As another methodologically interesting application, eq. 11 can be made use of for the stochastic characterization of relative velocities. For instance, the rate of motion (relative to the ambient ocean) of ships on the high seas might be determined by comparing the limiting current of oxygen obtained in a sample of sea water in a "calibration assembly" aboard, with the limiting current measured using the same indicator electrode immersed alongside the ship in the ocean.

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[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, THE AUSTRALIAN NATIONAL UNIVERSITY]

The Ion $Fe(CNS)_2^+$. Its Association Constant and Absorption Spectrum

BY D. D. PERRIN

RECEIVED DECEMBER 26, 1957

Association constants of the complexes $FeCNS^{++}$ and $Fe(CNS)_2^+$ have been calculated from absorbance and oxidation-reduction potential measurements. Values at 18° by the two methods are $K_1 = 145$ and 133; $K_2 = 14$ and 10, respectively, at ionic strengths of 0.56 and 0.65. Estimates at $\mu = 0$ are $K_1^0 = 1090$, $K_2^0 = 40$. The absorption spectrum of $Fe(CNS)_2^+$ shows a maximum near 4850 Å., with a molar absorbance index of 9800. $Fe(CNS)_2^+$ is the major light absorbing species for thiocyanate concentrations greater than 0.04 *M*.

Dilute aqueous solutions of ferric and thiocyanate ions contain the complex[1–4] $FeCNS^{++}$, for which consistent values of the association constant[3–6] and the molar absorbance index[4–6] have been derived from spectrophotometric measurements. Although qualitative evidence from a range of experimental methods indicates that at higher thiocyanate concentrations complexes of higher thiocyanate content are present,[1,4,5,7] few quantitative studies have been reported. Estimates of the association constants of the complexes, $Fe(CNS)_x^{(3-x)+}$, ($x = 1$ to 6), have been made using solvent distribution[5] and spectrophotometry,[8] but the results obtained were not in good agreement. A later estimate[6] of the association constant of $Fe(CNS)_2^+$, from kinetic studies, did not support earlier values.

The present investigation was undertaken in an endeavor to measure the association constant of the ion $Fe(CNS)_2^+$ and to obtain its absorption spectrum. In this way it was hoped to assess the significance of this species in the ferric thiocyanate system. Competitive complex formation was minimized by using perchlorate solutions since Rabinowitch and Stockmayer[9] found no evidence of complex formation by ferric ion with perchlorate concentrations of up to 3 *M*. Subsequent data[10] suggest that under the present experimental conditions about 2% of the ferric ion not present in thiocyanate complexes would exist as ferric perchlorate ion pairs. This would not significantly affect the results obtained.

Experimental Methods

Reagents.—All reagents were of A.R. grade and were used without further purification. Stock solutions of ferric perchlorate were prepared from ferric ammonium sulfate by precipitation of ferric hydroxide with ammonia; the precipitate was washed repeatedly with distilled water at the centrifuge and then redissolved in excess perchloric acid. Ferrous perchlorate was freshly prepared by double decomposition from ferrous sulfate and barium perchlorate solutions. Concentrations of freshly prepared sodium thiocyanate solutions were checked by argentometric titration.

Spectrophotometry.—All absorbance measurements were made at 18 ± 0.3°, using a Beckman model DU quartz photoelectric spectrophotometer. Silica inserts and a range of optical cells provided light paths from 0.14 to 100 mm.

Known concentrations of ferric perchlorate, perchloric acid, sodium perchlorate and sodium thiocyanate were mixed in that order and diluted to the desired volume. Absorbance measurements were commenced within two minutes of mixing, and a series of readings was taken at each wave length to allow correction for any observed fading. Fading was slight but significant only at higher thiocyanate concentrations. All readings were taken within 30 minutes of mixing.

Variation of Absorbance with Thiocyanate Concentration.—If, as appears to be generally accepted, thiocyanate ion forms a series of colored complexes with ferric ion, the variation of the absorbance of the system with increasing thiocyanate concentration should enable their association constants and absorption spectra to be calculated.

In a constant environment, from the law of mass action

$$Fe(CNS)_x^{(3-x)+}] = K_x[Fe(CNS)_{x-1}^{(4-x)+}]\theta = K_1K_2\ldots K_x[Fe^{+++}]\theta^x \quad (1)$$

$$[Fe^{+++}]_0 = \sum_{x=0}^{x=n}[Fe(CNS)_x^{(3-x)+}] = [Fe^{+++}](1 + K_1\theta + K_1K_2\theta^2 + \ldots + K_1K_2\ldots K_x\theta^n) \quad (2)$$

$$A_{1\ \text{cm.}} = \sum_{x=0}^{x=n}\epsilon_x[Fe(CNS)_x^{(3-x)+}] = [Fe^{+++}](\epsilon_1K_1\theta + \epsilon_2K_1K_2\theta^2 + \ldots + \epsilon_nK_1K_2\ldots K_n\theta^n) \quad (3)$$

where K_x is the association constant for the complex, $Fe(CNS)_x^{(3-x)+}$, θ is $[CNS^-]$, A is the absorbance, ϵ is the molar absorbance index, and $[Fe^{+++}]_0$ is the total ferric ion concentration. At the concentrations used in the present

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[2] H. E. Bent and C. L. French, THIS JOURNAL, **63**, 598 (1941).

[3] S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

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[5] J. Y. Macdonald, K. M. Mitchell and A. T. S. Mitchell, *J. Chem. Soc.*, 1574 (1951).

[6] R. H. Betts and F. S. Dainton, THIS JOURNAL, **75**, 5721 (1953).

[7] (a) H. I. Schlesinger and H. B. Van Valkenburgh, *ibid.*, **53**, 1212 (1931); (b) H. I. Schlesinger, *ibid.*, **63**, 1765 (1941); (c) R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942); (d) S. E. Polchlopek and J. H. Smith, *ibid.*, **71**, 3280 (1949); (e) S. Baldwin and W. J. Svirbely, *ibid.*, **71**, 3326 (1949); (f) A. K. Babko and V. S. Kodenskaya, *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R.*, **3**, 162 (1951); *C. A.*, **47**, 2575 (1953); (g) K. M. Mitchell and J. Y. Macdonald, *J. Chem. Soc.*, 1310 (1949).

[8] A. K. Babko, *Compt. rend. acad. sci. U.R.S.S.*, **52**, 37 (1946); *C. A.*, **41**, 1913, 4732 (1947).

[9] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[10] J. Sutton, *Nature*, **169**, 71 (1952).

work ferric ion gives no detectable absorption throughout the wave length range studied.

Elimination of $[Fe^{+++}]$ between equations 2 and 3 gives

$$\frac{A_{1\,\text{cm}}}{[Fe^{+++}]_0} = \frac{\epsilon_1K_1\theta + \epsilon_2K_1K_2\theta^2 + \ldots + \epsilon_nK_1K_2\ldots K_n\theta^n}{1 + K_1\theta + K_1K_2\theta^2 + \ldots + K_1K_2\ldots K_n\theta^n} \quad (4)$$

At low thiocyanate concentrations, where the only thiocyanate complex present in significant amounts is $FeCNS^{++}$,[4] equation 4 reduces to

$$A_{1\,\text{cm}}/[Fe^{+++}]_0 = \epsilon_1K_1\theta/(1 + K_1\theta)$$

which on rearranging becomes

$$[Fe^{+++}]_0/A_{1\,\text{cm}} = 1/\epsilon_1 + 1/\epsilon_1K_1\theta \quad (5)$$

Hence ϵ_1 and K_1 can be obtained from the plot of $[Fe^{+++}]_0/A_{1\,\text{cm}}$ against $1/\theta$.

At higher thiocyanate concentrations other complexes must also be considered. If it is assumed[6] that for thiocyanate concentrations less than 0.1 M the concentration of $Fe(CNS)_2^+$ is very much greater than of $Fe(CNS)_3$ and subsequent complexes, it becomes possible to determine the association constant K_2 of $Fe(CNS)_2^+$. Under these conditions equation 4 becomes

$$A_{1\,\text{cm}}/[Fe^{+++}]_0 = (\epsilon_1K_1\theta + \epsilon_2K_1K_2\theta^2)/(1 + K_1\theta + K_1K_2\theta^2)$$

which can be rearranged to give

$$\frac{A_{1\,\text{cm}}}{[Fe^{+++}]_0} = \epsilon_2 - \frac{1}{K_1K_2\theta^2}\left(\frac{A_{1\,\text{cm}}}{[Fe^{+++}]_0}(1 + K_1\theta) - \epsilon_1K_1\theta\right) \quad (6)$$

$$= \epsilon_2 - f(A)/K_1K_2\theta^2$$

where ϵ_2 is the molar absorbance index of $Fe(CNS)_2^+$. As K_1, ϵ_1, θ and Fe^{+++} are known it is possible to obtain ϵ_2 and K_2 from the plot of $A/[Fe^{+++}]_0$ against $f(A)/\theta^2$.

For thiocyanate concentrations exceeding 0.1 M, cubic and higher equations can be derived from which to evaluate subsequent association constants. However, uncertainty in the experimental measurements is too great to allow reliable constants to be obtained.

Oxidation-Reduction Potentials.—All measurements were made at 20 ± 0.1° with a Tinsley type 4046B potentiometer, easily readable to 0.1 mv., and a Cambridge Spot galvanometer. Two bright platinum electrodes were immersed in the ferric thiocyanate solution, which also contained a constant, known, concentration of ferrous ion. The reference electrode was saturated calomel, the liquid junction being established across a fine sintered disc. Commercial nitrogen freed from oxygen by passage through Fieser's solution was used to stir the solution and to maintain an inert atmosphere in the closed electrode vessel.

The potential of the cell

$$\text{Pt} \left| \begin{matrix} Fe^{+++} \\ Fe^{++} \end{matrix} \; ClO_4^- \right| \text{satd. KCl} \,\Big|\, \text{cal.}$$

is given by

$$E = E_0 - 2.3026(RT/F)\log(a_{Fe^{+++}}/a_{Fe^{++}}) + E_j$$

where E_0 is a constant and E_j is the liquid junction potential. At 20°, for $\mu = 0.69$, $E_0 + E_j$ was found to be −0.5280 v.

From the variation of E with concentration of thiocyanate ion the stability constants of the ferric thiocyanate complexes can be calculated if it is assumed that formation of ferrous complexes is negligible under the experimental conditions. This assumption is reasonable because it is known that where the formation of a metal complex is attended by a reduction of ionic charge the resulting large entropy change favorable to complex formation[11] is greater the smaller the ion and the higher its charge.[12] Ferric ion would therefore be expected to form much more stable complexes with anions than does ferrous ion. Electronegativity considerations point to the same conclusion.

At constant ionic strength, E_j and the activity coefficients of ferric and ferrous ions should be only slightly affected when some of the perchlorate ion is replaced by thiocyanate ion. If the concentration of ferrous ion is maintained constant the observed potential change enables the concentration of ferric ion to be calculated from

$$(E - E_0')/0.0581 = \log([Fe^{+++}]_0/[Fe^{+++}])$$

where E_0' and $[Fe^{+++}]_0$ refer to thiocyanate-free solutions. Values for $[Fe^{+++}]_0$, $[Fe^{+++}]$ and $[CNS^-]$ can then be substituted in

$$([Fe^{+++}]_0/[Fe^{+++}] - 1)/[CNS^-] = K_1 + K_1K_2[CNS^-] + K_1K_2K_3[CNS^-]^2 + \ldots \quad (7)$$

which is obtained from equation 2. By fitting a curve of the form $a + bx + cx^2 + \ldots$ to the plot of the left side of equation 7 against $[CNS^-]$ the successive association constants can be evaluated.

Results

In some preliminary experiments using the method of continuous variations,[13] a total ferric perchlorate, sodium thiocyanate concentration of 0.05 M gave a broad maximum which varied with wave length (Fig. 1). The observed scatter of the experimental points probably was due to variation in the length of the light path. A change of less than 3 degrees in the slope of the silica insert in the optical cell altered the cell length by 0.01 mm., that is, about 7%. Within this rather large experimental uncertainty the maximum at the lower wave lengths was near a molar ratio (Fe:CNS) of 1:1; at higher wave lengths it approached a ratio of 1:2. This result confirms earlier observations[7d] and suggests that at least two complexes, which are probably $FeCNS^{++}$ and $Fe(CNS)_2^+$, are present; also that the latter absorbs more strongly than $FeCNS^{++}$ at longer wave lengths.

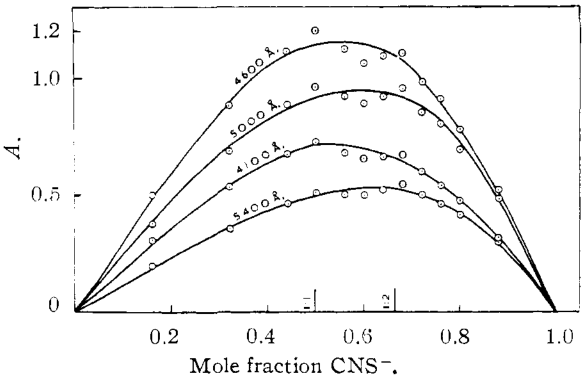

Fig. 1.—Method of continuous variations: $[Fe^{+++}]_0 + [CNS^-]_0$, 0.05 M; $[HClO_4]$, 0.50 M; 0.14 mm. light path. Solid lines calculated from association constants and molar absorbance indices for $FeCNS^{++}$ and $Fe(CNS)_2^+$.

From Fig. 2, ϵ_1K_1 was found to be 709000, 522000 and 247500, at 4600, 5000 and 5400 Å., respectively. Under the experimental conditions, $([CNS^-] \geq [Fe^{+++}])$, the intercept, $1/\epsilon_1$, was excessively sensitive to error, and it was necessary to use published values of ϵ_1 in evaluating K_1. The selected values of $\epsilon_{4600} = 4946$,[5] $\epsilon_{5000} = 3578$[5] and $\epsilon_{5400} = 1730$[5] (interpolated) are in good agreement with the figures of Betts and Dainton[6] but are slightly higher than those of Frank and Oswalt.[4] In this way K_1 was found to be 143.4, 145.9 and 143.0, average 144, at 18°, for $\mu = 0.56$. Correction for hydrolysis of ferric ion[14] increases K_1 by about 1%.

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[11] R. J. P. Williams, *J. Chem. Soc.*, 3770 (1952).

[12] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

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

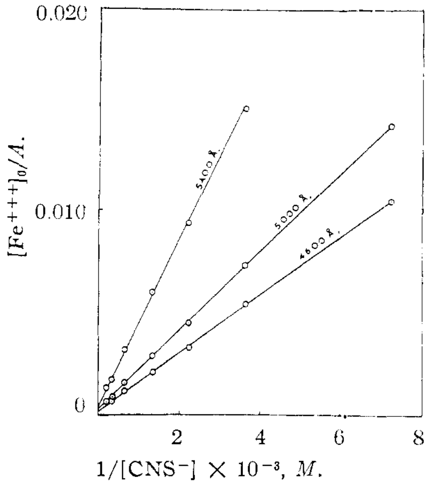

Fig. 2.—Estimate of $\epsilon_1 K_1$ from $[Fe^{+++}]_0/A = 1/\epsilon_1 + 1/\epsilon_1 K_1[CNS^-]$; $[Fe^{+++}]_0$, 2.0×10^{-4} *M*; $[HClO_4]$, 0.57 *M*.

For both Fig. 2 and 3 the thiocyanate concentrations were obtained by successive approximation, beginning with $[CNS^-] = [CNS^-]_0$. The corrections were small, amounting to about 3% at the lowest thiocyanate concentrations and diminishing to less than 1% above 0.014 *M*.

Over the thiocyanate range 0.006–0.123 *M*, the linearity of the results plotted in Fig. 3 confirms that $Fe(CNS)_2^+$ and $FeCNS^{++}$ are the main components present. The slopes of the lines lead to values of K_2 = 11.6, 14.5 and 15.7, average 14, at 18°, for μ = 0.56. The intercepts are somewhat uncertain owing to the long extrapolations but indicate molar absorbance indices for $Fe(CNS)_2^+$ of the orders of 9000, 9500 and 6300 at 4600, 5000 and 5400 Å. More accurate values were obtained using a solution 0.1229 *M* in thiocyanate, 0.567 *M* in perchloric acid and 2.0×10^{-4} *M* in ferric ion. The absorbance due to $FeCNS^{++}$ was calculated using the molar absorbance indices of Macdonald, *et al.*,[5] and taking K_1 = 146 and K_2 = 14. Subtraction from the measured absorbances gave the absorption spectrum for $Fe(CNS)_2^+$ recorded in Fig. 4, from which values were found to be: ϵ_{4600} = 8900, ϵ_{5000} = 9500, ϵ_{5400} = 6460.

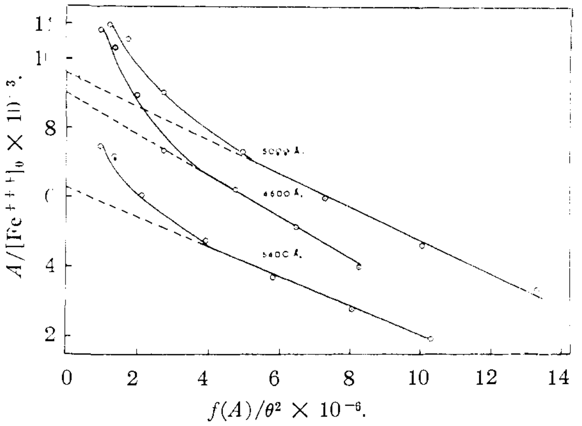

Fig. 3.—Evaluation of association constant and molar absorbance indices of $Fe(CNS)_2^+$: $[Fe^{+++}]_0$, 2.0×10^{-4} *M*; $[HClO_4]$, 0.56 *M*. Linear portions $[CNS^-]$, 0.0151 – 0.123 *M*. Higher concentrations are $[CNS^-]$, 0.31, 0.62, 0.92 *M*.

For thiocyanate concentrations exceeding about 0.2 *M*, the experimental values in Fig. 3 deviate increasingly from linearity, suggesting that higher complexes are present. However, the data are not sufficiently precise to permit the evaluation of higher association constants.

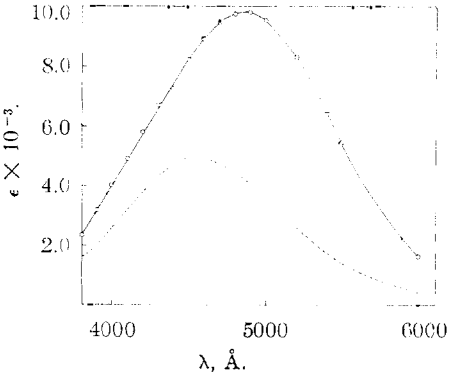

Fig. 4.—Absorption spectra of $Fe(CNS)_2^+$ (solid line) and $FeCNS^{+5}$ (broken line) in water.

The oxidation–reduction potential measurements provide an independent method of examining complex formation between ferric and thiocyanate ions. The results presented in Fig. 5 confirm that in thiocyanate concentrations at least up to 0.15 *M* only 1:1 and 1:2 ferric thiocyanate complexes are present in significant amounts. The good straight line obtained in Fig. 5 over this range leads to values of K_1 and K_2, at 20° and μ = 0.65, of 133 and 10.6, respectively. A subsequent experiment gave K_1 = 130, K_2 = 8.9, under similar conditions. The small correction for combined thiocyanate ion was made by successive approximation, commencing with $[CNS^-] = [CNS^-]_0 - ([Fe^{+++}]_0 - [Fe^{+++}])$. The temperature coefficient of K_2 should not be very different from that of K_1,[9] namely, ΔH =

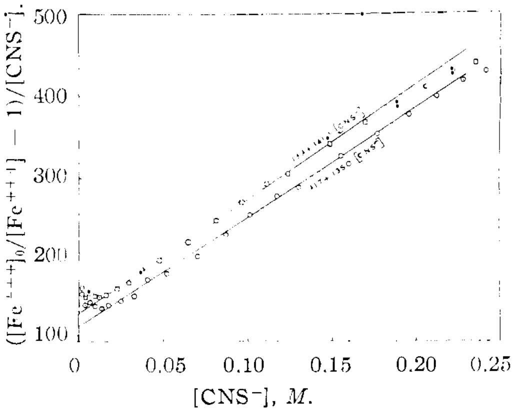

Fig. 5.—Estimate of association constants of $FeCNS^{++}$ and $Fe(CNS)_2^+$ from potentiometric measurements: $[Fe^{++}]$, 4.88×10^{-3} *M*; $[Fe^{+++}]_0$, 1.67×10^{-2} *M*; $[HClO_4]$, 0.569 *M*. Addition of 0.500 *M* NaCNS: ⊙, $[CNS^-]$ set equal to $[CNS^-]_0 - ([Fe^{+++}]_0 - [Fe^{+++}])$; ⊡, limiting values correcting for CNS^- in $FeCNS^{++}$ and $Fe(CNS)_2^+$.

−1.6 kcal./mole,[6] so that K_1 and K_2, corrected to 18°, are approximately 133 and 10.

The slight curvature shown by the results in Fig. 5 with increasing thiocyanate concentration is in the direction opposite to that expected for higher complex formation. This deviation from linearity, which was found to amount to 30% in a solution 0.8 M in thiocyanate ion and of ionic strength 1.08, is probably due to the increasing error in assuming constancy of liquid junction potential and ferric ion activity coefficients with change in thiocyanate concentration and ionic strength.

Discussion

The values for K_1 obtained spectrophotometrically and by potentiometric measurement are in good agreement and confirm previous data for perchlorate media, as listed in Table I.

TABLE I

ASSOCIATION CONSTANTS FOR $FeCNS^{++}$ IN PERCHLORATE SOLUTIONS AT 18°

	μ	K_1	$K_1°$at $\mu = 0$[d]
Present work[a]	0.65	133	1040
Present work[b]	.56	145	1140
Frank and Oswalt[4]	.5	138[c]	1050
Edmonds and Birnbaum[3]	1.0	127[c]	1020
Macdonald, *et al.*[5]	1.0	128	1030
Betts and Dainton[6]	1.28	121	920
Macdonald, *et al.*[5]	1.8	123	775

[a] Potentiometric. [b] Spectrophotometric. [c] At room temperature. [d] Extrapolation to $\mu = 0$, using equation of Rabinowitch and Stockmayer.[9]

Both methods also give values for K_2 reasonably close to the figure deduced by Betts and Dainton[6] (Table II).

TABLE II

ASSOCIATION CONSTANTS FOR $Fe(CNS)_2^+$ AT 18°

	Method	μ	K_2
Present work	Potentiometry	0.65	10[a]
	Spectrophotometry	0.56	14[a]
Betts and Dainton[6]	Kinetics	1.28	20 ± 5[a]
Macdonald, *et al.*[5]	Spectrophotometry	1.8	57[a]
	Spectrophotometry	1.8	105[b]
Babko[8]	Spectrophotometry		87[c]

[a] Perchlorate solutions. [b] Nitrate solutions. [c] Conditions not specified.

The conclusion that in solutions less than 0.15 M in thiocyanate ion the only complexes present are $FeCNS^{++}$ and $Fe(CNS)_2^+$ accounted quantitatively for the magnitudes of the absorbances that are used in Fig. 2 and 3. Over a range of thiocyanate concentration from 0.00014 to 0.123 M, values of the association constants and molar absorbance indices led to absorbances agreeing in almost all cases within 3% of the appropriate experimental value. Similarly a comparison was made with the experimental results in Fig. 1 by calculating from the initial ferric and thiocyanate ion concentrations the amounts of $FeCNS^{++}$ and $Fe(CNS)_2^+$ present, and hence their contributions to the absorbances. Results obtained in this way are shown by the solid lines in Fig. 1. Best fit for the data required that the cell length be taken as 0.144 mm.; measurement by micrometer gave 0.14 mm. The scatter of the experimental values about these lines is within the estimated experimental uncertainty.

Similarly for a solution 0.33 M in ferric nitrate and 0.67 M in potassium thiocyanate a value of $A^{5000}_{0.038\ \text{mm.}} = 1.5$ was predicted. This is in satisfactory agreement with the reported[7d] value of 1.7 (temperature not stated).

The fractions present as Fe^{+++}, $FeCNS^{++}$ and $Fe(CNS)_2^+$ for varying thiocyanate concentrations have been calculated using $K_1 = 146$, $K_2 = 14$ and are plotted in Fig. 6. As the absorption maxima for $FeCNS^{++}$ and $Fe(CNS)_2^+$ occur near 4530[5] and 4850 Å., respectively, the variation of the ratio of these complexes with increasing thiocyanate concentration leads to a shift of the absorption maximum to longer wave lengths.

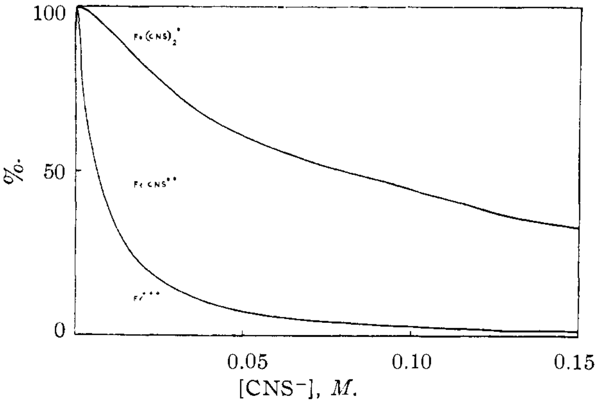

Fig. 6.—Variation in fractions of ferric ion present as complexes in solutions containing thiocyanate ion. Vertical distances between lines give percentage as Fe^{+++}, $FeCNS^{++}$ and $Fe(CNS)_2^+$.

The molar absorbance index at the maximum increases with thiocyanate content in the ferric complexes, from $\epsilon_{4530} = 5000$[6] for $FeCNS^{++}$ to $\epsilon_{4850} = 9800$ for $Fe(CNS)_2^+$. For the complex, believed to be $Fe(CNS)_3$, obtained by extraction of an aqueous ferric solution, 1.5 M in thiocyanate, ion, with an equal volume of amyl alcohol, ϵ_{4950} was about 13,800.

Association constants and molar absorbance indices point to $Fe(CNS)_2^+$ as the main light absorbing species for thiocyanate concentrations greater than 0.04 M.

By assuming that the activity coefficients of the ferric thiocyanate system are similar to those for ferric chloride complexes, estimates can be obtained of K_1^0 and K_2^0. Extrapolation to $\mu = 0$, using the same function as Rabinowitch and Stockmayer,[9] gives $K_1^0 = 1090$. Similarly from the function of Bray and Hershey,[15] $K_2^0 = 40$. The ratio of $K_1^0/K_2^0 = 27$ lies between the values of 6.7, for Fe^{+++}, Cl^{-9}, and 175 for Fe^{+++}, OH^-.[15] A "statistical" factor of 6 would be anticipated for a mechanism involving simple substitution; the difference may indicate less ionic binding in the complex.[9] From simple electrostatic considerations[9] it is predicted that K_3^0/K_2^0 is appreciably smaller than K_2^0/K_1^0. This has been confirmed for

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

the similar molybdenum(V) thiocyanate system.[16] The potentiometric measurements reported above also suggest that K_3 is numerically small.

Estimation of Iron as Thiocyanate.—The present results indicate the need to maintain a constant, high, thiocyanate concentration in any spectrophotometric method for the estimation of ferric ion by formation of thiocyanate complexes. The association constants of these complexes are not large and, as is apparent from Fig. 6, almost complete conversion to any one complex does not occur, even at high thiocyanate concentrations. Also, although ferric hydroxyl complex formation can be reduced to negligible proportions by using sufficiently acid solutions, ferric ion forms with many other anions complexes of stabilities comparable with, or exceeding, those with thiocyanate. Except under carefully controlled conditions such a method is, therefore, not likely to be capable of high precision. When greater accuracy is desired reduction to ferrous ion and the use of much more strongly complex-forming reagents such as α,α'-dipyridyl ion or *o*-phenanthroline appears to be preferable.

CANBERRA, AUSTRALIA

(16) D. D. Perrin, THIS JOURNAL, **80**, 3540 (1958).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BAYLOR UNIVERSITY]

Equilibrium Studies of the Copper(II) Oxalate Complex Between an Aqueous Solution and an Anion-exchange Resin[1]

BY LEONE D. COCKERELL AND PATRICK H. WOODS[2]

RECEIVED JULY 26, 1957

The equilibrium of the copper(II) oxalate complex existing between an aqueous solution and an ion-exchange resin has been studied. The copper(II) bioxalate complex is stable on the resin, although it does not exist in a dilute aqueous solution. Evidence for a coördination number of six for copper(II) is given. A high *p*H and low oxalate in solution favor the uptake of copper(II) on an anion-exchange resin.

Introduction

The copper(II) oxalate complex has been investigated and its formula and stability constant in solutions of an oxalate salt determined. In 1936 Britton and Jarrett[3] in an electrometric investigation of the copper(II) oxalate complex in solutions of sodium oxalate showed the complex to have the formula $Cu(C_2O_4)_2^{=}$. This work has been confirmed several times, most recently by Meites[4] in 1950 by polarographic means. The purpose of the present work was to study the equilibrium of the copper(II) oxalate complex existing between an aqueous solution and an ion-exchange resin. The general approach used was that of Stokes and Walton[5] and/or Salmon.[6] The use of an ion-exchange resin previously saturated with the ligand is suggestive of Fronaeus[7] but his treatment was not applicable in this case. The metal ion concentration was much too high (7×10^{-2} *M*) and the existence of the uncharged complex could not be assumed. Instead, the data were plotted after the manner of Bjerrum.[8]

Experimental

Materials.—Reagent grade chemicals were used throughout the investigation except for primary standard sodium oxalate and potassium dichromate which were used for standardization purposes.

Amberlite IRA-401, a strongly basic quaternary ammonium type resin was used, because it has a low degree of cross-linkage which permits the exchange of large anions. The chloride form of the resin was converted to the oxalate form with concentrated solutions of sodium oxalate. It was washed until the effluent was free of the oxalate ion, back-washed, column dried and finally air dried before use. The moisture content, determined by drying at 110° for 3 hr., was 35.9%. The swollen volume (in water) of the air-dried resin was determined pycnometrically. The dry volume of the air-dried resin was determined by displacement of hexane.[9] The values are: swollen volume, 1.682 cc./g. of air-dried resin; dry volume, 0.888 cc./g. of air-dried resin; internal solution volume, 0.794 cc./g. of air-dried resin.

To obtain the ion capacity, a weighed quantity of the oxalate form of the resin was placed in sulfuric acid and the eluted oxalate ion was titrated with potassium permanganate. This value was checked by converting to the hydroxide form, adding excess nitric acid and back titrating with standard sodium hydroxide. The exchange capacity per gram of air dried resin was 1.150 meq./g.

Preparation of Solution.—The copper(II) oxalate complex solution used for equilibration was prepared by bringing solid copper oxalate (J. T. Baker Analyzed >99.5%) into solution with sodium oxalate. Standardization was done by potassium permanganate for the oxalate and iodometrically for the copper.

Equilibration Technique.—One gram (1.150 meq.) of the oxalate resin was placed in a 130-ml. polyethylene bottle with a measured volume of the solution containing the complex and free sodium oxalate. Water was added to make a total of 100 ml. of solution. This was agitated at 30° for 18 hr. Preliminary runs had shown that equilibrium was attained shortly after 12 hr.

Analytical.—Copper content, total oxalate and *p*H were determined on the solution after equilibration. The *p*H was measured with a Beckman Model G meter. Copper and oxalate were determined as in the original analysis of the solution containing the complex. The analysis of the resin was done by difference since all ionic species were known. No attempt was made to correct for activities as available constants are not thermodynamic ones. No attempt was made to maintain constant ionic strength because this would have required addition of another salt whose anions would have entered the resin and caused unnecessary complications.[10]

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(2) Taken from a thesis presented by Patrick H. Woods in partial fulfillment of requirements for the Doctor of Philosophy degree.

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