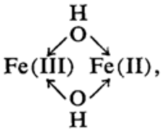
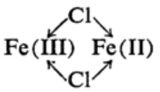
In order to account for magnetic observations on the reaction between iron(III) and thiocyanate ions, the present writer has proposed the formations of three kinds of dimers in solutions and discussed their roles in reactions. The results have been reported in the previous paper[1].





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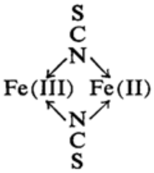

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[1] C. Miyake, This Bulletin, 33, 867 (1960).

There seems to be much remaining to be investigated. One of the problems to be clarified first is which dimer of the three is the most abundant and stable one in the solution. In this paper are reported the experimental data which are conceivably useful for considering the above-mentioned problems.

Experimental

Materials. — The iron(III) solution and potassium thiocyanate solution were prepared by the same method as that previously described. Acetic acid was purified by distillation until it became negative for the test of the iron ion. Sulfuric acid of analytical grade was used without further purification. It was confirmed that the test of the iron ion was negative. The sample solution was prepared by adding appropriate amounts of sulfuric acid (or acetic acid) and potassium thiocyanate to the iron stock solution. Before each measurement, the solution was diluted to the desired concentration.

Measurements. — The methods of measurements are the same as those described in the previous paper.

Experimental Results

Magnetic Data. — Fig. 1 shows that the magnetic moment of iron in solutions of various acids with the same normality decreases with time. Fig. 2 shows that the magnetic moment of iron in sulfuric acid of various normalities decreases with time.

Spectrophotometric Data. — The spectral curves of thiocyanatoiron(III) complexes in solutions of sulfuric acid or acetic acid are shown in Fig. 3. The absorption maxima at about 460 mμ are due to thiocyanatoiron(III) complexes in the solutions. Other maxima at about 300 mμ seem to be due to sulfatoiron(III) and acetatoiron(III) complexes. The curves of thiocyanatoiron(III) complexes in sulfuric acid of various normalities are shown in

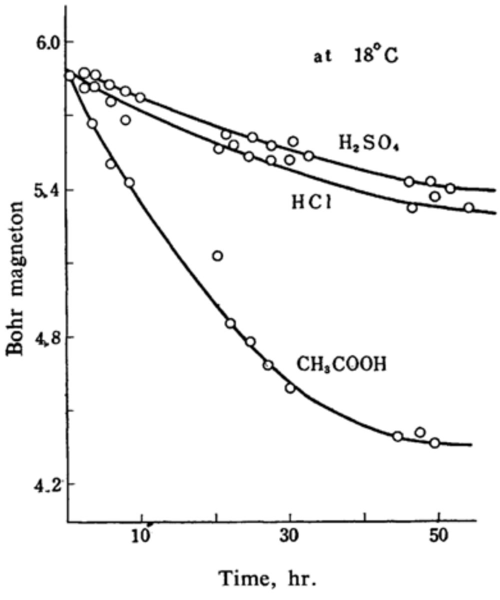

Fig. 1. Dependency of decrease in magnetic moment of iron upon kind of acid. (0.005 M iron(III), 0.5 M thiocyanate ion, 0.12 N-each acid solutions).

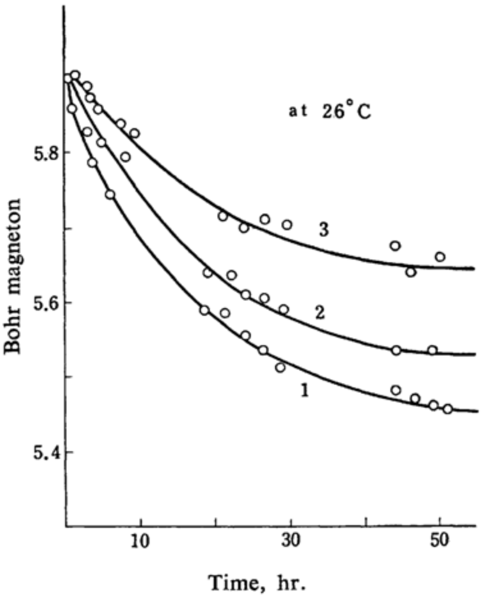

Fig. 2. Dependency of decrease in magnetic moment of iron upon concentration of sulfuric acid (0.005 M iron(III), 0.05 M thiocyanate ion solutions).
1 : 0.012 N H_2SO_4, 2 : 0.12 N H_2SO_4, 3 : 1.2 N H_2SO_4.

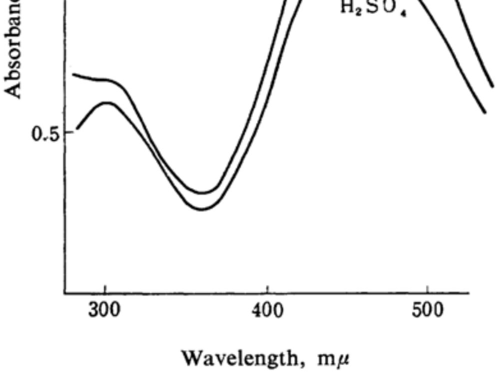

Fig. 3. Absorption spectra of thiocyanato iron(III) complexes in sulfuric or acetic acid solutions.

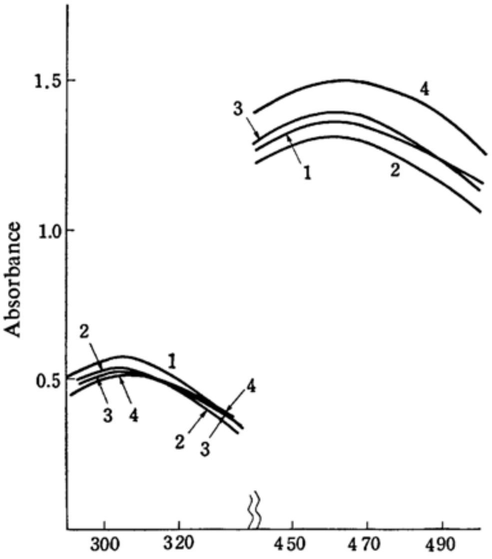

Fig. 4. Absorption spectra of thiocyanatoiron(III) complexes in solutions with varying concentration of sulfuric acid (0.005 M iron(III), 0.05 M thiocyanate ion solutions).
1 : 3.6N, 2 : 1.2 N, 3 : 0.6 N, 4 : 0.12 N.

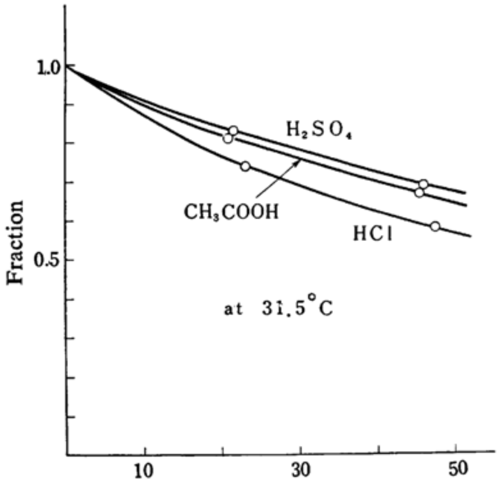

Fig. 5. Dependency of decrease in absorbance at about 470 mμ upon kind of acid (0.005 M iron(III), 0.5 M thiocyanate iron, 1.2 N each acid solutions).

Fig. 4. Fig. 5 shows the time dependency of absorbance values at the peak wavelength, about 460 mμ of the complexes in various acid solutions having the same normality. Fig. 6 represents the time dependency of absorbance values at the peak wavelength, about 460 mμ of the complexes whose time dependency of magnetic moment values is already shown in Fig. 2. The relations between the concentration of the hydrogen or thiocyanate ion and the above-mentioned absorbances at about 460 mμ and 320 mμ are tabulated in Table I, which can afford some knowledge about the effects of hydrochloric and sulfuric acids upon the nature of decoloration and of the formation of the dimer.

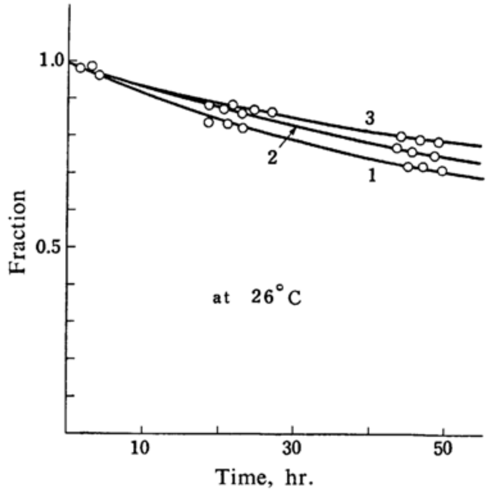

Fig. 6. Decrease of absorbance at about 460 mμ of thiocyanatoiron(III) complexes in solutions.
1 : corresponds to 1 in Fig. 2.
2 : 〃 2 〃
3 : 〃 3 〃

Discussion

The magnetic moment of thiocyanatoiron-(III) complexes in sulfuric acid and acetic acid solutions, when measured within fifteen minutes after the preparation, was found to be 5.91 and 5.88 Bohr magnetons, respectively. The values are characteristic of the outer orbital type of binding of the iron(III) complexes as in the case of the complexes in hydrochloric acid. As is seen in Fig. 3, no noticeable difference from the absorption for the complexes in hydrochloric acid solutions can be seen with respect to the absorption at about 460 mμ. As shown in Figs. 1 and 5, the decrease of the magnetic moment with time, which suggests the formation of complexes having the inner orbital type of binding, is also remarkable in both the solutions. However, the decrease is rather conspicuous in the acetic acid solution. This seems to be due to the unknown magnetic interaction between iron ions and acetate ions. Werbel et al.[2] pointed out that this kind of interaction makes the magnetic moment of the solution smaller while other authors proposed the formation of trimers. Some interpretation

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[2] B. Werbel, V. Debeler and W. C. Vosborgh, *J. Am. Chem. Soc.*, 65, 2329 (1943).

TABLE I. EFFECTS OF CONCENTRATIONS OF BOTH HYDROGEN IONS AND THIOCYANATE IONS TO ABSORBANCES AT ABOUT 470 mμ AND 320 mμ

	Increase of $[\mathrm{NCS}^-]$	Increase of $[\mathrm{H}^+]$
	Absorbance at about 470 mμ	
Wavelength of max. absorbance	Bathochromic	Constant*
Absorbance	Increase	Decrease*
Rate of decrease in absorbance	Increase	Decrease
	Absorbance at about 320 mμ	
Wavelength of max. absorbance	Bathochromic*	Bathochromic
Absorbance	Decrease*	Increase
Rate of decrease in absorbance	Constant*	Decrease

* The absence of any noticeable effect.

for the time dependency of the magnetic moment of the acetic acid solution should be postponed to the future when sufficient data are available.

In the present paper the discussion will be conducted with the data of sulfuric and hydrochloric acid solutions. The most important fact is to determine which dimer of the three is most likely existing and prevailing during the course of reaction. According to the present author's results shown in Figs. 2 and 5 or those also given in Table I, the increase in the acidity of the solution suppresses the progress of reactions which conceivably brings about the decrease of the magnetic moment. If it is assumed that the second type of dimers containing chloride or sulfate ions may exist, the formation of dimers should increase with the increasing concentrations of acids, resulting in a great decrease of the magnetic moment. This expected relation can not be supported by the afore-mentioned experimental results. Consequently the existence of the second type of dimers is thought to be very unlikely.

A question is raised whether the dimer with hydroxo bridges or that with thiocyanate bridges is more stable. The latter dimer may tentatively be considered to be stable in the solution in which the magnetic moment decreases with the increasing concentrations of thiocyanate ions (as shown in Fig. 2 in the previous paper). However, it should be noticed that the degree of decrease of the magnetic moment can increase even at a constant concentration of the thiocyanate ion, if the acidity of the solution decreases. Therefore, it will be safely concluded that the existence of dimers through hydroxo bridges is more likely than their existence through thiocyanate bridges.

Summary

Magnetic and spectrophotometric measurements have been carried out for the purpose of determining which of the proposed three types of dimers is most probable. The results obtained show that the second one with chloride ion bridges can safely be neglected. The existence of the first type with hydroxo bridges can be considered to be plausible.

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