Complex Formation of Ferric Iron with 7-Iodo-8-hydroxy-quinoline-5-sulphonic Acid (Ferron)

Å. R. STORM and F. J. LANGMYHR

University of Oslo, Chemical Institute A, Blindern, Norway

The complex formation of ferric iron with 7-iodo-8-hydroxyquino-line-5-sulphonic acid (ferron) was studied by potentiometric and spectrophotometric methods. Titrations of mixtures of the ligand and metal ion with standard alkali indicated the presence of complexes with ligand metal ratios 1:1, 2:1 and 3:1. On the basis of the titrations, the stability constants at $25.0° \pm 0.1°C$ and in the presence of 0.10 M potassium chloride were calculated to: log $K_{MA} = 8.9 \pm 0.2$, log $K_{MA_2} = 8.4 \pm 0.15$ and log $K_{MA_3} = 7.9 \pm 0.15$. By spectrophotometry, absorption curves and curves of continuous variation at different pH values were plotted. The photometric measurements confirmed the results obtained by potentiometry as to the number of complexes present, and showed that in the visible range the three complexes have absorption maxima which are only $10-15 \, m\mu$ apart.

In connection with the application of 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) in the simultaneous spectrophotometric determination of iron and aluminium it is of importance to know the composition and stability of the complexes formed. In a previous work [1] the authors studied the system aluminium-ferron and found evidence of complexes with ferron metal ratios 1:1, 2:1 and 3:1. In addition, hydroxo-compounds of the 1:1 and 2:1 complexes were found to be present.

The interaction of ferric iron with ferron has earlier been investigated by Yoe and Hall [2] and by Nortia [3]. The former authors concluded from colorimetric methods that a complex with ferron metal ratio 3:1 was formed. The latter author confirmed this result and in addition predicted the existence of a 1:1 complex with the composition Fe(OH)A.

The inconclusiveness as to the number of complexes present in the system ferric iron-ferron made further studies desirable. The present investigation was started with the purpose of determining the species present in the system, and at the same time to procure data on the stability of the compounds formed.

EXPERIMENTAL

Methods. The methods employed in this investigation were potentiometric titration and spectrophotometry. Ferron was titrated with standard alkali in the absence of and in the presence of ferric ions. During the titrations the temperature was $25.0 \pm 0.1°C$, and the ionic strength was kept relatively constant by maintaining a concentration of 0.10 M potassium chloride and by keeping a low concentration of ligand and metal ion. Mixing was effected by passing a stream of nitrogen through the solutions. Hydrogen ion concentrations were taken directly from the pH values measured. Absorption curves were plotted at different pH of solutions containing the ligand and the metal in the ratios 1:1, 2:1 and 3:1. To determine the composition of the complexes, curves of continuous variation were plotted at varying pH. The photometric measurements were carried out at room temperature $(20 \pm 2°C)$ and in the presence of 0.10 M potassium chloride.

Instruments. Extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1.000 cm glass and quartz cells. For the potentiometric titrations and the measurement and regulation of pH a Beckman Zeromatic pH meter (glass and calomel reference electrodes) was employed. The solutions to be titrated were placed in an ultra-thermostat.

Reagents. All chemicals were of reagent grade quality. The ferron used (Hopkin and Williams) contained (according to the producers' specification) not less than 98.0 % of $C_9H_6O_4NSI$ and a maximum amount of 0.1 % of sulphated ash. The iron compound applied was ferric chloride $(FeCl_3 \cdot 6H_2O)$.

Standard solutions. For the potentiometric titrations the following standard solutions were prepared. A 5×10^{-3} M solution of ferron was prepared by dissolving 1.7556 g in boiled distilled water, adding potassium chloride and diluting to 1 000 ml. Solutions of ferron decompose slowly on standing and were therefore not stored for more than one week. A standard solution of ferric iron was prepared by dissolving 54.16 g of $FeCl_3 \cdot 6H_2O$ in about 100 ml of distilled water containing about 0.5 ml of concentrated nitric acid. The solution was boiled and all iron was found to be in the ferric state (no colour formed with a freshly prepared solution of potassium ferricyanide). After dilution to 1 000 ml, the concentration of iron was determined gravimetrically and was found to be 11.165 g of iron per 1 000 ml, corresponding to a 0.20 M solution. By pipetting out 25 ml of this solution, adding potassium chloride and diluting to 1 000 ml with distilled water, a 5×10^{-3} M solution of ferric iron was obtained. A 0.09953 N solution of potassium hydroxide was used for the titrations, the solution being added from a calibrated 10 ml burette graduated to 0.01 ml. For the photometric measurements 5×10^{-3} M standard solutions of ferron and ferric iron were prepared, but these solutions did not contain inert salt. Potassium chloride was, however, added later during the preparation of the separate solutions.

Acid dissociation constants of ferron. The values determined previously by the authors [1] were employed in this investigation ($pK_1 = 2.50$ and $pK_2 = 7.11$ at $25.0 \pm 0.1°C$ and in the presence of 0.10 M potassium chloride).
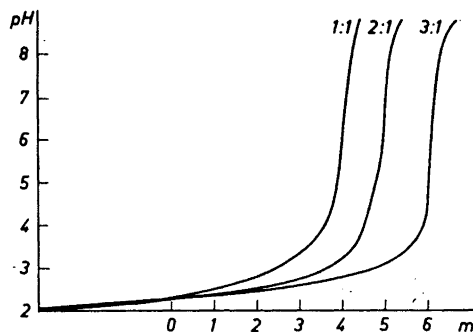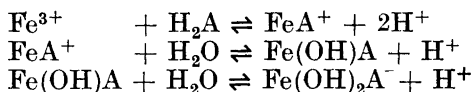

Fig. 1. Titration curves for solutions with ferron/ferric iron ratios 1:1, 2:1 and 3:1. m = equivalents of base added per mole of metal.

Potentiometric titrations. Solutions containing 1:1, 2:1 and 3:1 molar ratios of ligand to metal ion were titrated with standard alkali. From the 5×10^{-3} M solution of iron 25 ml were pipetted into a beaker and 25,50 or 75 ml of 5×10^{-3} M ferron solution were added. After thermal equilibrium was reached, standard alkali was added in small increments and the corresponding pH data were recorded as soon as constants values were obtained.

In Fig. 1 a set of titration curves is reproduced.

RESULTS

The 1:1 curves. Titration of equimolar amounts of ligand (H_2A) and metal ion resulted in a single inflection obtained after the addition of four equivalents of base per mole of metal. This result probably corresponded to the reactions:

$$Fe^{3+} \quad + H_2A \rightleftharpoons FeA^+ + 2H^+$$
$$FeA^+ \quad + H_2O \rightleftharpoons Fe(OH)A + H^+$$
$$Fe(OH)A + H_2O \rightleftharpoons Fe(OH)_2A^- + H^+$$

No precipitate was observed at any time during the titration. The increasing slope of the curve in the region two to four equivalents of alkali was believed to indicate that the formation of hydroxo-complexes took place by overlapping reactions. At the start of the titrations the solutions were green, but changed to red at the inflection. (A red colour is typical of iron-phenolate compounds.)

The 2:1 curves. The titration curves of solutions containing ferron and ferric iron in the ratio 2:1 exhibited one inflection corresponding to the addition of five equivalents of base per mole of metal. The following reactions probably took place:

$$Fe^{3+} + 2H_2A \rightleftharpoons FeA_2^- + 4H^+$$
$$FeA_2^- + H_2O \rightleftharpoons Fe(OH)A_2^{2-} + H^+$$
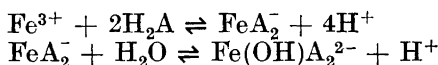
During these titrations the colour also changed from green to red. No precipitates were seen.

The 3:1 curves. These curves showed an inflection after the addition of six equivalents of base, probably corresponding to the reaction:

$$Fe^{3+} + 3H_2A \rightleftharpoons FeA_3^{3-} + 6H^+$$
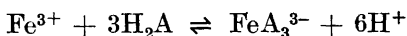
Two or three titration curves were plotted of each mixture. The separate curves of one set did not differ by more than 0.01 to 0.02 pH units in the ranges employed for the calculation of the stability constants.

Stability constants. Stability constants for the complexes not containing hydroxyl were calculated according to the method by Bjerrum [4] on the basis of a titration curve of the 3:1 complex. The average number of moles of ligand bound per mole of metal ion, designated by $\bar{n}$, were plotted against pA, the negative logarithm of the concentration of ligand. In Fig. 2, the fully drawn line resulted from calculations in which the amount of acid originating from the iron solution was included in the formula employed. The initial amount of acid was determined graphically from the plot of the titration curves. To obtain data of pA at $\bar{n}$ values below about 1.5, the broken line (Fig. 2) was drawn.

The values of pA at $\bar{n} = 0.5$, 1.5 and 2.5 were taken as log K_{MA}, log K_{MA_2} and log K_{MA_3}, respectively.
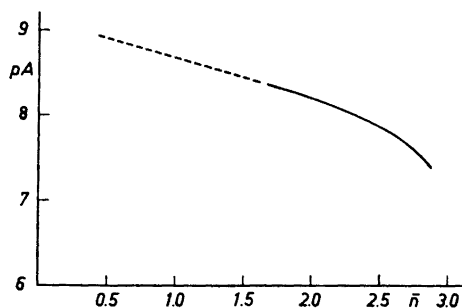
Fig. 2. Variation of degree of formation $\overline{n}$ for ferric iron/ferron complexes as a function of concentration of ligand pA.

The effect of a variation of $\pm$ 0.02 pH (the reproducibility of the pH meter) on the stability constants was calculated, and the data were used to estimate the limits of variation given below. (The pA *versus* $\overline{n}$ curve obtained by using a formula not including the amount of acid initially present, fell within the limits calculated for the pH variation of $\pm$ 0.02.)

The constants calculated were:

$\log K_{MA} = 8.9 \pm 0.2$, $\log K_{MA_2} = 8.4 \pm 0.15$ and
$\log K_{MA_3} = 7.9 \pm 0.15$.

Photometric measurements

In addition to the early colorimetric studies made by Yoe [5] and Yoe and Hall [2], spectrophotometric investigations of the system ferron-ferric iron have been carried out by Davenport [6], Swank and Mellon [7] and Nortia [3].

Davenport [6] plotted absorption curves at different pH values of some solutions containing ferric iron and excess of ligand, and recommended a pH of 5.0 for the analytical determination of iron. Swank and Mellon [7] plotted in more detail similar absorption curves, which showed, for the maximum around 600 mμ, a shift to lower wavelengths with increasing pH values. In another experiment these authors kept a constant concentration of metal ion, a contant pH of 3.0, and examined the effect of varying concentration of ferron. They found that increasing amounts of ferron increased the extinction of the solutions. A study of their absorption curves also showed that by increasing the concentration of ferron the maximum around 600 mμ shifted to lower wavelengths.

Nortia [3] studied the effect of the ligand-metal ratio on the absorption at 600 mμ by measuring the extinction of a series of unbuffered solutions. He found the resulting curves to be typical of systems where successive compounds are formed, or where the stability of the complex is not high. He also plotted absorption curves in the range 400—700 mμ and at different pH values for solutions in which hydrous ferric oxide and ferron or 8-hydroxyquinoline-5-sulphonic acid had reacted. The curves obtained for the two systems were similar in form. The curves reproduced by Nortia for the latter system also

showed that increasing pH values resulted in a shift of the maximum around 600 mμ to lower wavelengths.

The present potentiometric investigation indicated the presence of complexes with ligand metal ratios 1:1, 2:1 and 3:1. In the opinion of the authors, it seemed probable that the variations of the absorption maximum around 600 mμ with pH (*vide supra*) were due to the presence of different complexes. These complexes probably have slightly different absorption curves and different ranges of existence depending on pH. In order to confirm these assumptions, some photometric measurements were carried out.

Absorption curves. A series of solutions were prepared by pipetting into 100 ml volumetric flasks 3 ml of 5 $\times$ 10^{-3} M ferric iron solution, 3, 6 or 9 ml of 5 $\times$ 10^{-3} M ferron solution and 10 ml of 1.0 M potassium chloride. pH was regulated without the use of buffers and the solutions were diluted to volume with distilled water. The extinctions were then measured in the wavelength range 550 to 700 mμ against distilled water (ferron does not absorb in this wavelength region). The absorption curves are reproduced in Fig. 3.
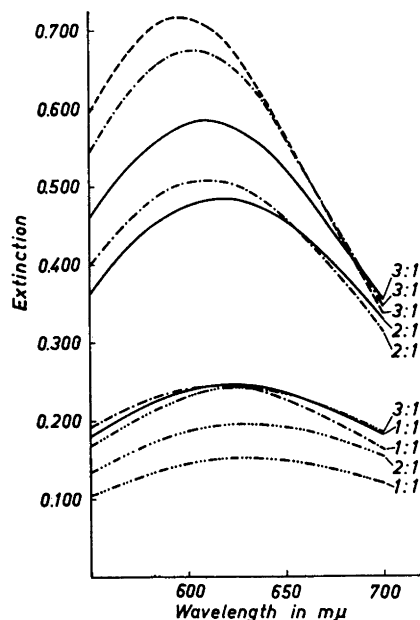

Fig. 3. Absorption curves at different pH values for solutions with ferron/ferric iron ratios 1:1, 2:1 and 3:1. Solutions with pH 1.30 —···—···—, pH 2.70 ——————, pH 3.50 —·—·—·—· and pH 5.0 — — — — —.

Solutions containing equimolar amounts of ligand and metal ion and having the pH values 1.30, 2.70 and 3.50 exhibited absorption curves which were similar in form and with maxima at the same wavelength, 625 mμ. The extinction of the solutions increased with pH. These solutions probably all contained mainly the 1:1 complex, the varying extinction being caused by the

difference of pH. Solutions containing ferron and metal ion in the ratios 2:1 and 3:1 and maintained at pH 1.30 exhibited curves which were similar to the 1:1 curves and with maxima at the same wavelength. At this low pH, the 2:1 and 3:1 complexes were probably not formed, the only stable compound being the 1:1 complex. The 2:1 and 3:1 curves plotted at higher pH values showed maxima at lower wavelengths and considerable higher extinctions. The maxima of the 2:1 curve at pH 2.70 and 3.50 were found at 618 and 613 mμ, respectively. In this pH range, the 2:1 complex was probably predominating. For solutions containing the ligand and metal ion in the ratio 3:1, the maximum varied considerably with pH. At pH 1.30 the 1:1 complex was believed to be formed, at intermediary pH values the 2:1 complex appeared and finally, at pH 5.00, the 3:1 complex was formed with absorption maximum at 595 mμ. Solutions of the 1:1 and 2:1 compounds at pH 5.00 probably contained phenolate compounds and the corresponding curves are not reproduced in Fig. 3.

Curves of continuous variation. Curves of continuous variation were plotted at 600 mμ for series of solutions with pH 1.25, 2.30, 3.25 and 4.90. In Fig. 4 these curves are given.
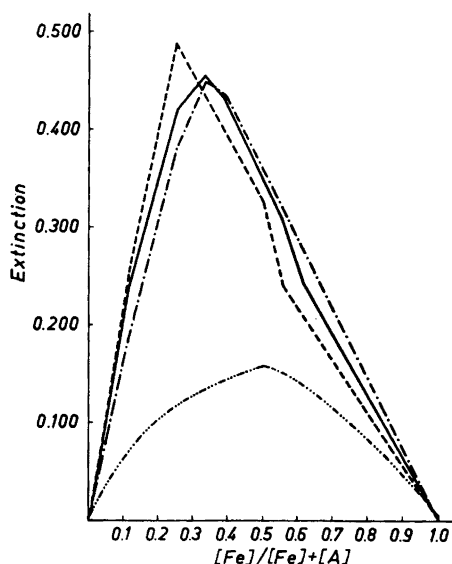

Fig. 4. Curves of continuous variation measured at 600 mμ. Solutions with pH 1.25 —···—···—, pH 2.30 —·—·—, pH 3.25 ————, and pH 4.90 —————.

The presence of three different complexes is indicated by the curves, the form of which also reflects the increasing stability when going from the 1:1 to the 3:1 complex.

DISCUSSION

The earlier observed change of the absorption maximum around 600 mμ with pH, or by varying the ferron metal ratio at a constant pH (*vide supra*) is explained by the presence of three complexes.

From this study conclusions can also be drawn as to the most suitable conditions for spectrophotometric determination of iron. An excess of ferron and a relatively high pH value should favour the formation of the 3:1 complex, which also has the highest extinction coefficient. The pH value given by Davenport[6], *viz.* 5.0 can thus be recommended.

It is of interest to compare the absorption curves of the present work with the data given by Phillips[8] for the complexes of ferric iron with 8-hydroxy-quinoline-5-sulphonic acid. Phillips reported that the 1:1 and 3:1 complexes with 8-hydroxyquinoline-5-sulphonic acid had absorption maxima at 625 and 580 mμ, respectively, while the maxima for the ferron complexes of the same composition in the present study were found at 625 and 595 mμ. The introduction of iodine in the 7-position does therefore not seem to change the visible absorption curves of the ferric iron complexes appreciably. It is highly probable, that the system 8-hydroxyquinoline-5-sulphonic acid/ferric iron is similar to that of ferron/ferric iron, the only difference being that higher stability constants can be expected in the former system.

REFERENCES

1. Langmyhr, F. J. and Storm, Å. R. *Acta Chem. Scand.* **15** (1961) 1461.
2. Yoe, J. H. and Hall, R. T. *J. Am. Chem. Soc.* **59** (1937) 872.
3. Nortia, T. *Ann. Acad. Sci. Fennicae Ser. A*, II, No. 86 (1957).
4. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, P. Haase and Son, Copenhagen, 1941.
5. Yoe, J. H. *J. Am. Chem. Soc.* **54** (1932) 4139.
6. Davenport, W. H. *Anal. Chem.* **21** (1949) 710.
7. Swank, H. W. and Mellon, M. G. *Ind. Eng. Chem., Anal. Ed.* **9** (1937) 406.
8. Phillips, J. P. *J. Am. Chem. Soc.* **72** (1950) 3159.