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

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By potentiometric methods the two dissociation constants of ferron were found to be: $pK_1 = 2.50$ and $pK_2 = 7.11$ at $25.0 \pm 0.1°C$ and in the presence of 0.10 M potassium chloride. Potentiometric titrations of mixtures of ferron (H_2A) and aluminium indicated the presence of the following complexes: AlA^+, $Al(OH)A$ (slightly soluble), $Al(OH)_2A^-$, AlA_2^-, $Al(OH)A_2^{2-}$ and AlA_3^{3-}. The stability constants of the complexes not containing hydroxyl were found to be: $\log K_{MA} = 7.6$, $\log K_{MA_2} = 7.1$ and $\log K_{MA_3} = 5.6$ at $25.0 \pm 0.1°C$ and in the presence of 0.10 M potassium chloride. Under the same conditions the $\log K$ for the equilibrium $[AlA_2^-]/[Al(OH)A_2^{2-}]$ $[H^+]$ was calculated to 5.0.

7-Iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) was originally proposed as analytical reagent for iron by Yoe [1]. By colorimetric methods he studied the colour formation of ferron with various metal ions and found that aluminium did not develop any colour. Swank and Mellon [2] later investigated the interaction of ferron with aluminium and ferric iron by spectrophotometric methods and reported that aluminium interfered in the ferron method for iron. They found that the interfering effect was caused by the formation of an aluminium ferron complex with a colour similar to that of ferron itself. Davenport [3] found that this complex absorbed in the ultraviolet region (absorption maximum 370 mμ), and utilized the difference of absorption maximum of the ferric iron and aluminium complexes to determine the elements simultaneously.

By colorimetry Yoe and Hall [4] investigated in more detail ferron and its reaction with ferric iron, and found evidence of only one complex pointing to a ferron metal ratio 3:1. Nortia [5] studied the interaction of ferron with a series of metal ions including ferrous and ferric iron, and deduced from pH measurements that the ferric iron complex had the ligand metal ratio 3:1. He further predicted the existence of a ferric iron complex with the ferron metal ratio 1:1 and the composition Fe(OH)A. No references were found in the literature as to the composition and stability of the complexes formed between ferron and aluminium.

Ferron is an important reagent in the simultaneous spectrophotometric determination of aluminium and iron, and in this connection it is of interest to know the composition and stability of the complexes formed. As seen above no data are available on the system aluminium ferron, while the data on the ferric iron ferron system are inconclusive. The present paper describes a redetermination of the dissociation constants of ferron and an investigation of the system aluminium ferron.

EXPERIMENTAL

Methods. The interaction of aluminium with ferron was studied by potentiometric tiration, solutions of the ligand being titrated with standard alkali in the absence of and in the presence of aluminium ions. 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 ions. The titrations were carried out at $25.0 \pm 0.1°C$. Mixing was obtained by passing a stream of nitrogen through the solutions. The hydrogen ion concentrations were obtained directly from the pH values measured.

Instruments. A Beckman Zeromatic pH meter (glass and calomel reference electrodes) was employed. The solutions to be titrated were placed in an ultrathermostat.

Reagents. Aluminium solutions were prepared from super pure metal (99.997 %) which contained the following amounts of impurities: silicon — 0.0014 %, iron — 0.0007 %, copper — 0.0008 % and zinc — 0.0002 %. The ferron (Hopkin and Williams) contained, according to the producer's specification, not less than 98.0 % of $C_9H_6O_4NSI$ and a maximum amount of 0.1 % of sulphated ash. All other chemicals were of reagent grade quality.

Standard solutions. A 5×10^{-3} M solution of ferron was prepared by dissolving 1.7556 g in boiled distilled water. Potassium chloride was added and the solution was diluted to 1 000 ml. Ferron solutions decompose slowly on standing and were therefore not used for more than one week. A 0.2 M solution of aluminium was prepared by dissolving 5.3942 g in hydrochloric acid and diluting to 1 000 ml. A 5×10^{-3} M standard solution of the metal was prepared by pipetting out 25 ml of 0.2 M solution, adding potassium chloride and diluting to 1 000 ml. A 0.09953 N solution of potassium hydroxide was used for the titrations.

ACID DISSOCIATION CONSTANTS OF FERRON

The acid dissociation constants were determined on the basis of potentiometric titrations of ferron with standard alkali. From the 5×10^{-3} M solution of ferron 50 ml were pipetted into a beaker placed in the thermostat. After thermal equilibrium was reached, a number of pH readings were plotted after the addition of small increments of base. The titration curve exhibited two distinct inflections, probably corresponding to the neutralization of the two hydrogen ions of ferron. The calculation of the dissociation constants was based on the following equilibria:

$$H_2A \rightleftharpoons H^+ + HA^-; \quad K_1 = [H^+][HA^-]/[H_2A]$$

$$HA^- \rightleftharpoons H^+ + A^{2-}; \quad K_2 = [H^+][A^{2-}]/[HA^-]$$
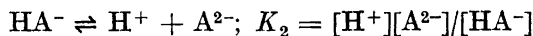
When T_A represents the total concentration of the species of ligand present and a the number of moles of base added per mole of ligand, it follows for the lower buffer region, assuming that no A^{2-} ions were present:

$$T_A = [H_2A] + [HA^-] \text{ and } aT_A + [H^+] = [HA^-] + [OH^-]$$

Table 1. Determination of first dissociation constant of ferron.

a	pH	$[H+] \times 10^3$	$T_A \times 10^3$	$K_1 \times 10^3$	pK_1
0.3	2.785	1.641	4.8450	2.901	2.537
0.4	2.855	1.396	4.8215	3.101	2.508
0.5	2.945	1.135	4.7983	3.173	2.498
0.6	3.050	0.8913	4.7752	3.286	2.483
0.7	3.190	0.6457	4.7524	3.288	2.483

Average value of $pK_1 = 2.50$ at $25.0 \pm 0.1°C$ and in the presence of 0.10 M potassium chloride.

And similarly for the upper buffer region, assuming that no H_2A was present:

$$T_A = [HA^-] + [A^{2-}] \text{ and } (a-1)T_A + [H^+]-[OH^-] = [A^{2-}]$$

Substitution and solving for K_1 and K_2 gives:

$$K_1 = \frac{[H^+] \ (aT_A + [H^+]-[OH^-])}{T_A-(aT_A + [H^+]-[OH^-])} \text{ and}$$

$$K_2 = \frac{[H^+] ((a-1)T_A + [H^+]-[OH^-])}{T_A-((a-1)T_A + [H^+]-[OH^-])}$$

Values for K_1 and K_2 were calculated for 5 different additions of base in the lower and in the upper buffer region. In Tables 1 and 2 the experimental and calculated data are given. The pH values in Tables 1 and 2 were determined graphically to the nearest 0.005 pH from a large scale plot of the titration curves.

COMPOSITION AND STABILITY CONSTANTS OF THE ALUMINIUM FERRON COMPLEXES

For the determination of composition and stability constants, solutions containing 1:1, 2:1 and 3:1 molar ratios of ligand to metal ion were titrated with standard alkali according to the method of Bjerrum [6]. From the aluminium standard solution 25 ml were pipetted into a beaker, and 25, 50, or 75 ml

Table 2. Determination of second dissociation constant of ferron.

a	pH	$[H+]$	$[OH^-]$	$T_A \times 10^3$	$K_2 \times 10^8$	pK_2
1.3	6.745	1.799×10^{-7}	5.559×10^{-8}	4.675	7.711	7.113
1.4	6.940	1.148×10^{-7}	8.710×10^{-8}	4.653	7.792	7.108
1.5	7.110	7.762×10^{-8}	1.288×10^{-7}	4.631	7.762	7.110
1.6	7.290	5.129×10^{-8}	1.950×10^{-7}	4.609	7.693	7.114
1.7	7.490	3.236×10^{-8}	3.090×10^{-7}	4.587	7.548	7.122

Average value of $pK_2 = 7.11$ at $25.0 \pm 0.1°C$ and in the presence of 0.10 M potassium chloride.
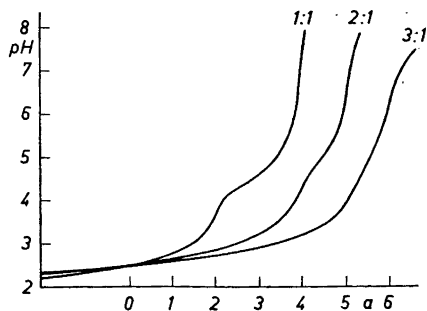
Fig. 1. Titration curves for solutions with ferron aluminium ratios 1:1, 2:1 and 3:1. a = equivalents of base added per mole of metal.
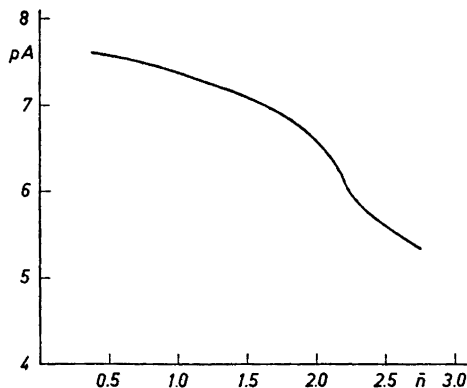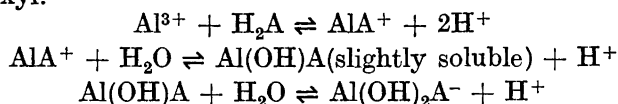
Fig. 2. Variation of degree of formation $\bar{n}$ for aluminium ferron complexes as a function of concentration of ligand pA.

of ferron standard solution were added. After thermal equilibrium was reached in the thermostat, standard alkali was added in small increments, and the corresponding pH data were recorded when constant values were obtained with the pH meter. The curves obtained by repeated titrations did not differ by more than $\pm$ 0.02 pH units. A set of curves is reproduced in Fig. 1.

The 1:1 curve. The curves obtained for equimolar amounts of ferron and aluminium showed two inflections, corresponding to the addition of two and four equivalents of alkali per mole of metal. During these titrations a precipitate also appeared after the addition of more than two equivalents of base. The precipitate disappeared again after the addition of four equivalents of alkali. The following reaction mechanism is suggested for the initial interaction of equimolar amounts of ligand and aluminium, and the later stepwise incorporation of hydroxyl:

$$Al^{3+} + H_2A \rightleftharpoons AlA^+ + 2H^+$$
$$AlA^+ + H_2O \rightleftharpoons Al(OH)A(\text{slightly soluble}) + H^+$$
$$Al(OH)A + H_2O \rightleftharpoons Al(OH)_2A^- + H^+$$

Hydroxo-complexes were thus probably not present at pH values below 3.6.

The 2:1 curve. The titration curves for solutions with ferron metal ratios 2:1 also exhibited two inflections, *viz.* after the addition of four and five equivalents of base. Precipitates were not observed during these titrations. The reactions taking place are believed to be:

$$Al^{3+} + 2H_2A \rightleftharpoons AlA_2^- + 4H^+$$
$$AlA_2^- + H_2O \rightleftharpoons Al(OH)A_2^{2-} + H^+$$
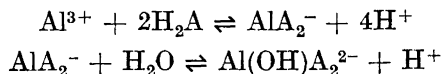
The hydroxo-complex is believed not to be formed before the addition of more than four equivalents of base, or at pH values below about 4.2.

The 3:1 curve. In these titration curves an inflection appeared after the addition of 6 equivalents of base, probably corresponding to the reaction:

$$Al^{3+} + 3H_2A \rightleftharpoons AlA_3^{3-} + 6H^+$$
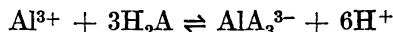
Hydroxo-complexes are probably not present in the pH range investigated.

From the inflections of the titration curves it was possible to establish graphically the starting point of the titrations in the absence of acid originating from the aluminium solution, and at the same time to determine the amount of acid added. The stability constants could then be calculated both with and without taking into account the acid originally present in the aluminium solution. The stability constants were calculated for the three complexes AlA^+, AlA_2^- and AlA_3^{3-}. The calculations were based on the 3:1 curve, but the data obtained were controlled by using the acid ranges of the two other curves in which hydroxo-complexes were not present.

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. 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. The formation function curve obtained is reproduced in Fig. 2. The stability constants calculated were: $\log K_{MA} = 7.6$, $\log K_{MA_2} = 7.1$ and $\log K_{MA_3} = 5.6$ at $25.0 \pm 0.1°C$, in the presence of 0.10 M potassium chloride and with $pK_1 = 2.50$ and $pK_2 = 7.11$ as the dissociation constants of ferron.

On the basis of the 2:1 curve, and assuming that in the interval 4 to 5 equivalents of base the reaction:

$$AlA_2^- + H_2O \rightleftharpoons Al(OH)A_2^{2-} + H^+$$

takes place, the equilibrium constant:

$$K = \frac{[AlA_2^-]}{[Al(OH)A_2^{2-}][H^+]}$$

was found to be $10^{5.0}$.

Due to the presence of a solid phase, similar data for the 1:1 complexes were not calculated.

DISCUSSION

Ferron. The two sharp inflections obtained by potentiometric titration of ferron probably corresponded to the following neutralization reactions:

The pK values of 2.50 and 7.11 may be compared with those obtained colorimetrically by Feldman and Powell[7] and potentiometrically by Näsänen and Ekman[8]. The former authors got the values 2.45 and 7.15 without indicating the ionic strength and temperature at which the measurements were made. The latter authors obtained the values 2.42 and 7.09 at a temperature of 25°C and an ionic strength of 0.1. It is further of interest to note the increasing acidity when going from 8-hydroxyquinoline (pK values determined, *e.g.*, by

Table 3. Determined and estimated stability constants of complexes of aluminium with 7-iodo-8-hydroxyquinoline-5-sulphonic acid, 8-hydroxyquinoline-5-sulphonic acid and 8-hydroxyquinoline. The estimated data are given in parenthesis.

	$\log K_1$	$\log K_2$	$\log K_3$
7-Iodo-8-hydroxyquinoline-5-sulphonic acid	7.6	7.1	5.6
8-Hydroxyquinoline-5-sulphonic acid	(10.0)	(9.5)	(8.0)
8-Hydroxyquinoline	(12.5)	(12.0)	(10.5)

Näsänen, Lumme and Mukula [9] to 5.02 and 9.81 at zero ionic strength and the temperatures 20° and 25°C, respectively), to 8-hydroxyquinoline-5-sulphonic acid (pK values determined, *e.g.*, by Richard, Gustafson and Martell [10] to 3.84 and 8.35 at 25°C and in the presence and 0.10 M potassium chloride), and to 7-iodo-8-hydroxyquinoline-5-sulphonic acid with the pK values 2.50 and 7.11.

The aluminium ferron complexes. In the literature [11] no data were found on the stability of complexes of aluminium with 8-hydroxyquinoline or its derivatives. The data published deal mainly with bivalent metals which do not form hydroxocomplexes at lower pH values.

The decreasing basicity observed when going from 8-hydroxyquinoline to 8-hydroxyquinoline-5-sulphonic acid and finally to 7-iodo-8-hydroxyquinoline-5-sulphonic acid is reflected in a correspondingly lower stability of the respective metal complexes. Richard, Gustafson and Martell [10] compared the stability constants of four bivalent metal ions with 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulphonic acid, and found the average decrease of $\log K_1 = 3.0$ and $\log K_2 = 3.2$ when going from the former to the latter ligand. On the basis of the stability constants determined in this investigation it is possible to estimate roughly the expected stability constants for the complexes of aluminium with 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulphonic acid. A $\Delta \log K$ value of about 2.5 was considered probable in these estimations. In Table 3 determined and estimated stability constants are given.

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