

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MISSOURI]

The Structure of Ferric Thiocyanate and its Dissociation in Aqueous Solution

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Various formulas have been assigned to the colored complex present in aqueous solutions of ferric thiocyanate.^{1a,2-8} In recent years the work of Schlesinger and Van Valkenburgh has led rather generally to the adoption of the formula $\text{Fe}(\text{CNS})_6^{\equiv}$. The investigation about to be described was undertaken with the objective of determining the equilibrium constant for the dissociation of this complex. Contrary to our expectations, we found no evidence for the above complex in aqueous solution but did find rather definite proof for the formula FeCNS^{++} . The equilibrium constants for the dissociation of this complex and also for the corresponding chloro complex were determined.

Several methods of attacking this problem were investigated. The first to be tried was that of establishing the formula by studying the dependence of the color of the solution on the ionic strength. Since previous investigators have postulated several different compounds, it seemed desirable to verify the formula for the colored complex. The quantitative determination of the effect of change in ionic strength on the color should give information regarding the charge on the colored complex, or more specifically the difference in the squares of the charges of the reactants and products of the reaction. These early experiments were not carried far, in as much as they did not indicate the presence of either $\text{Fe}(\text{CNS})_6^{\equiv}$ or the neutral molecule $\text{Fe}(\text{CNS})_3$.

The second method of attack was to carry out a series of dilutions in Nessler tubes, starting with a solution with a large excess of thiocyanate and assuming the complex to be largely associated in this solution. By matching pairs of tubes, one of

which was diluted by a known fraction and the other diminished in quantity by a known fraction, it was found that one could assume the presence of neither of the above compounds. These results were not precise and little attention was paid to them until near the end of the investigation. It was then found, on returning to these data, that they substantiated the assumption of the ion FeCNS^{++} .

Precise determinations of the molecular extinction coefficient were then obtained in two series of experiments. In one the total concentration of iron was kept constant and the optical density was determined as a function of the thiocyanate concentration, keeping the ionic strength constant. In the other series the thiocyanate concentration was kept constant and in a similar manner the iron concentration varied. This procedure enables one to determine independently the number of each of the ions involved in the reaction which gives rise to the colored complex.

Similar experiments were carried out in which the concentrations of iron and thiocyanate were kept constant and the concentration of chloride ion was varied, keeping the ionic strength constant by varying the concentration of sodium perchlorate. This permitted the calculation of the equilibrium constant for the dissociation of the chloro complex. In this last experiment the thiocyanate complex is being used essentially as an indicator to permit the study of other equilibria involving the iron ion. This suggests the possibility of using this method to study various other equilibria involving iron and thiocyanate.

Finally experiments were carried out on the migration of ions by the moving boundary method. Schlesinger and Van Valkenburgh have reported that the color around the anode is darker, indicating the migration of a negative ion into this region. Our postulate of a positive ion would suggest that the color should move with the positive ions toward the cathode. In order to test these conflicting hypotheses, several different experiments were performed. The study of a moving boundary with the aid of agar or gelatin is out of the question since the thiocyanate solution was decolorized by these solutions. Finally experi-

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(1a) G. Krüss and H. Moraht, *J. Chem. Soc.*, **46**, I, 1129 (1889); **64**, I, 185 (1893).

(2) A. Rosenheim and R. Cohn, *Z. anorg. Chem.*, **27**, 280 (1901); *J. Chem. Soc.*, **60**, I, 455 (1901).

(3) G. Magnanini, *Z. physik. Chem.*, **8**, 1 (1891); *J. Chem. Soc.*, **60**, 1150 (1891).

(4) N. Tarugi, *Gazz. chim. ital.*, **34**, 326 (1904).

(5) C. Bongiovanni, *ibid.*, **37**, 472 (1907); *J. Chem. Soc.*, **92**, I 833 (1907).

(6) K. C. Bailey, *Proc. Roy. Irish Acad.*, **37B**, 6 (1924).

(7) B. A. Golzschmidt, *Ivanovo-voznensensk polytekh. Izvest.*, **11**, 51 (1928).

(8) H. I. Schlesinger and H. B. Van Valkenburgh, *This Journal*, **53**, 1212 (1931).

ments were performed with a tube of a shape similar to the letter W. At the center a fine capillary was attached, leading to a funnel. The tube was filled with a 1 *N* solution of sodium perchlorate of *pH* 2. Then the ferric thiocyanate solution, made up to an ionic strength of about 0.5 with sodium perchlorate and a *pH* of 2 with perchloric acid was added through the capillary. A good boundary was formed between the ferric thiocyanate solution and the colorless solution of sodium perchlorate on each side of the center of the "W." The greater density of the sodium perchlorate solution prevented turbulence and mixing of the two solutions. Reference marks were placed on the tube and the levels on the two side arms checked to be sure there was no change in the position of liquid as a whole. A potential gradient of about one volt per centimeter was found to give rise to a slight movement of color across the boundary in the direction of the cathode, but no appreciable movement toward the anode. This we interpret to mean that the colored ion is positively charged, but that as it migrates into the solution of sodium perchlorate it dissociates sufficiently to shift the equilibrium in the solution, destroying the color and leading to the formation of thiocyanate ion which migrates back into the colored solution. Hence one could not expect any larger amount of color across the boundary due to the above dissociation of the complex.

The major part of the work of Schlesinger and Van Valkenburgh dealt with nonaqueous solutions and therefore could not conclusively establish the formula in aqueous solutions.

In the experimental part of this paper details are given, to save space, for only the precise determination of the optical density as a function of the concentration of iron or thiocyanate. The success of these experiments is due first to the precision of measurement of the optical density with an apparatus⁹ which has been described recently and to the large range in cell length used permitting the study of a large range of optical density and concentration. These cells varied from 0.0385 cm. to 10.324 cm.

Experimental

All solutions were carefully prepared and analyzed. Salts were recrystallized where necessary. Distilled water was redistilled from alkaline permanganate. Solu-

(9) S. Jacobsohn, H. E. Bent and A. J. Harrison, *Rev. Sci. Instruments*, **11**, 220 (1940).

tions were allowed to stand for several months in order to permit settling of suspended material which would pass through an analytical filter paper. In order to avoid changes in concentration due to distillation to the upper surface of the storage bottles while standing for long periods of time these were painted black and an incandescent bulb mounted in the cupboard above these bottles.

Cells for the absorption measurements were constructed with windows cemented to Pyrex tubes in order to facilitate cleaning of the windows. Central Scientific "Sealstix" was found satisfactory as a cement. Short cells were constructed by grinding a hole in a glass plate and cementing a plate to each side. A section was also removed from one side of the hole to permit filling the cell. In the measurement of the most dense solution these short cells were used and microscope slides suspended in the opening in order further to diminish the thickness of the solution in the light path.

Measurements of the optical density were obtained by means of the spectrophotometer previously mentioned. This instrument, which used a Martens photometer, has a sensitivity which permits setting to better than 0.01° on the scale. The vernier reads to 0.01°, which makes this the limit of accuracy of the instrument. Readings of the zero point are taken before and after each reading on a solution. If these zero readings differ by more than 0.02° the measurements are repeated.

Fading of the ferric thiocyanate solution was reduced to a minimum by keeping the cell in the dark until it was placed in the photometer. The cell was wrapped with dark paper in order to eliminate all light except the monochromatic beam used for the measurement. Approximately twenty minutes elapsed between the time of mixing and the determination of the optical density. A series of measurements was then carried out over approximately half an hour and the optical density calculated by extrapolation to a standard time of fifteen minutes from the time of mixing. The amount of fading in a period of fifteen minutes varied from 0.05 to 3.4%, the average being 0.9%.

Plates were obtained with a Hilger medium quartz spectrograph covering the region from the near ultraviolet well up into the visible and these plates were measured with a Leeds and Northrup recording microphotometer.¹⁰ These plates indicate that the most suitable wave length for measurements of the absorption is 500 $m\mu$ which is very near the maximum in the absorption curve for the ferric thiocyanate and far enough away from the absorption curve for ferric chloride to introduce but a small correction term for the presence of this compound. These photographs with the Hilger instrument indicate that there is no change in the shape of the absorption curve with concentration and no evidence of a second compound at the higher concentration which has a different spectrum.

The determination of the structure of the colored complex was accomplished by varying the concentration of thiocyanate with a constant concentration of iron as shown in Fig. 1 and by vary-

(10) We are indebted to Dr. V. R. Ellis, who is in charge of the University spectrographic laboratory, for these plates and the measurements upon them.

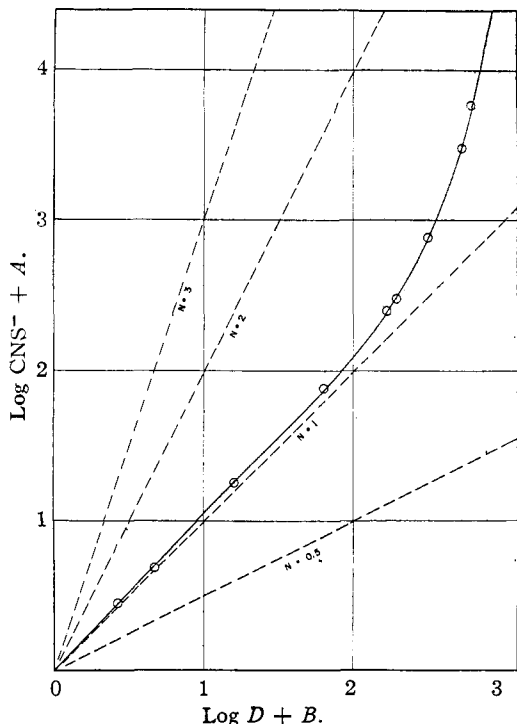


Fig. 1.—The logarithm of the total concentration of thiocyanate is plotted against the logarithm of the optical density, constants being added in order to give scales starting at zero. The total concentration of FeCl_3 is kept constant at $0.003582 M$, the concentration of HCl at $0.011 M$ and the ionic strength at 0.665 , sodium chloride being added to give the required ionic strength. The slope of the curve at the lower end gives the number of thiocyanate ions in the complex. Circles are experimental points, the solid curve is that obtained by the method of least squares.

ing the concentration of iron with a constant concentration of thiocyanate as shown in Fig. 2. The significance of the various straight lines in these figures will be evident from the following equations and equilibrium expressions.

If we write as a general expression for the reaction to be considered the equation



the charge on the complex being determined by the values of m and n , then the expression for the equilibrium constant for the reverse reaction will be

$$K = \frac{(\text{Fe}^{+++})^m (\text{CNS}^-)^n}{\text{Fe}_m(\text{CNS})_n}$$

If we now take the logarithm of both sides of this expression we may write

$$\log \text{Fe}_m(\text{CNS})_n = m \log \text{Fe}^{+++} + n \log \text{CNS}^- - \log K$$

If we keep the concentration of one of the ions constant, we then have the equation for a straight line if we plot the log of the optical density, which

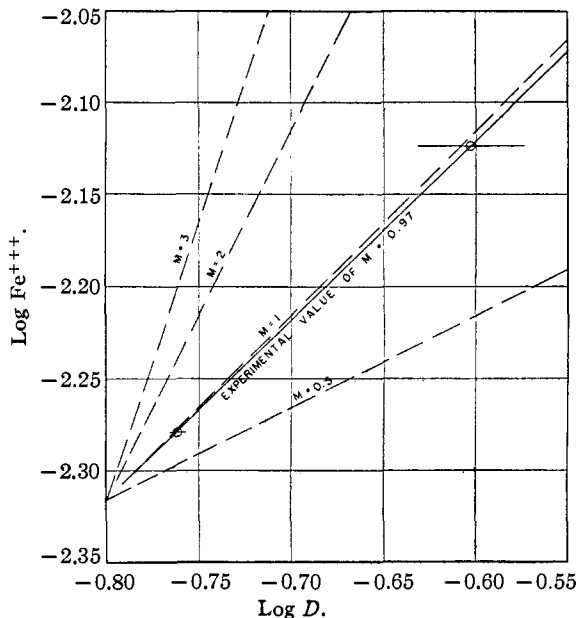


Fig. 2.—The logarithm of the total concentration of ferric ion is plotted against the logarithm of the optical density. The circles are the experimental points, the large error at the upper point being due to the fact that the cell used in the measurement was longer than desirable. Higher precision could have been obtained but seemed unnecessary in order to establish the slope of the curve as unity.

is proportional to the concentration of the colored complex, against the logarithm of the concentration of the other ion. The slope of this straight line then gives the value of n or m the reciprocals of which are given as N or M in Fig. 1 or 2. In these figures we have plotted not the logarithm of the concentration of the ion at equilibrium as would be required by the above logarithmic expression but rather the logarithm of the total concentration of this ion. In dilute solution where the colored complex is largely dissociated this will give a straight line, but deviations will occur as soon as an appreciable fraction of the ion is present in the form of the complex. Considerable care was taken in obtaining the data for Fig. 1 inasmuch as the chief question at issue is the number of thiocyanate radicals in the complex. The data for Fig. 2 were not obtained in as much detail or with as much care since no question has been raised regarding the number of iron ions in the complex. It is evident from these two figures that the data indicate the presence of a complex ion of the formula FeCNS^{++} .

The Value of the Equilibrium Constant and the Molecular Extinction Coefficient.—The

method used in determining the values of the equilibrium constant and the molecular extinction coefficient is suggested in part by Fig. 1. The circles represent the experimental determinations of the logarithm of the thiocyanate concentration plotted against the logarithm of the optical density. Since more than one equilibrium may be involved and since the introduction of each new colored compound introduces two arbitrary constants, the equilibrium constant and the molecular extinction coefficient, it seemed necessary to go to some pains to secure the best curve through the experimental points. Consequently using the method of least squares an equation was obtained for the solid curve drawn through the experimental points. This equation is

$$\log(\text{CNS}^-) + 3.9626 = (1.05197)(\log \epsilon Ml + 1.3221) - (0.0060496)(\log \epsilon Ml + 1.3221)^4 + (0.000322216)(\log \epsilon Ml + 1.3221)^8$$

its complexity being due to the fact that the curve with which we are dealing is so nearly straight at the lower end.

The lower end of the curve is nearly straight due to the fact that the compound is largely dissociated in this region. The curvature at the upper end is probably due largely to the fact that as the concentration of thiocyanate increases more and more of the iron is used up, the curve probably being asymptotic to the line representing complete association. It is possible, however, that other equilibria are involved at higher concentrations which are partly responsible for the shape of the curve in this region.

The first attempt to reproduce the curve was by assuming but one equilibrium, namely, that giving rise to the ion FeCNS^{++} . Values were obtained for the equilibrium constant and for the molecular extinction coefficient which reproduced the least squares curve with an average deviation of 0.038. This value may be compared with the deviation of the experimental points from the least squares curve, the average of these values being 0.012. It would appear that this assumption is too simple to account completely for the experimental results.

The next assumption was that an additional complex ion of the formula $\text{Fe}(\text{CNS})_2^+$ is present at higher concentrations of thiocyanate. This introduces two new constants and, as one might expect, a much better agreement may be obtained with the experimental points. The evaluation of the constants is a laborious procedure by suc-

cessive approximations. The final calculated results gave deviations from the least squares equation of the same magnitude as the experimental points, and even gave deviations of the same sign in most cases. This indicates that the form of the equation used in the method of least squares, which was intentionally arbitrary in nature, is not capable of fitting the experimental results as well as one based on the presence of two equilibria.

Similarly the assumption was made that two compounds are present, the second one having the formula $\text{Fe}(\text{CNS})_3$. The values of the constants obtained by successive approximations, however, did not give as good an agreement with the experimental curve as either of the two assumptions made above.

Finally the assumption was made that the iron is involved in the formation of two complex ions, FeCNS^{++} and FeCl^{++} , the latter affecting the measurements chiefly through its alteration in the concentration of the ferric ion.¹¹ The equilibrium involving the chloride ion was studied by using the thiocyanate as an indicator. Working with the following concentrations: FeCl_3 , 0.003482 *M*; HCl , 0.011 *M*; NaCNS , 0.0001090 *M*; total ionic strength, 0.665 *M*, the concentration of sodium chloride was reduced, replacing it by sodium perchlorate. The optical density as a consequence increased, as shown by the following figures.

Cl ⁻ concn.	Optical density
0.655	0.4053
.412	.4696
.123	.6028
.022	.7037
.000	.71 (extrapolated)

Since in these solutions the ferric thiocyanate is largely dissociated, we can calculate values for the equilibrium constant for the dissociation of the chloro complex. This turns out to be 0.78 ± 0.10 , which may be compared with the value obtained by Bray and Hershey¹² in solutions of zero ionic strength of 0.05. If we estimate from the data of these authors the value for the equilibrium constant at the ionic strength which we employed,

(11) The results of the investigation up to this point were presented as a preliminary report at the Cincinnati meeting of the American Chemical Society. We are greatly indebted to discussion with W. R. Brode, M. Kilpatrick and V. K. LaMer following the presentation of the paper which led to additional experiments on the chloro complex.

(12) W. C. Bray and A. V. Hershey, *THIS JOURNAL*, **56**, 1889 (1934).

we obtain a value of 0.3, which is considerably lower than ours but probably agrees as well as can be expected in view of this rather long extrapolation of their data to values of the ionic strength used in our experiments.

Using this value for the chloro complex equilibrium we have again calculated values for the FeCNS^{++} equilibrium by successive approximations, obtaining values which deviate from the least squares equation by 0.032, as compared with the deviations for the experimental points of 0.012. Doubtless a better agreement could be obtained by considering two complex ions with thiocyanate in addition to the chloro ion, but the solution of such a problem is obviously futile since the number of constants involved in the equations is so large as to make the agreement meaningless.

One more equilibrium must be considered before giving final values for equilibrium constants. This is the hydrolysis of the iron to give the complex ion FeOH^{++} . It is convenient to consider this equilibrium last, inasmuch as the activity of the hydrogen ion was kept constant in all of our experiments and consequently the ratio of FeOH^{++} to Fe^{+++} must also remain constant. We may therefore multiply the concentration of ferric ion involved in all of our equilibria by a constant factor in order to take account of the amount involved in the hydrolysis. Bray and Hershey obtained a value for the equilibrium constant for the reaction



of 60×10^{-4} at zero ionic strength and a value of 18×10^{-4} at the ionic strength used in our experiments. More recently Lamb and Jacques¹³ have obtained a value of 35×10^{-4} at zero ionic strength. If we extrapolate the data of these latter authors to zero ionic strength by drawing a curve with the limiting slope predicted by the Debye-Hückel theory, we obtain a value of 30×10^{-4} . Taking into account the effect of the ionic strength as indicated by Bray and Hershey and the value at zero ionic strength of Lamb and Jacques, we will use the value of 0.001 for this equilibrium constant at our ionic strength. This means that as a result of hydrolysis the concentration of Fe^{+++} must be reduced by the factor 1.09. This factor does not

(13) A. B. Lamb and A. G. Jacques, *THIS JOURNAL*, **60**, 1215 (1938).

need to be applied to the equilibrium constant for the chloride equilibrium since this was determined colorimetrically and no absolute values of the concentration were used except for the chloride ion. The equilibrium constant for the thiocyanate equilibrium must be corrected, however, by dividing it by this factor.

Our final value for the dissociation constant of FeCNS^{++} is found to be 0.033 ± 0.002 and for the molecular extinction coefficient 7882 ± 550 .

TABLE I
EXPERIMENTAL DATA^a

Molar concn. NaCNS	Molar concn. NaCl	Ionic strength	Cell length	Density at 15 min.
0.6322	0	0.665	0.0385 = 1.6 %	1.1234 = 0.66%
.3270	0.305	.665	.0385 1.6 %	0.9689 .2 %
.08284	.549	.665	.0385 1.6 %	.5771 .3 %
.0327	.599	.665	.0385 1.6 %	.3573 .3 %
.02725	.577	.637	.1415 0.4 %	1.1370 .4 %
.008284	.624	.665	.1415 .4 %	.4247 .2 %
.001962	.630	.665	.611 .5 %	.4656 .2 %
.0005232	.631	.665	2.857 .07%	.6547 .3 %
.0003052	.633	.666	7.633 .04%	.9705 .1 %
.0001090	.633	.666	10.324 .01%	.4918 .4 %

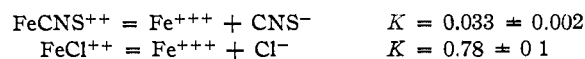
^a All solutions 0.003582 *M* with respect to FeCl_3 and 0.011 *M* with respect to HCl .

Summary

The dependence of the molecular extinction coefficient of aqueous solution of ferric thiocyanate at constant *pH* and ionic strength on the concentration of ferric ion and on thiocyanate ion has been determined. These results indicate that the colored substance is the ion FeCNS^{++} . Dilution experiments and experiments on the migration of ions in an electric field substantiate this conclusion.

Values for the dissociation constant of the above ion have been calculated, correcting for hydrolysis and the amount of iron combined with chloride ion. The equilibrium constant for this reaction with chloride ion also has been calculated.

The numerical results are as follows:



The ionic strength in both cases is 0.665.

The molecular extinction coefficient of FeCNS^{++} as defined by the equation $\log I_0/I = \epsilon Ml$ in which *M* is the molar concentration and *l* is the length of the cell in centimeters is found to be 7880 ± 550 at a wave length of 500 μm .