COMPLEXES OF IRON(III) WITH DERIVATIVES OF 8-QUINOLINOL

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MASTER OF SCIENCE

BY

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ABSTRACT

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The organic ligands 5- and 7- methyl-8-hydroxyquinoline have been synthesised and shown to form green, water soluble, 1:1 complexes with iron(III) and thus to possess the same composition as the complexes with 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline previously reported.

Thermodynamic formation constants for the 1:1 complexes of 2-, 5-, and 7-methyl-8-hydroxyquinoline with iron(III) have been determined spectrophotometrically as 5.5×10^{14}, 2.9×10^{15} and 3.6×10^{15} $mole^{-1}dm^3$ respectively at 25.0°C and $I = 0.1M$.

When compared with the value 8.5×10^{14} for 8-hydroxyquinoline itself the results support the theory that methyl substitution affects the stability of these complexes by increasing the basicity of the nitrogen atom. The lesser stability of the 2-methyl complex, however, indicates an opposing steric effect of a bulky substituent in the 2-position.

CHAPTER I

INTRODUCTION

CHAPTER II

PREPARATIVE WORK

CHAPTER I

INTRODUCTION

8-Hydroxyquinoline (HOx;Oxine) reacts with ferric ions in dilute mineral acid medium to give a soluble green complex.

The formation of this complex has been used in the indirect absorptiometric determination of magnesium [1]. An acid solution of the magnesium oxinate is treated with ferric ion, and the concentration of the green complex so formed is determined absorptiometrically. In 1949 Sandell and Spindler [2] showed that the complex had a one : one mole ratio, and determined the value of the thermodynamic formation constant, K^{T}_{FeOx} defined by

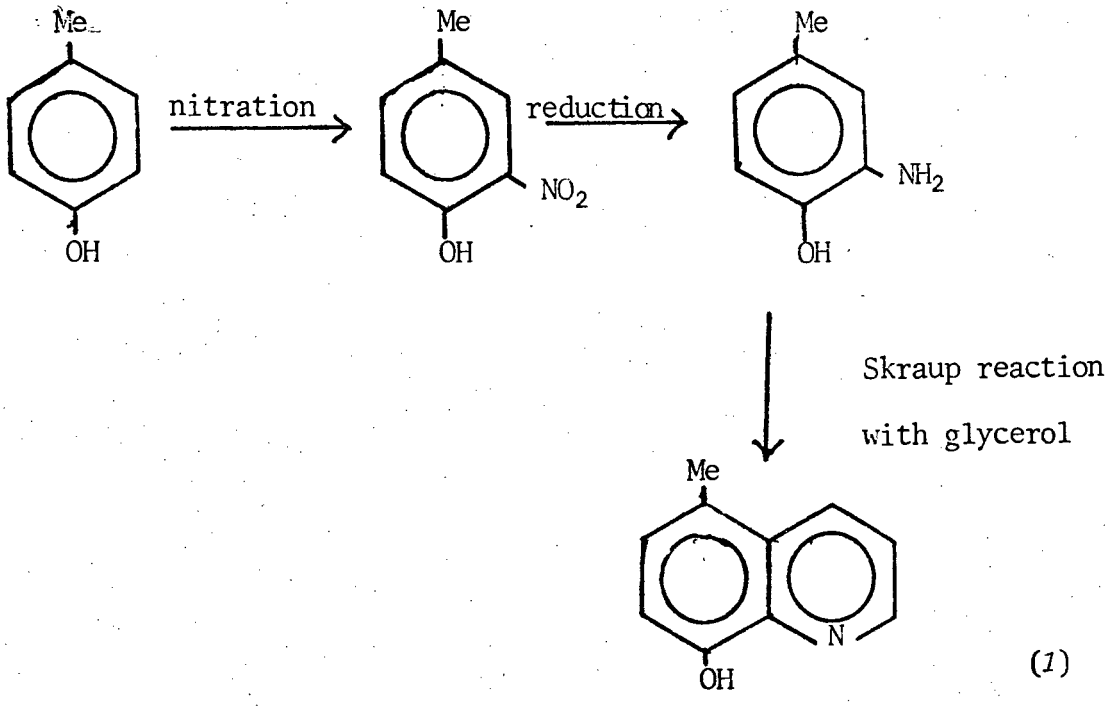
$$K^{T}_{FeOx} = \{FeOx^{2+}\} / \{Fe^{3+}\}\{Ox^{-}\} = 3.33 \times 10^{14} \qquad (1)$$

It was observed that various methyl-substituted oxines also gave green-coloured complexes, and it was clearly of interest to find the composition of these complexes, and to see how methyl substitution has affected their stability. The methyl group would be expected to increase the basicity of the nitrogen atom, which would result in an increase in the stability of the complex. There may, however, be an opposing steric effect of a methyl group in the 2-position [3].

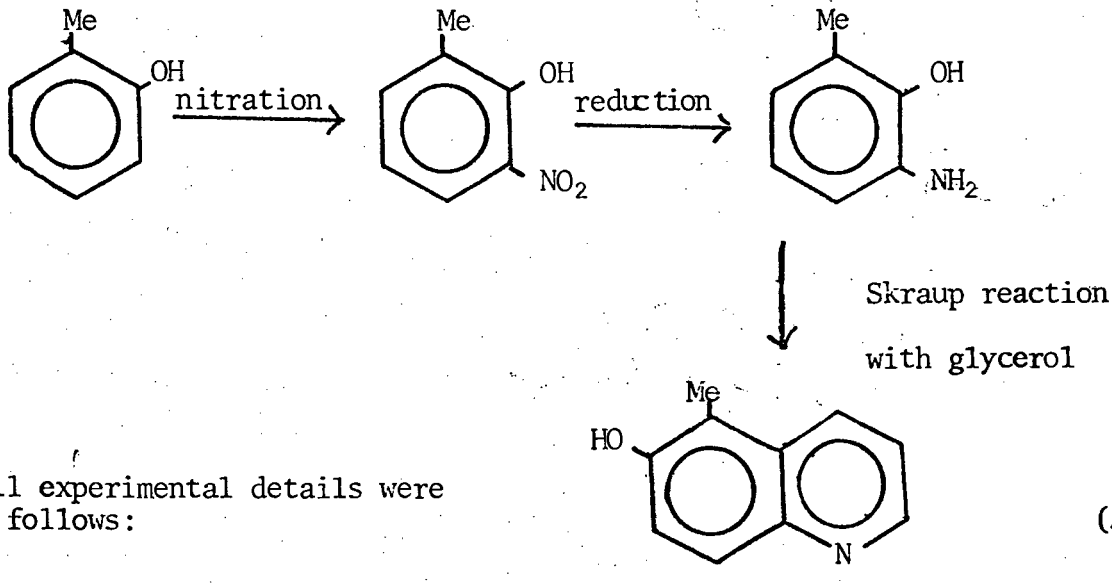
CHAPTER II

PREPARATION OF METHYL-SUBSTITUTED OXINES

A pure sample of 8-hydroxyquinaldine (2-methyl-8-hydroxyquinoline) was available in the laboratory, but to investigate complex formation between Fe(III) and ligands where steric effects would not operate, 5-methyl-8-hydroxyquinoline (*1*) and 7-methyl-8-hydroxyquinoline (*2*) were prepared by the following series of reactions:



(*1*)



(*2*)

Full experimental details were as follows:

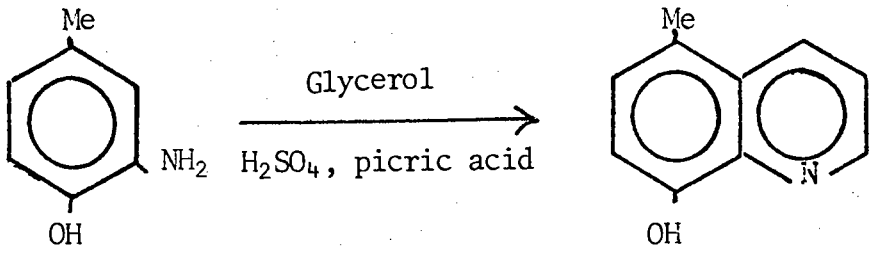
A. Preparation of 5-Methyl-8-hydroxyquinoline

(i) Preparation of *o*-Nitro-*p*-cresol. *p*-Cresol (200 g) was dissolved in benzene (400 g). To this solution was added over 1-1½ h a mixture of concentrated HNO_3 (200 ml) and water (300 ml). The reaction mixture was stirred continuously and its temperature kept below 20°C. As the reaction proceeded the solution became a dark red-brown colour. Finally the solution was transferred to a separating funnel and the lower nitric acid layer run off. The benzene solution was then steam distilled. The benzene came over first and, as it contained only small quantities of the nitro-compound, it was discarded. The desired compound eventually collected as a brilliant yellow solid which was filtered off and dried. (Yield 94.7 g, 33.2%)

(ii) Reduction of *o*-nitro-*p*-cresol. The nitro-compound (94.7 g) and ethanol (140 ml) together with some Raney nickel were placed in a pressure bottle. While the bottle was agitated hydrogen gas was led in for 48 hours. The apparatus was not adapted to show the amount of hydrogen absorbed, and so thin layer chromatograms were run at intervals; after 48 hours most of the nitro-compound had been reduced. At this stage the reduction was stopped and it was hoped that any nitro-compound still remaining in the mixture could be used as an oxidant in the subsequent Skraup reaction.

While being cooled some of the base had crystallized out and a small amount of ether was added to redissolve it. The Raney nickel was filtered off on a sintered glass filter and the filtrate divided into three portions which were worked up separately. Alcohol and ether were evaporated off using a Buchi rotary evaporator and the crude base collected.

(iii) The Skraup Reaction



This reaction was carried out on the crude base in the same flask in which it had been isolated. With the first portion of base, the condensation reaction was carried out without the addition of picric acid, in the hope that there was enough nitro-compound available in the crude mixture to act as an oxidant and give a good yield of the desired product. Although the yield was good, it was improved when picric acid was added in a second preparation.

To the base was added glycerol (46 g), dry picric acid (4 g) and concentrated H_2SO_4 (40 g). The reaction flask, to which was attached a long air condenser, was warmed to initiate the reaction after which the contents were heated gently under reflux for 3½ hours. The reaction mixture, after being cooled and diluted with water, was first made just alkaline with strong sodium hydroxide solution.

Glacial acetic acid was next added in excess and the whole was then steam distilled. The yellow distillate was made neutral with 2N-ammonia and the precipitated 5-methyl-8-hydroxyquinoline was filtered off and dried. Different batches of the product were white, colourless and grey and melted over the range 117-120°C. The combined product was recrystallised 3 times from ethanol (and animal charcoal) to give a crop of colourless crystals (12.9 g) mp 121-123°C. The literature value is 122-4°C. [4].

B. Preparation of 7-Methyl-8-hydroxyquinoline

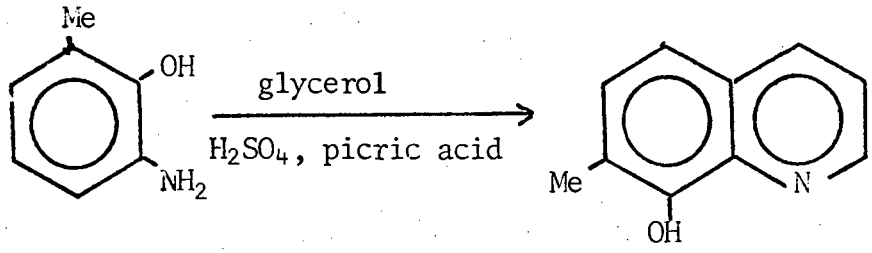
(i) Preparation of 3- and 5-nitro-*o*-cresols [5, 6]. A mixture of concentrated nitric acid (107 ml) and glacial acetic acid (300 ml) was stirred in a freezing mixture at -15°C while a mixture of *o*-cresol (100 g) and glacial acetic acid (100 ml) was added in the course of 2 hours when a thick magma of crystals separated. After standing for 2 hours in the freezing mixture, the whole was poured into water (5 litre). The crystals which separated were collected and submitted to steam distillation.

Crude 3-nitro-*o*-cresol containing a small proportion of 3,5-dinitro-*o*-cresol distilled first and was collected, filtered and submitted to steam distillation again. 5-nitro-*o*-cresol with a little 3,5-dinitro-*o*-cresol then remained in the flask as an oil. The crude distillate was steam distilled and the various fractions (200 ml) were collected and after being dried their melting points were taken.

The first fractions gave deposits of deep yellow plates of nearly pure 3-nitro-*o*-cresol (49 g; 34%; 63.65°C), the last gave pure 3, 5-dinitro-*o*-cresol in well-defined colourless prisms [5,6].

(ii) Reduction of the nitro compound. The nitro-compound (46.1 g) and ethanol (300 ml) together with some Raney nickel were placed in a pressure bottle. While this was continuously shaken hydrogen gas was led in until no more was absorbed. A small amount of ether was added to dissolve the base which had crystallized out in the bottle on cooling. After filtering off the Raney nickel, the alcohol and ether were removed by evaporation under reduced pressure, and the crude base isolated.

(iii) The Skraup Reaction [4]



This reaction was carried in the same flask in which the base had been isolated in order to reduce losses involved in transference to another vessel. To the base was added glycerol (109.7 g, 87 ml), dry picric acid (9.53 g) and concentrated sulphuric acid (95.3 g) The reaction flask, to which was attached a long air condenser, was warmed to initiate the reaction, and then the contents were heated gently under reflux for 3½ hours. After being cooled and diluted with water the reaction mixture was first made just alkaline with strong sodium hydroxide solution and then just acid with glacial acetic acid. It was then steam distilled until ammonium hydroxide no longer produced a precipitate when added to the distillate. The combined yellow coloured distillate was neutralised with 5*M*-ammonia and the precipitated 7-methyl-8-hydroxyquinoline was collected and dried. Recrystallisation from ethanol (containing animal charcoal) gave a pure white solid (17.9 g; 37.3%; m.p. 64-66°C).

CHAPTER III

THE SOLUBLE COMPLEX OF 5-METHYLOXINE AND FERRIC ION

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THE SOLUBLE COMPLEX OF 5-METHYLOXINE AND FERRIC ION

Preliminary experiments were performed on the complex formation between 5-methyl-8-hydroxyquinoline and ferric ions to investigate the effects of pH, ionic strength, and any change of absorbance with time. The first of these experiments involved the investigation of the absorption spectrum of the complex. Since ferric ion forms complexes with halide ions and with carboxylic acids, ferric perchlorate was used for the standard solution.

Equal volumes (10 ml) of $7.525 \times 10^{-4} M$ iron perchlorate and $7.525 \times 10^{-4} M$ 5-methyloxine were mixed. The addition of 10 ml of $Fe(ClO_4)_3$ produced no change in the pale yellow colour. Presumably the acid produced by the hydrolysis of the iron(III) salt was sufficient to drive the following equilibrium to the left:

$$Fe^{3+} + nHL \rightleftarrows FeL_n^{3-n} + nH^+ \qquad (2)$$

On adding dilute ammonium hydroxide dropwise, each drop first produced a dark green-black suspension, which dissolved on shaking and the colour darkened slightly. At a particular stage, a green colour was noticed, but one more drop of alkali changed the colour to a brown-green and a permanent precipitate formed.

From this was deduced that the subsequent experiments would have to be carried out in a restricted range of acidity. If the solution was too acidic, very little green complex would be formed : if the solution was too alkaline, extensive hydrolysis of ferric ion would occur. Buffer solutions could not be used in the adjustment of the pH because of the formation of complexes between ferric ion and the respective anions, such as acetate and phthalate .

(i) Effect of pH

A 1:1 mixture of $7.525 \times 10^{-4} M$ iron perchlorate and $7.525 \times 10^{-4} M$ 5-methyloxine (20 ml) was placed in a 25 ml volumetric flask. Varying volumes of 0.343*M* ammonium hydroxide were added and the volume was made up to 25 ml with glass distilled water. The absorption spectra of such solutions were then measured in the visible region using a Varian Superscan 3 Ultraviolet-Visible Spectrophotometer using 4 cm matched quartz cells. The results are shown in Figure 1. Two peaks were observed for each complex with maximum wavelengths, (λ_{max}) at 670 nm and 470 nm respectively. Both peaks were very broad but since the ratio of the absorbancies at the two maxima remained substantially constant (0.795 ± 6%), it was concluded that only one species was present, absorbing at both wavelengths. The absorbance rose to a maximum as the pH was increased from 1.13 to 3.02. Precipitation occurred with the addition of a few more drops of alkali.

Individual spectra of the two reagents, $Fe(ClO_4)_3$ and 5-methyloxine, determined over the range 400-800 nm with an expanded scale (0-0.5) showed that the absorbancy of both Fe^{3+} and the ligand were negligible at the wavelength of maximum absorption, 670 nm. Actual measured absorbancies of the green complex could, therefore, be used without correction for the method of continuous variations (Job curves).

(ii) Change of absorbance with time

It was observed that the green solutions took a certain period of time to reach their maximum colour intensity, after which the colour began to fade. Absorbance readings were taken immediately after mixing the components and at intervals over a period of about three and a half hours. From the plot of absorbance against time (Figure 2), it appeared that the maximum

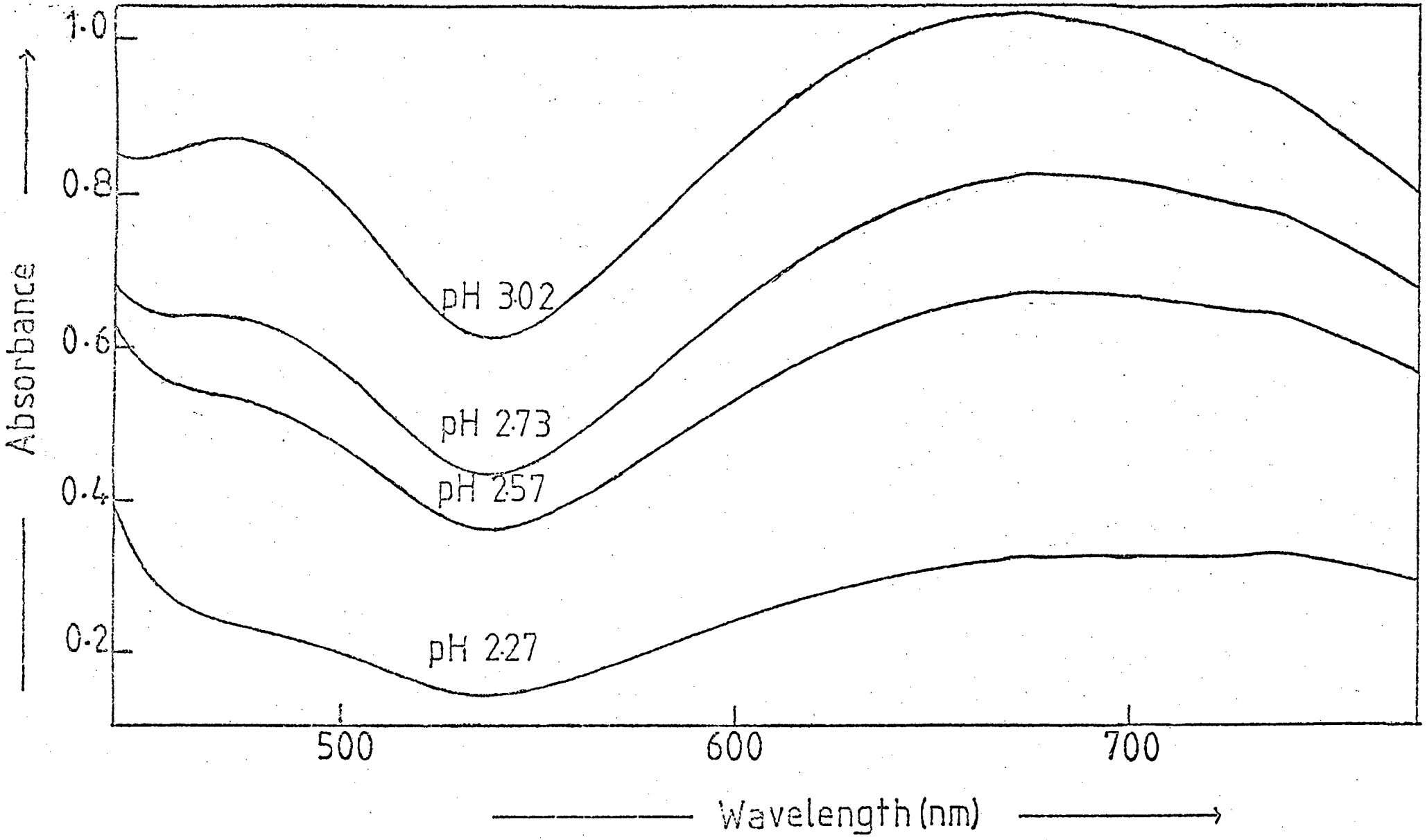

FIGURE 1 : Absorption spectra of 1:1 mixtures of 5-methyl-8-hydroxyquinoline and $Fe(ClO_4)_3$ as pH is increased from 2.27 to 3.02

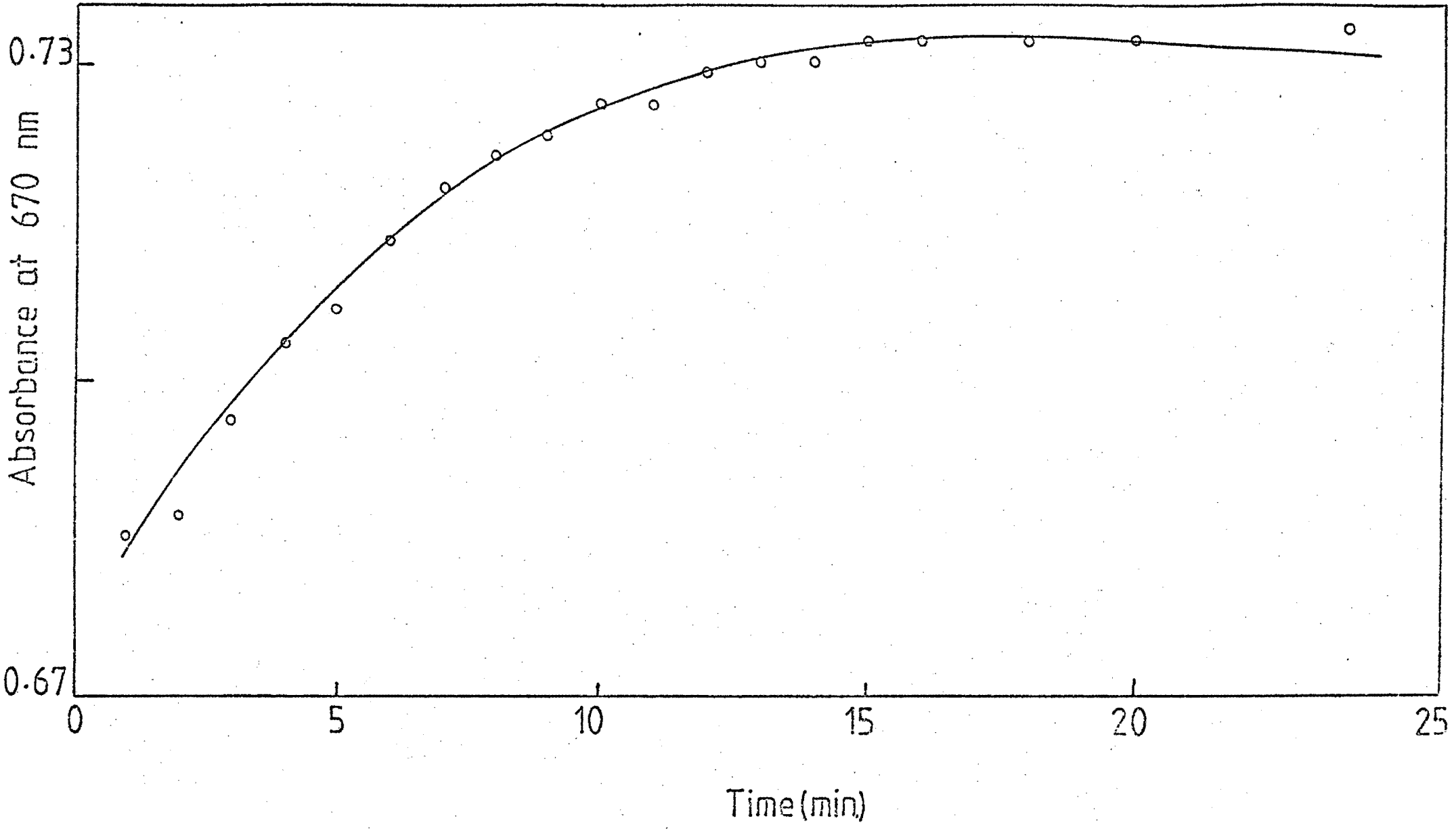

FIGURE 2 : Plot of change in absorbance with time of 1:1 mixture of ∿ 8.01 x 10^{-4}M solutions of 5-methyl-8-hydroxyquinoline and $Fe(ClO_4)_3$.

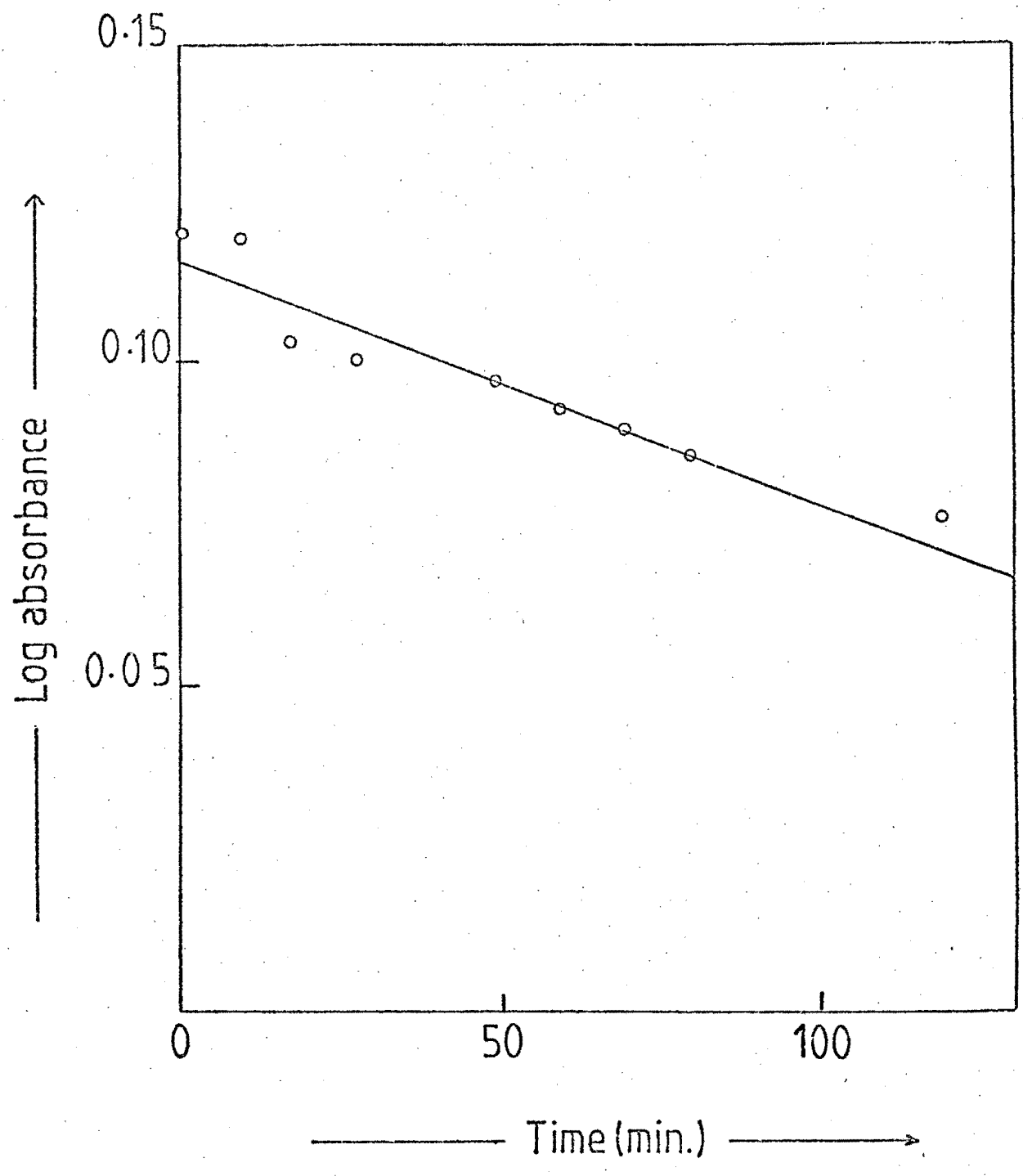

FIGURE 3 : Plot of the log of absorbance at 670 nm against time of the 1:1 mixture of 5-methyl-8-hydroxyquinoline and $Fe(ClO_4)_3$ after reaching maximum colour intensity.

colour was attained approximately twenty minutes after mixing. Thereafter decomposition appeared to follow first order kinetics over the first two-hour period (Figure 3). The rate of decomposition was 3.9×10^{-4} absorbance units per minute over this period. Thus over the brief time required to take a reading decomposition could be regarded as negligible. All subsequent readings were taken twenty minutes after mixing. Similar plots of absorbance against time were made for complexes of each of the methyl homologues of 8-hydroxyquinoline as well as for that of 8-hydroxyquinoline itself. The green complexes were found to behave similarly and to be relatively stable. The complex formed by 2-methyloxine was exceptional in that the green colour began to disappear almost immediately after mixing.

(iii) Effect of changing the ionic strength.

7.025 g (0.5 mole) of sodium perchlorate was added to 100 ml of a 1 : 1 mixture of iron(III) and 5-methyloxine. As expected, the pH and absorbance of the mixture were both altered greatly by the change in ionic strength, confirming that it would thus be necessary to maintain this constant throughout all the subsequent experiments This could be achieved by making up all solutions in perchloric acid of a constant, known strength, and by the appropriate addition of sodium perchlorate.

CHAPTER IV

JOB CURVES

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In the method of continuous variations (Job's method) [7,8] the absorbance of mixtures of two components A and B each of identically the same concentration, C, is measured at a suitable fixed wavelength, the mole fraction, x of one component being varied from 0 to 1 as that of the other is reduced from 1 to 0. It can be shown that if a complex AB_n is formed the maximum absorbance is attained when $x = 1/(n + 1)$.

Clearly each Job curve must refer to a fixed, known pH. One would, at first glance, imagine that the simplest means of controlling pH would be to adjust the pH of the two reagents before mixing. However, on mixing, there is a release of hydrogen ions due to complex formation (see equation 2), so causing a change in pH. The extent of this will vary with each different ratio of iron to reagent and with the value of C. Since it is impossible to bring all solutions to exactly the same pH, and also to retain the same total concentration, C, a novel method of interpolation had to be used.

Method in Interpolation

For each concentration ratio, $[Fe^{3+}]/([Fe^{3+}] + [HL])$ a number of absorbance measurements were made at λ_{max} 670 nm at gradually increasing alkalinities produced by adding increasing small amounts of 0.343*M* ammonia. The ionic strength of the ammonia was kept constant at 0.1138 by addition of sodium perchlorate. Because of the small buffering capacity of these solutions, the exact pH could not be predicted and had to be measured immediately after the determination of the absorbance. pH measurements were made with a PHM62 Standard pH-Meter. By this means a family of curves was obtained at the maximum wavelength of absorbance and when colour development

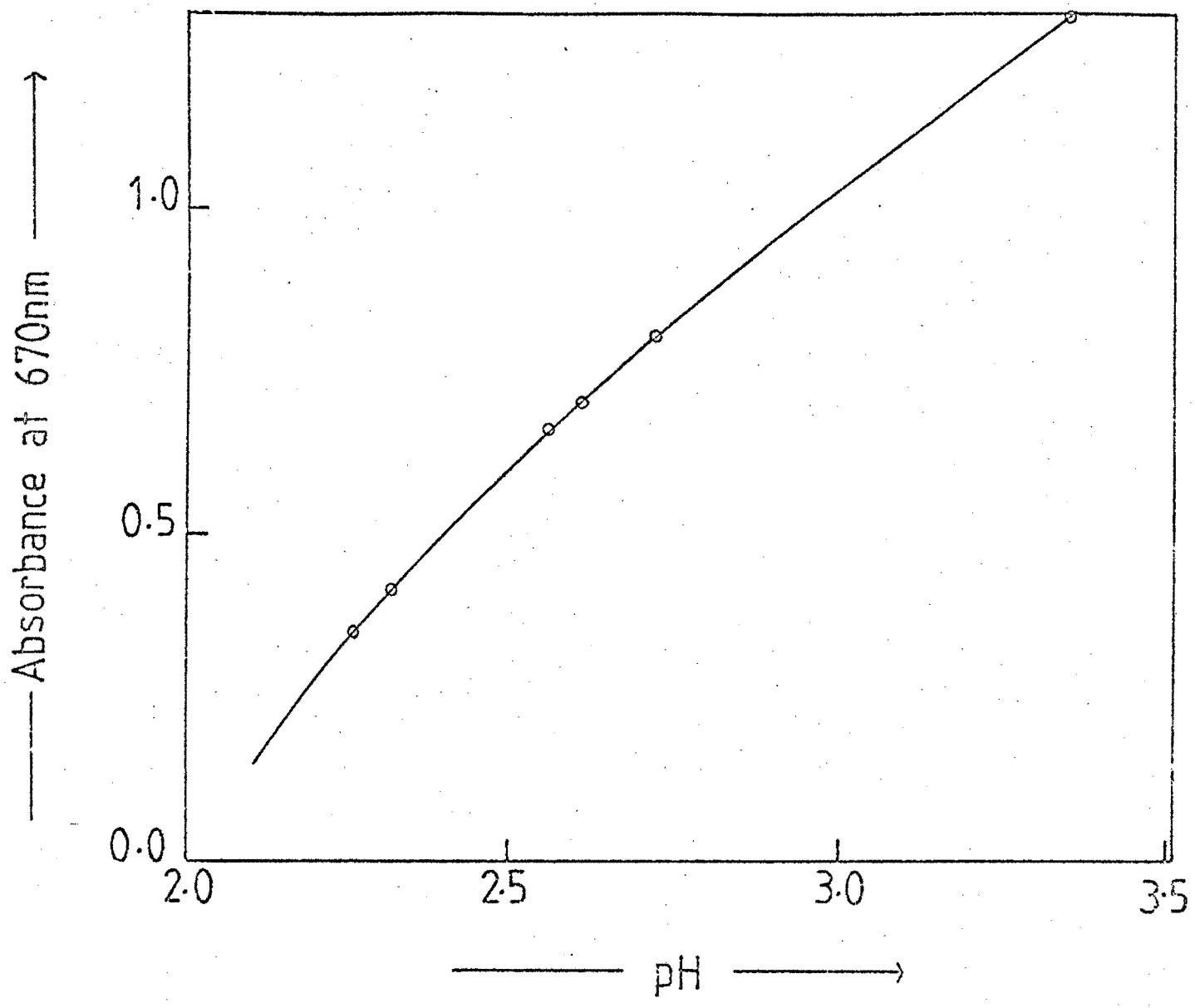
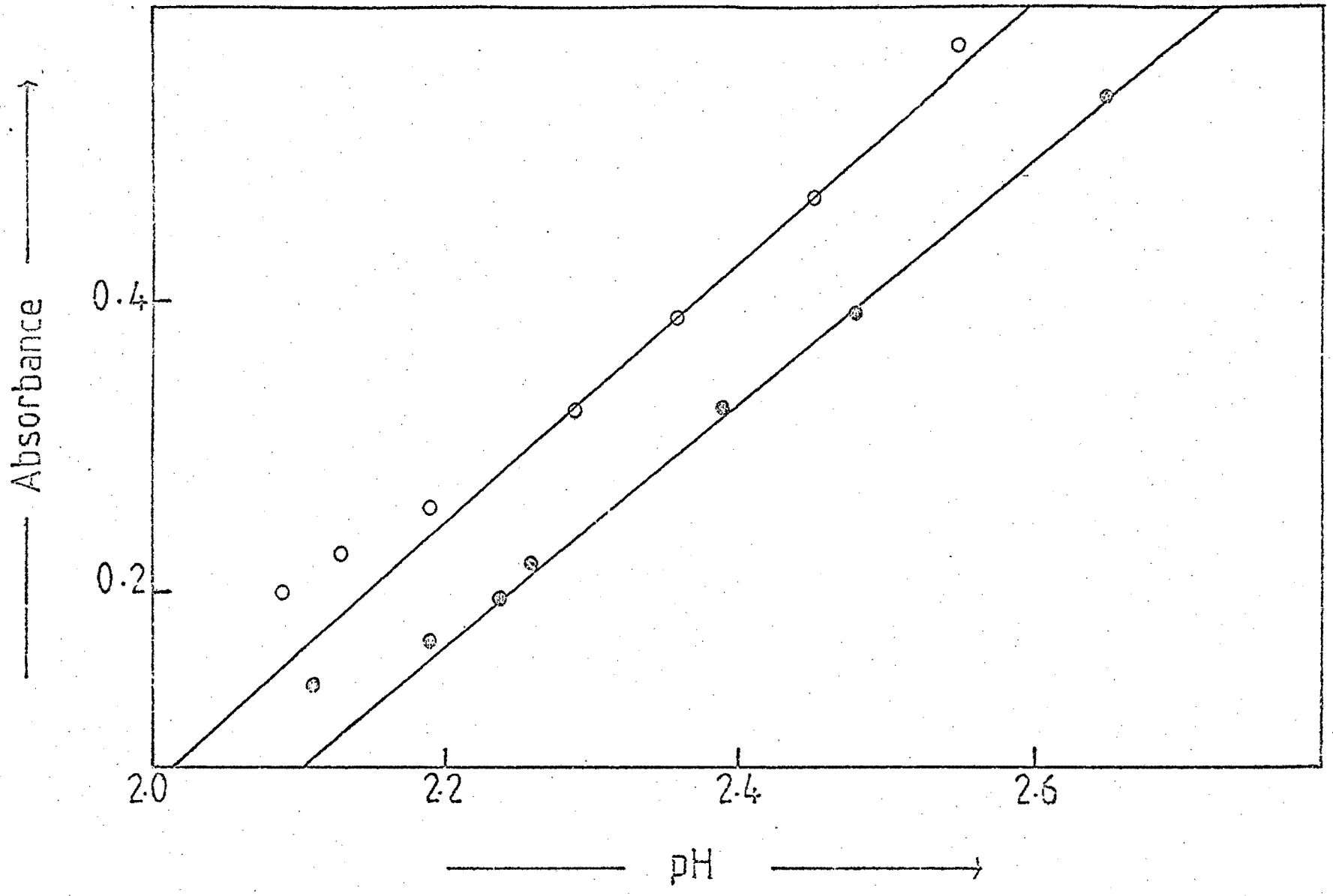


FIGURE 4 : Plot of absorbance at 670 nm measured 20 minutes after mixing against pH for a 1:1 mixture of $\sim 8.01 \times 10^{-4}$ solutions of 5-methyl-8-hydroxy-quinoline and $Fe(ClO_4)_3$.



○ $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.6$ ◎ $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.2$

FIGURE 5 : Plot of variation of absorbance at 670 nm with pH for 2 different ratios of $[Fe^{3+}]/([Fe^{3+}] + [HL])$. (To avoid confusion only 2 sets are shown).

no longer increased : one curve for each molar ratio of iron to ligand thus relating the variation in absorbance to pH. An example of one of these curves is shown in Figure 4, and the appearance of other such sets is shown in Figure 5.

From these curves it was a simple matter to interpolate the absorbancies corresponding to any arbitrarily chosen pH for each mixture of reagents of known molar ratio, thereby providing the required data for a series of Job's curves. (See Table 1). The complete set of results for all these measurements are given in Tables 2-8 in the experimental section. Two such Job's curves for pH 2.14 and 2.54 are shown in Figure 6.

In each case a maximum was attained for the mole fraction 0.5. This proved conclusively that the complex formed had the 1 : 1 composition corresponding to the formula Fe(5-methyloxine)$^{2+}$ If the formula of the complex had been Fe(5-methyloxine)$_2^+$ the maximum of the curve would have come at the mole ratio 0.33. This was obviously not the case.

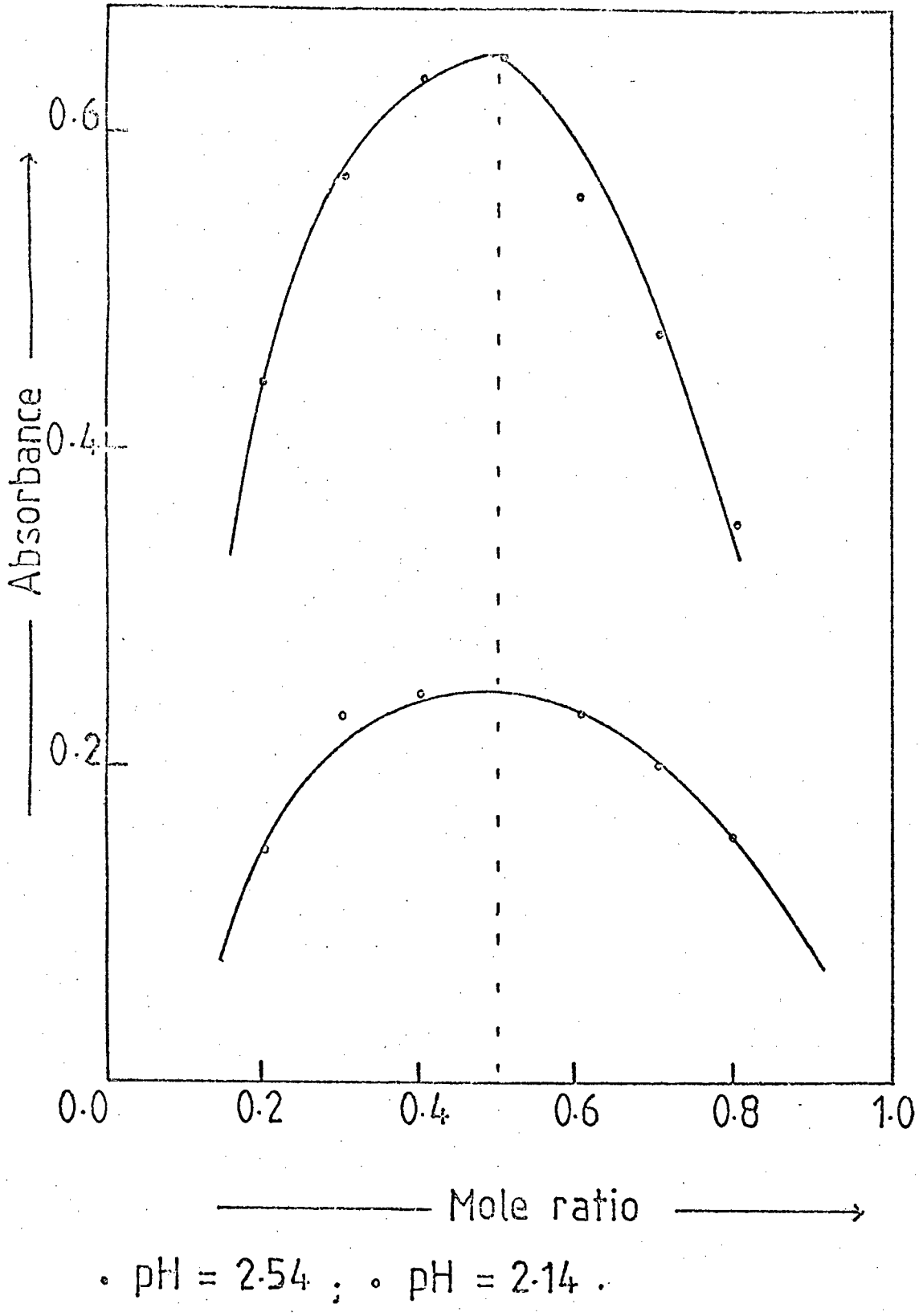


FIGURE 6 : Job curves plotting absorbance against mole fraction for mixtures of 5-methyl-8-hydroxyquinoline and $Fe(ClO_4)_3$ at pH 2.54 and 2.14 respectively.

EXPERIMENTAL

Solutions of iron perchlorate ($8.0119 \times 10^{-4} M$) and 5-methyl-8-hydroxyquinoline ($8.0119 \times 10^{-4} M$) were mixed in varying proportions to a total volume of 20 ml. The amounts of ammonia shown in the tables were introduced with a pipette, and the solutions were made up to 25 ml with glass distilled water. Absorbance measurements were taken in a 4 cm quartz cell at 670 nm twenty minutes after initial mixing and the pH was measured afterwards. Each of the following tables refers to a particular value of the ratio $[Fe^{3+}] / ([Fe^{3+}] + [HL])$.

TABLE 1 : INTERPOLATED VALUES OF ABSORBANCE FOR DIFFERENT MOLE RATIOS, $[Fe^{3+}] / ([Fe^{3+}] + [HL])$, FOR pH = 2.14 AND 2.54

x = mole ratio
A = absorbance (using 4 cm cells)

pH = 2.14

x	A
0.2	0.148
0.3	0.232
0.4	0.245
0.5	0.256
0.6	0.232
0.7	0.202
0.8	0.156

pH = 2.54

x	A
0.2	0.441
0.3	0.572
0.4	0.633
0.5	0.646
0.6	0.560
0.7	0.474
0.8	0.353

TABLES 2 - 8 : EXPERIMENTAL RESULTS FOR DIFFERENT VALUES OF THE MOLAR RATIO $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.2$

TABLE 2 : $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.2$

16 ml of ligand solution:
4 ml of Fe^{3+} solution

Volume of ammonia added / ml.	Absorbance	pH
3.60	0.536	2.65
3.55	0.391	2.48
3.50	0.324	2.39
3.45	0.218	2.26
3.40	0.195	2.24
3.35	0.166	2.19
3.30	0.137	2.11

TABLE 3 : $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.3$

14 ml of ligand solution
6 ml of Fe^{3} solution

Volume of ammonia added / ml	Absorbance	pH
3.60	0.703	2.66
3.55	0.553	2.52
3.50	0.472	2.43
3.45	0.303	2.26
3.40	0.278	2.22
3.30	0.207	2.07

TABLE 4 : $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.4$

12 ml of ligand solution:
8 ml of Fe^{3+} solution.

Volume of ammonia added / ml	Absorbance	pH
3.60	0.658	2.56
3.55	0.515	2.44
3.50	0.394	2.32
3.45	0.310	2.24
3.35	0.227	2.11
3.30	0.194	2.07

TABLE 5 : $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.5$

10 ml of ligand solution:
10 ml of Fe^{3+} solution

Volume of ammonia added / ml.	Absorbance	pH
3.60	0.646	2.54
3.55	0.563	2.46
3.50	0.385	2.33
3.45	0.334	2.44
3.40	0.279	2.19

TABLE 6 : $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.6$

8 ml of ligand solution:
12 ml of Fe^{3+} solution

Volume of ammonia added / ml.	Absorbance	pH
3.60	0.574	2.55
3.55	0.471	2.45
3.50	0.386	2.36
3.45	0.324	2.29
3.40	0.258	2.19
3.35	0.227	2.13
3.30	0.199	2.09

TABLE 7 : $[Fe^{3+}]/([Fe^{3+}] + [HL] = 0.7$

6 ml of ligand solution:
14 ml of Fe^{3+} solution

Volume of ammonia added / ml.	Absorbance	pH
3.60	0.484	2.55
3.55	0.362	2.39
3.50	0.318	2.33
3.45	0.261	2.25
3.40	0.226	2.18
3.35	0.198	2.13
3.30	0.160	2.08

TABLE 8 : $[Fe^{3+}]/([Fe^{3+}] + [HL]) = 0.8$

4 ml if ligand solution:
16 ml of Fe^{3+} solution

Volume of ammonia added / ml.	Absorbance	pH
3.60	0.315	2.48
3.55	0.282	2.43
3.50	0.237	2.31
3.45	0.195	2.24
3.40	0.164	2.18
3.35	0.144	2.13
3.30	0.119	2.06

CHAPTER V

THE FIRST AND SECOND THERMODYNAMIC DISSOCIATION CONSTANTS OF THE LIGAND ACID

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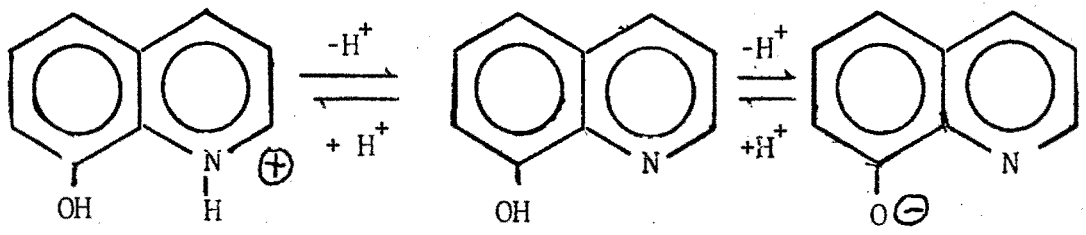
THE FIRST AND SECOND THERMODYNAMIC DISSOCIATION CONSTANTS OF THE LIGAND ACID.

In order to calculate values of $\{Ox^-\}$ needed for substitution in equation (1) it is necessary to determine the first and second acid dissociation constants of the ligand acid H_2Ox^+

In the equilibria



(H_2Ox^+) (HOx) (Ox^-)

or

$$H_2Ox^+ \underset{}{\overset{K^T_{1,Ox}}{\rightleftharpoons}} HOx \overset{K^T_{2,Ox}}{\rightleftharpoons} Ox^-$$

we define

$$K^T_{1,Ox} = \frac{\{H^+\}\{HOx\}}{\{H_2Ox^+\}} = \frac{(aH^+)\,[HOx]f_0}{[H_2Ox^+]f_1} \qquad (3)$$

and

$$K^T_{2,Ox} = \frac{\{H^+\}\{Ox^-\}}{\{HOx\}} = \frac{(aH^+[Ox^-]f_1}{[HOx]f_0} \qquad (4)$$

where (aH^+) is the hydrogen-ion activity as given directly from pH readings. Here HOx is taken to represent 8-hydroxyquinoline itself or any one of its methyl-substituted homologues.

From (3) and (4) it follows that

$$pH \equiv p(aH^+) = pK^T_{1,Ox} + \log \frac{[HOx]f_0}{[H_2Ox^+]f_1} \qquad (5)$$

and $$pH \equiv p(aH^+) = pK^T_{2,Ox} + \log \frac{[Ox^-]}{[HOx]f_0} \qquad (6)$$

Here the activity coefficients f_0 and f_1 refer respectively to the uncharged ligand HOx or to the singly charged species H_2Ox^+ or Ox^-, the same value being adopted for simplicity's sake for each ion.

Two different techniques were used to obtain the two acid dissociation constants; one based on titrimetry (A), the second on spectrophotometric observations (B).

A.1. pH TITRATIONS AT CONSTANT TEMPERATURE

The procedure is to titrate a saturated solution of a methyl-substituted oxine containing excess of the formally uncharged solid, HOx, with (a) standard hydrochloric acid and (b) standard carbon-dioxide-free sodium hydroxide following the changes in pH as the solid gradually dissolves as H_2Ox^+ or Ox^- respectively. The temperature is maintained constant at 25.0°C with a thermostat. Knowing the values of the activity coefficients f_0 and f_1 (q.v.) it is possible to calculate $pK^T_{1,Ox}$ from equation (5) if the values of [HOx] and $[H_2Ox^+]$ are available. The latter term is

assumed to be equivalent to the concentration of acid added and [HOx] will be constant throughout and equal to the solubility of the formally uncharged ligand acid - since the solution remains saturated throughout.

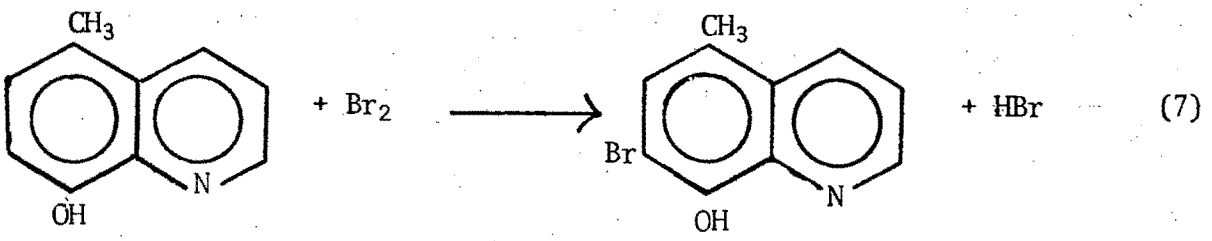
Similar $pK^{T}_{2,Ox}$ follows from equation (6) and a knowledge of the magnitude of $[Ox^{-}]$ which is taken to be equal to the concentration of alkali added.

The first step is therefore to determine the solubility of the uncharged species [HOx] at the temperature of measurement.

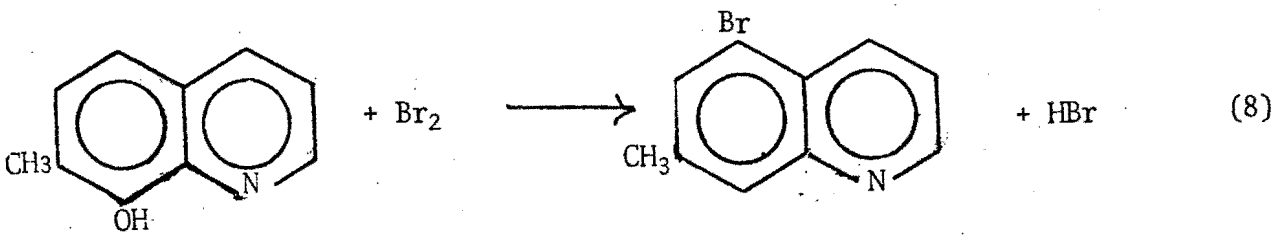
A.2. DETERMINATION OF SOLUBILITIES

The solubilities in water of 2-, 5-, and 7-methyl-8-hydroxyquinolines were determined by the analysis of saturated aqueous solutions. This was to be carried out by bromination (by bromate in the presence of excess bromide), a method previously used for the determination of oxine itself and a number of its metal complexes, notably aluminium tris-oxinate, $Al(Ox)_3$.

It was first necessary to determine in what way each of the methyl-substituted oxines would react with bromine and to establish whether the bromination is quantitative. Titrations on solutions of pure 5- and 7-methyl-8-hydroxyquinoline of accurately known concentration showed that one bromine atom entered the 7- (or 5-) position respectively and that the following reactions were stoichieometric:-

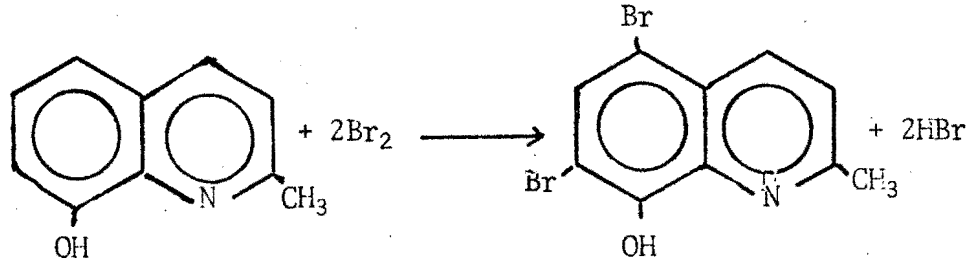


(7)



(8)

In the case of 2-methyloxine however two bromine atoms entered in the 5- and 7-positions to give the known 5,7-dibromo-8-hydroxyquinoline as follows:-



(9)

The above modes of bromination were assumed in calculating the concentrations of portions of solutions saturated at 25°C as fully described in the experimental section. The results are shown in Table 9.

TABLE 9. MOLAR SOLUBILITIES AT 23°C OF METHYL SUBSTITUTED 8-HYDROXYQUINOLINES

Derivative	Solubility/mole dm^{-3}
2-Methyl-8-hydroxyquinoline	$2.60 \pm 0.03 \times 10^{-3}$
5-Methyl-8-hydroxyquinoline	$3.70 \pm 0.006 \times 10^{-3}$
7-Methyl-8-hydroxyquinoline	$3.80 \pm 0.03 \times 10^{-3}$

A.3. CALCULATION OF ACTIVITY COEFFICIENTS

In order to calculate thermodynamic acid dissociation constants according to equations (5) and (6) the relevant activity coefficients are needed. Sufficiently precise values could be obtained from the approximate equation

$$-\log f_1 = A\sqrt{I}/(1 + aB\sqrt{I})$$

$$\cong 0.5\sqrt{I}/(1 + \sqrt{I})$$

where I is the ionic strength, A = 0.509 in water at 25°C, B = 3.3×10^7 and a the effective diameter of the ions H_2Ox^+ and Ox^- which has been estimated as 3×10^{-8}.

The ionic strength can only be calculated from the definition $I = 0.5\ \Sigma\ cz^2$ if the concentration, c, and the ionic charge, z, of each species is known. In a saturated solution of the uncharged oxine, HOx there will be H_2Ox^+ and Ox^- in equilibrium but the total analytical concentration

$$c_{tot} = [HOx]\left\{\frac{(aH^+)f_0}{K^T_{1,Ox}f_1} + 1 + \frac{K^T_{2,Ox}f_0}{(aH^+)f_1}\right\} \qquad (10)$$

At the isoelectric point $[H_2Ox^+] = [Ox^-]$ and using the values $pK^T_{1,Ox} = 5.5$ and $pK^T_{2,Ox} = 10.95$ subsequently calculated for 2-methyl-8-hydroxyquinoline it is easy to show that $pH = \frac{1}{2}(pK^T_1 + pK^T_2) = 8.23$. In the very dilute solution of ions existing in a saturated solution of HOx it is reasonable to assume that f_0 and f_1 are $\cong 1$.

Then $$c_{tot} = [HOx]\left\{\frac{10^{-8.23}}{10^{-5.5}} + 1 + \frac{10^{-10.95}}{10^{-8.23}}\right\}$$

$$= 1.004[HOx] \qquad (11)$$

which means that less than 0.5% of the dissolved oxine will be present as ions and it will be easy to calculate the value of [HOx] from the titrimetrically determined value of c_{tot}.

It follows that the contributions of the ions H_2Ox^+ and Ox^- to the ionic strength will be negligibly small. In the actual titrations with HCl (or NaOH) the ionic strength will be essentially due to the ions H_2Ox^+ and Cl^- (or Ox^- and Na^+) and hence readily computed. It was shown that throughout the range of pH values used in the titrations (*q.v.*) ionic contributions arising from the solubility of undissociated oxine (equation 10) were negligible.

For an uncharged species $\log f_0 = kI$ where k is some small constant. Since I never exceeded 0.2 M it was shown that $f_0 \cong 1$.

A.4. EXPERIMENTAL. pH TITRATIONS

All titrations were carried out in a cell containing a glass electrode and a calomel reference electrode. The cell was thermostatted at 25.0°C and an atmosphere of nitrogen gas was maintained above the solution at all times to prevent the ingress of carbon dioxide.

(i) 5-Methyl-8-hydroxyquinoline. 5-Methyloxine (0.0985 g; excess) was added to 20 ml of boiled-out distilled water in the titration cell and a saturated solution was prepared by successive warming and cooling and finally allowing the solution to equilibrate at 25°C for several hours. The pH-meter was standardised against a buffer of pH 4.01 at 25°C.

Titration was carried out with 0.1761*M* hydrochloric acid, and after each addition the contents were thoroughly mixed until the pH reading was constant.

An exactly similar procedure was adopted for a titration with 0.1050*M* carbonate-free sodium hydroxide but in this case the PHM64 pH-meter was standardised against a buffer of pH 9.18 at 25°C. The results are shown in the following Tables.

TABLE 10. PH READINGS FOR TITRATION OF 0.0985 g 5-METHYL-8-HYDROXYQUINOLINE WITH 0.1761*M* HCl AT 25°C

Observation	Volume of HCl/ml	pH	Observation	Volume of HCl/ml	pH
1	0.00	6.04	11	1.55	3.59
2	0.02	5.70	12	1.60	3.57
3	0.05	5.70	13	2.00	3.48
4	0.10	4.91	14	2.30	3.42
5	0.15	4.63	15	2.80	3.35
6	0.20	4.46	16	3.30	3.09
7	0.30	4.25	17	3.50	2.78
8	0.60	3.92	18	3.70	2.57
9	1.00	3.69	19	3.80	2.50
10	1.50	3.63			

TABLE 11. pH READINGS FOR TITRATION OF 0.0901 g 5-METHYL-8-HYDROXYQUINOLINE WITH 0.1050*M* NaOH AT 25°C.

Observation	Volume of HCL/ml	pH	Observation	Volume of HCl/ml	pH
20	0.00	6.31	28	2.45	11.60
21	0.05	9.59	29	3.45	11.73
22	0.10	10.21	30	4.65	11.81
23	0.15	10.35	31	5.85	11.90
24	0.25	10.64	32	7.15	11.96
25	0.40	10.85	33	8.35	12.01
26	0.65	11.09	34	9.55	12.05
27	1.45	11.38	35	10.22	12.06

An identical procedure was adopted with (ii) 2-methyl-8-hydroxyquinoline and (iii) 7-methyl-8-hydroxyquinoline giving the results summarised in Tables 12, 13, 14 and 15.

(ii) 2-Methyl-8-hydroxyquinoline

TABLE 12. pH READINGS FOR TITRATION OF 0.1606 g 2-METHYL-8-HYDROXY-QUINOLINE WITH 0.1761*M* HCl AT 25°C

Observation	Volume of HCl/ml	pH	Observation	Volume of HCl/ml	pH
72	0.00	7.13	84	1.75	4.83
73	0.10	6.08	85	1.95	4.75
74	0.15	5.92	86	2.15	4.78
75	0.25	5.70	87	2.35	4.70
76	0.35	5.54	88	2.55	4.69
77	0.45	5.41	89	2.85	4.59
78	0.55	5.35	90	3.15	4.43
79	0.75	5.12	91	3.45	4.13
80	0.95	5.07	92	3.95	3.28
81	1.15	4.91	93	4.15	3.06
82	1.35	4.99	94	4.55	2.73
83	1.55	4.84			

TABLE 13. pH READINGS FOR TITRATION OF 0.1240 g 2-METHYL-8-HYDROXY-QUINOLINE WITH 0.1050*M* NAOH AT 25°C

Observation	Volume of HCL/ml	pH	Observation	Volume of HCL/ml	pH
95	0.00	7.29	104	1.75	11.28
96	0.05	9.33	105	3.55	11.52
97	0.10	9.58	106	4.55	11.67
98	0.20	9.97	107	5.75	11.79
99	0.35	10.38	108	6.95	11.87
100	0.50	10.60	109	8.15	11.97
101	0.70	10.75	110	9.35	12.05
102	0.90	11.06	111	10.33	12.08
103	1.25		112	11.83	12.11

(iii) 7-Methyl-8-hydroxyquinoline

TABLE 14. pH READINGS FOR TITRATION OF 0.09740 7-METHYL-8-HYDROXYQUINOLINE WITH 0.1761*M* HCl AT 25°C

Observation	Volume of HCl/ml	pH	Observation	Volume of HCl/ml	pH
36	0.00	6.44	46	1.55	3.88
37	0.05	5.21	47	1.80	3.84
38	0.10	4.99	48	1.90	3.78
39	0.15	4.85	49	2.10	3.71
40	0.25	4.59	50	2.30	3.63
41	0.35	4.41	51	2.50	3.50
42	0.50	4.24	52	2.70	3.38
43	0.75	4.04	53	2.90	3.16
44	1.15	3.99	54	3.20	2.73
45	1.25	3.94	55	3.40	2.56

TABLE 15. pH READINGS FOR TITRATION 0.0962 OF 7-METHYL-8-HYDROXYQYINOLINE WITH 0.1050*M* NaOH AT 25°C

Observation	Volume of NaOH/ml	pH	Observation	Volume of NaOH/ml	pH
56	0.00	6.45	64	1.70	11.37
57	0.05	9.71	65	2.60	11.39
58	0.10	10.00	66	3.60	11.64
59	0.15	10.28	67	4.60	11.75
60	0.25	10.54	68	5.70	11.86
61	0.40	10.73	69	6.90	11.94
62	0.60	10.93	70	8.20	12.01
63	1.00	11.10	71	9.52	12.06

A.5. EXPERIMENTAL SOLUBILITY DETERMINATIONS

Saturated solutions of the three methyl-derivatives were prepared by adding excess of the appropriate solid to boiled out distilled water, and alternatively warming and cooling the solutions and finally allowing them to stand in a thermostat at 25°C. for several hours in order to reach equilibrium.

Aliquat portions of each solution (50 ml) were treated with concentrated hydrochloric acid (20 ml) followed by the addition of potassium bromide (1.5 g). A few drops of methyl red indicator were added and standardised potassium bromate (o.0172*M*) was run in until an excess was indicated by the colour change from pink to yellow. The solutions were then diluted to 150 ml and the excess bromine was determined by adding solid potassium iodide (1.5 g) and titrating the liberated iodine to a starch indicator endpoint with standard 0.01*M* sodium thiosulphate. The tables below show the volumes of potassium bromate and sodium thiosulphate used.

TABLE 16. VOLUMES OF BROMATE AND THIOSULPHATE USED IN THE DETERMINATION OF THE SOLUBILITY OF 2-METHYL-8-HYDROXYQUINOLINE

Volume potassium bromate (0.0172*M*) = x ml
Volume sodium thiosulphate (0.01*M*) = y ml
Volume potassium bromate (0.0172*M*) equivalent to 50 ml sample = z ml

x/ml	y/ml	z/ml
5.60	4.85	5.13
5.57	5.19	5.07
5.56	5.39	5.04
5.19	1.39	5.06
5.23	2.76	4.96

TABLE 17. VOLUMES OF BROMATE AND THIOSULPHATE USED IN THE DETERMINATION OF THE SOLUBILITY OF 5-METHYL-8-HYDROXYQUINOLINE

x/ml	y/ml	z/ml
1.24	9.07	0.361
1.77	10.80	0.362
1.64	9.48	0.361
1.50	8.00	0.362

TABLE 18. VOLUMES OF BROMATE AND THIOSULPHATE USED IN THE DETERMINATION OF THE SOLUBILITY OF 7-METHYL-8-HYDROXY-QUINOLINE

x/ml	y/ml	z/ml
1.51	7.90	0.372
1.49	7.72	0.371
1.49	7.64	0.375

From the above results the mean volumes of potassium bromate (0.0172*M*) which are equivalent to 50 ml aliquot portions of 2-, 5- and 7-methyloxines were calculated to be 5.05 ± 0.06, 0.36 ± 0.001 and 37 ± 0.003 ml respectively. From equations (7), and (9) it can be seen that one mole of bromine reacts with one mole of both 5-methyloxine and 7-methyloxine, and that 2 moles of bromine react with one mole of 2-methyloxine. Since bromine is released from bromate in the following way :

$$BrO_3^- + 5\ Br^- \times 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The solubility of each methyl derivative may be calculated in moles per litre. These results are summarized in Table 9 above.

A.6. CALCULATION OF THERMODYNAMIC ACID DISSOCIATION CONSTANTS

All the data has now been assembled for calculating the values of $pK^{T}_{1,Ox}$ and $pK^{T}_{2,Ox}$ according to the equations (5) and (6). The results are summarised in Tables 19, 20 and 21. The greatest precision results from using points from the midpoint regions of the titration curves.

TABLE 19. CALCULATED VALUES OF $pK^{T}_{1,Ox}$ AND $pK^{T}_{2,Ox}$) FOR 5-METHYL-8-HYDROXYQUINOLINE

Observation number	$pK^{T}_{1,Ox}$	I(calc.)	Observation number	$pK^{T}_{2,Ox}$	I (calc.)
9	5.00	0.09	28	10.16	0.11
10	5.10	0.11	29	10.16	0.12
11	5.08	0.11	30	10.16	0.14
12	5.07	0.11	31	10.14	0.15
13	5.06	0.13	32	10.16	0.17
Mean Values	5.07 ± 0.01			Mean Values	10.16 ± 0.01

TABLE 20. CALCULATED VALUES OF $pK^{T}_{1,Ox}$ AND $pK^{T}_{2,Ox}$ FOR 2-METHYL-8-HYDROXYQUINOLINE

Observation number	$pK^{T}_{1,Ox}$	I(calc.)	Observation number	$pK^{T}_{1,Ox}$	I (calc.)
83	5.50	0.11	107	10.90	0.15
84	5.52	0.12	108	10.92	0.16
85	5.47	0.13	109	10.97	0.17
86	5.54	0.13	110	11.02	0.18
87	5.49	0.14	111	11.02	0.19
88	5.51	0.14	112	11.02	0.20
89	5.45	0.15			
Mean Values	5.49 ± 0.03			Mean Values	10.95 ± 0.05

TABLE 21. CALCULATED VALUES OF $pK^{T}_{1,Ox}$ AND $pK^{T}_{2,Ox}$ FOR 7-METHYL-8-HYDROXYQUINOLINE

Observation number	$pK^{T}_{1,Ox}$	I(calc.)	Observation number	$pK^{T}_{2,Ox}$	I(calc.)
46	5.35	0.11	67	10.10	0.14
47	5.37	0.12	68	10.14	0.15
48	5.33	0.12	69	10.16	0.16
			70	10.18	0.17
			71	10.18	0.18
Mean Values	5.35 ± 0.2		Mean Values	10.16 ± 0.03	

B. SPECTROPHOTOMETRIC DETERMINATION OF FIRST AND SECOND THERMODYNAMIC ACID DISSOCIATION CONSTANTS AT CONSTANT TEMPERATURE AND IONIC STRENGTH

B.1. The method used to determine the above constants was based on that of Stenstrom and Goldsmith [11]. The ultraviolet absorption spectra of accurately prepared $10^{-3}M$ solutions of 8-hydroxyquinoline and its methyl-substituted derivatives were measured in acidic, neutral, and alkaline media. These spectra are shown in Figures 8, 9, 10, and 11. The neutral molecule HOx does not absorb strongly in the visual region and the absorption bonds due to the ions H_2Ox^+ and Ox^- are similar. Absorbance measurements of solutions of the parent oxine and its methyl derivatives were recorded at a fixed wavelength, that of maximum absorption, as the pH was varied through the ranges 1-7 and then 7-13 respectively, by means of buffers of constant ionic strength. The constant total amount of ligand used in each experiment is such that the absorbance is a linear function of concentration for each of the three absorbing species. In a sufficiently acidic medium, H_2Ox^+ would be the predominant species and its molar extinction coefficient can be obtained directly from the absorbance in this medium. Similarly, in a sufficiently alkaline medium, a value may be obtained for the molar extinction coefficient of the species Ox^-.

According to Stenstrom and Goldsmith [11], at the mid-point of the plot of absorbance against pH in the lower pH region, $pH = pK^B_{1,Ox}$ where $K^B_{1,Ox}$ is the first (Brønsted) acid dissociation constant, defined as

$$K^B_{1,Ox} = (aH^+)[HOx]/[H_2Ox^+].$$

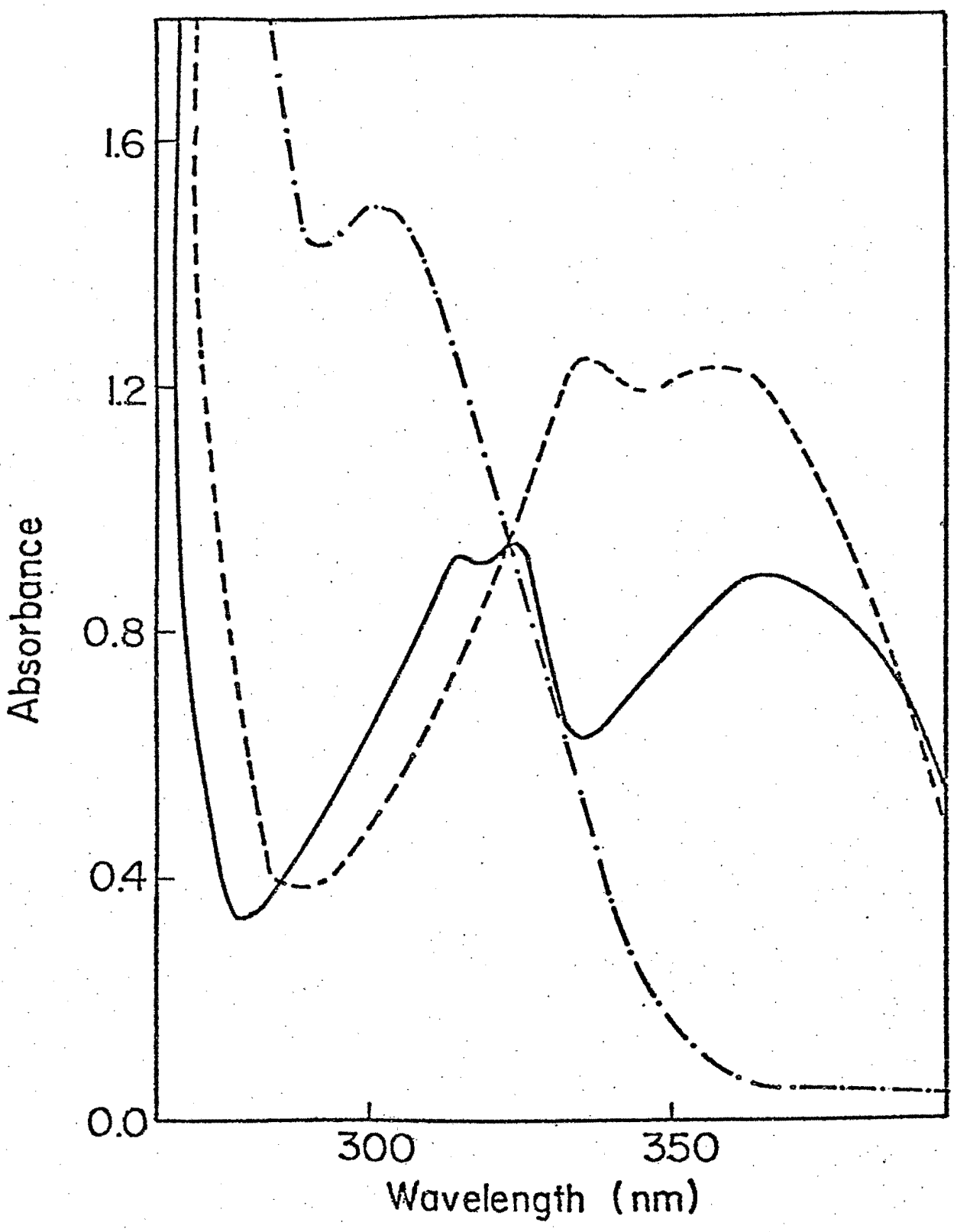


FIGURE 8 : Absorption Spectra of 4.396×10^{-3} 8-hydroxyquinoline (1 ml) in 10 ml of (i) buffer pH 7, (ii) concentrated HCl and (iii) 5*M* NaOH

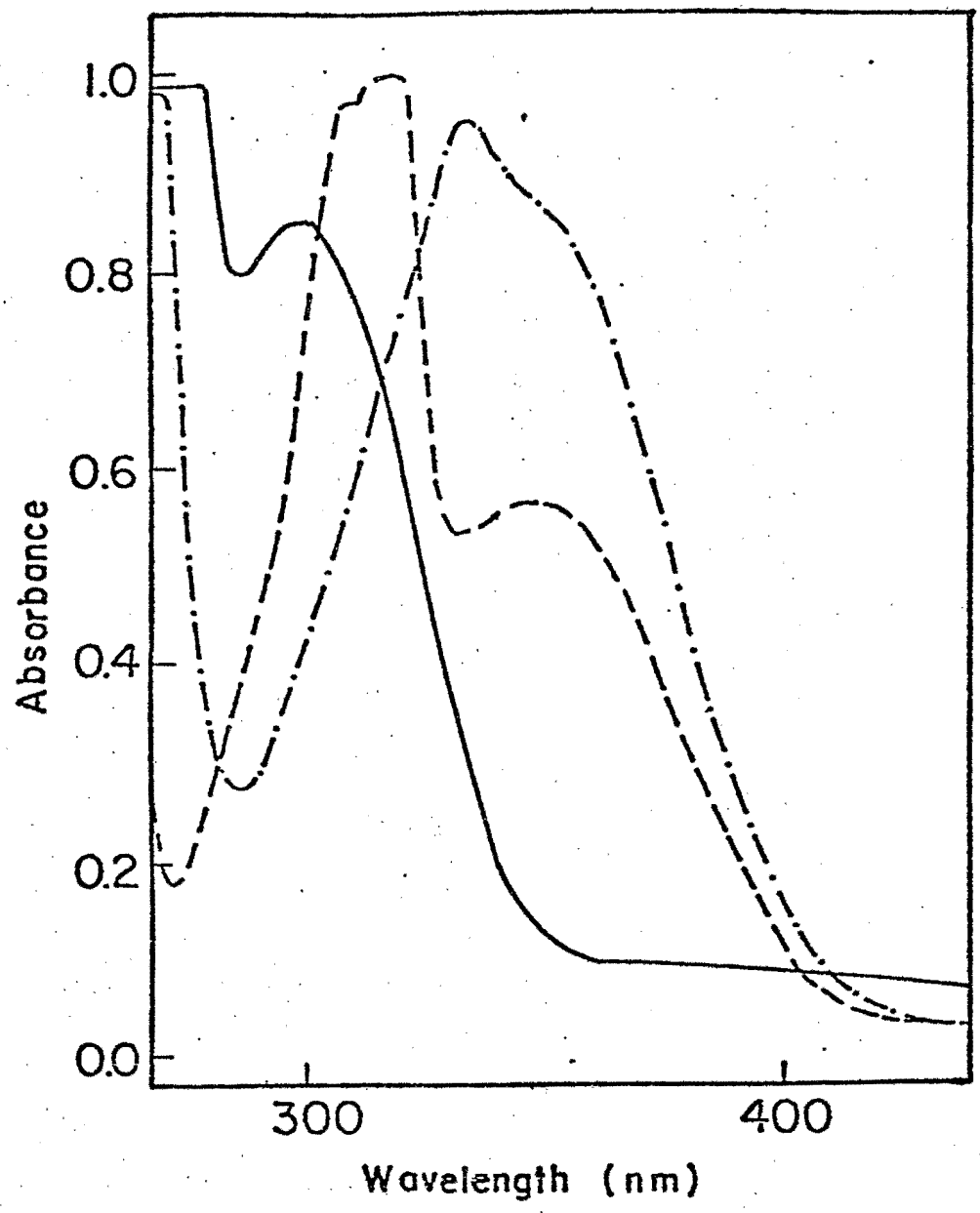


FIGURE 9 : Absorption spectra of $3.289 \times 10^{-3} M$ 2-methyl-8-hydroxy-quinoline (1 ml) in 10 ml of (i) 5*M* NaOH, (ii) concentrated HCl and (iii) buffer pH 7

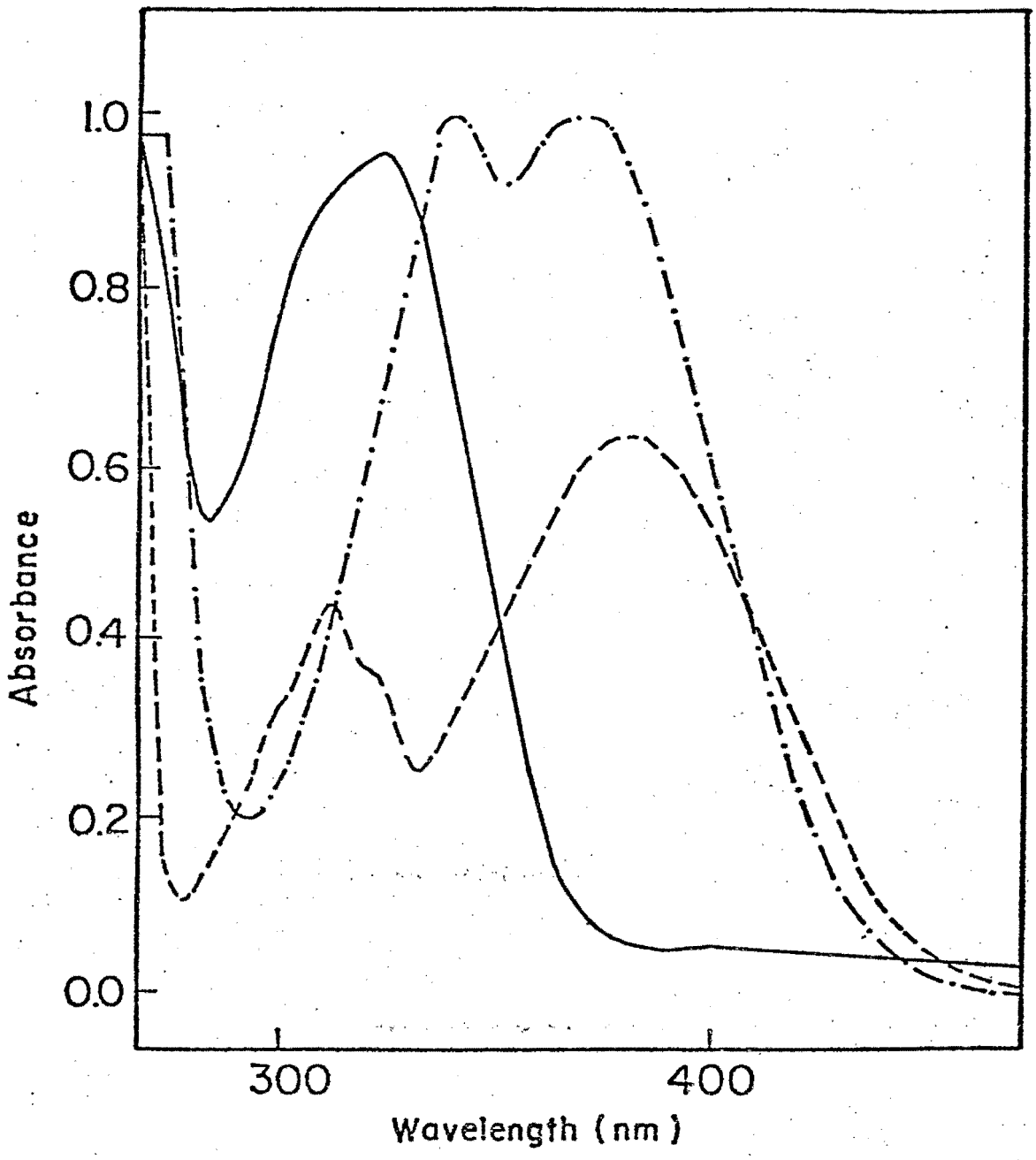


FIGURE 10 : Absorption spectra of 3.509 x 10^{-3} *M* 5-methyl-8-hydroxyquinoline (1 ml) in 10 ml of (i) 5*M* NaOH, (ii) concentrated HCl and (iii) buffer pH 7

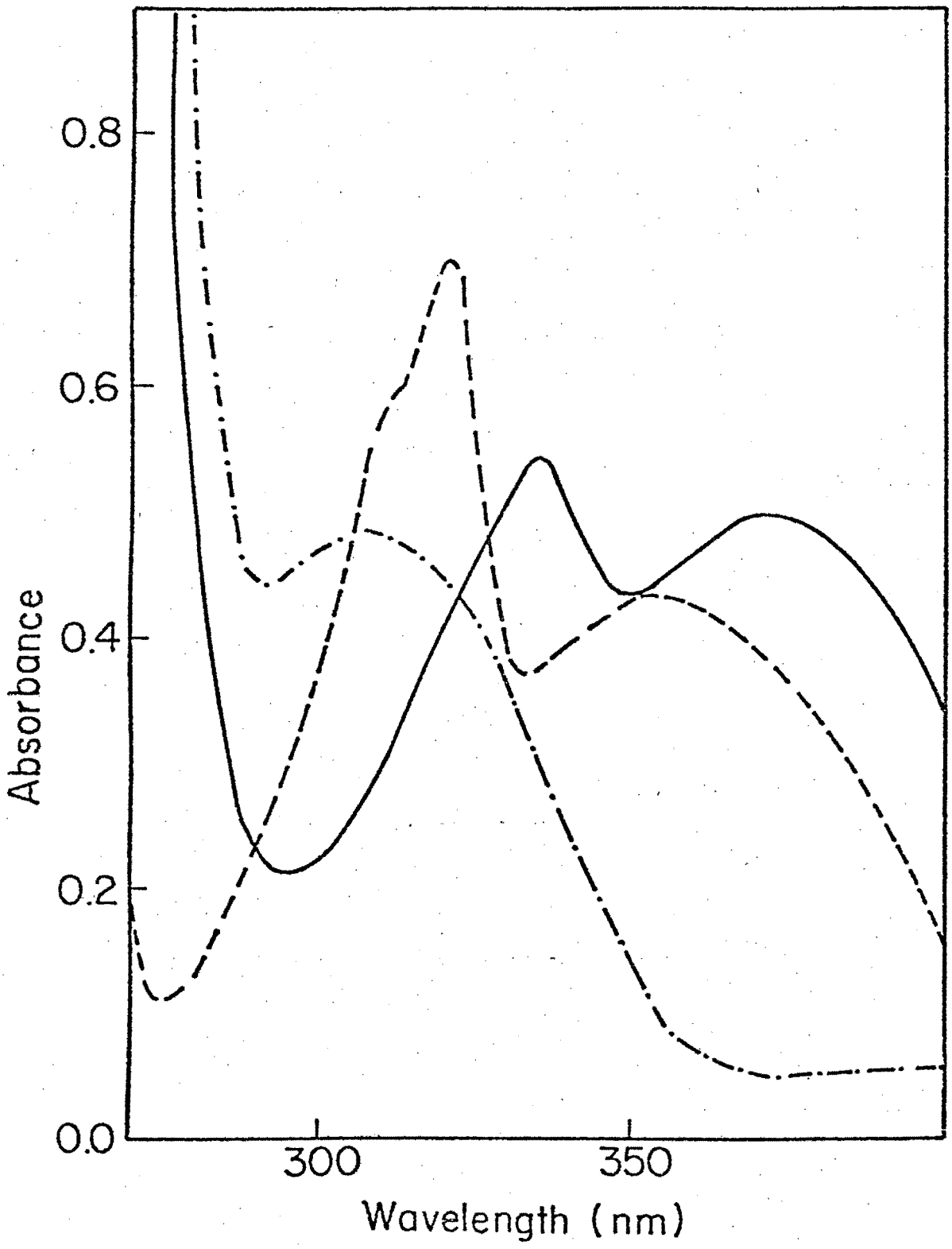
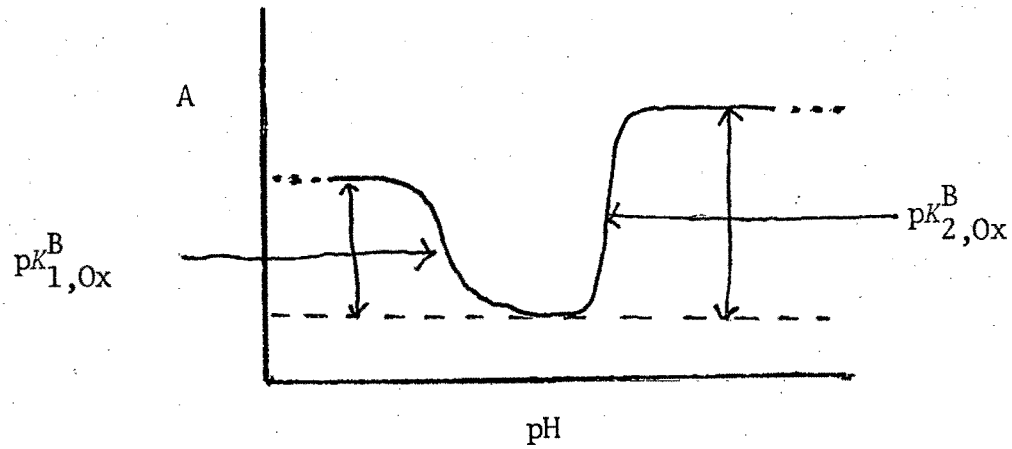


FIGURE 11 : Absorption spectra of $3.425 \times 10^{-2}M$ 7-methyl-8-hydroxyquinoline (0.1 ml) in 20 ml of (i) buffer pH 7 (ii) 5*M* NaOH and (iii) concentrated HCl



Brønsted dissociation constants were thus obtained by a graphical determination of the pH at which the absorbance is halfway between its values in acidic and in neutral solution. By analogy, the graphical determination of the pH at which the absorbance was halfway between its value in neutral and alkaline solutions gave $pK^B_{2,Ox}$ where

$$K^B_{2,Ox} = (aH^+)\,[Ox^-]/[HOx]$$

These were converted into thermodynamic constants, $pK^T_{1,Ox}$ and $pK^T_{2,Ox}$ after calculating the relevant activity coefficients from the (known) ionic strength of the solution. Specifically,

$$K^T_{1,Ox} = K^B_{1,Ox}\, f_0/f_1 \qquad \text{and } K^T_{2,Ox} = K^B_{2,Ox}\, f_1/f_0.$$

The calculation of $pK^B_{1,Ox}$ and $pK^B_{2,Ox}$ values from the spectra data was based on the following considerations.

Consider the general equilibrium

$$H_2Ox^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HOx \overset{K_2}{\rightleftharpoons} Ox^-$$

If c is the total concentration of the ligand in all its forms, and ε_{H_2Ox}, ε_{HOx} and ε_{Ox} are the molar extinction coefficients of the species $H_2Ox_2^+$, HOx and Ox^-, then for a 1 cm cell the measured absorbance at a particular wavelength is

$$A = [H_2Ox^+]\varepsilon_{H_2Ox} + [HOx]\varepsilon_{HOx} + [Ox^-]\varepsilon_{Ox}$$

and $$c = [H_2Ox^+] + [HOx] + [Ox^-]$$

In an acidic medium, the term $[Ox^-]$ becomes negligible.

Thus $c = [H_2Ox^+] + [HOx]$

and $$A = [H_2Ox^+]\varepsilon_{H_2Ox} + [HOx]\varepsilon_{HOx}$$

Now $K^B_{1,Ox} = [HOx][aH^+]/[H_2Ox^+]$

and so $$c = [HOx]\left\{\frac{[aH^+]}{K^B_{1,Ox}} + 1\right\} \qquad (12)$$

and $$A = [HOx]\left\{\frac{[aH^+]}{K^B_{1,Ox}}\varepsilon_{H_2Ox} + \varepsilon_{HOx}\right\} \qquad (13)$$

Whence $$K^B_{1,Ox} = \frac{[aH^+]\{A - c\varepsilon_{H_2Ox}\}}{\{c\varepsilon_{HOx} - A\}}$$

and $$pK^B_{1,Ox} = p(aH^+) - \log \frac{\{(A/c) - \varepsilon_{H_2O}\}}{\{\varepsilon_{HOx}(A/c)\}} \qquad (14)$$

If ε_{H_2Ox} is obtained as described above, then $K^B_{1,Ox}$ may be calculated for each pH and absorbance value. Calculations were, however, performed only for the points in the midpoint region of the curve. A similar equation given below may be derived for the calculation of the second (Brønsted) acid dissociation constant

$$pK^B_{2,Ox} = p(aH^+) \log \frac{\{A/c) - \varepsilon_{HOx}\}}{\{\varepsilon_{Ox} - (A/c)\}} \qquad (15)$$

All experimental data are given in the experimental section, and the corrected thermodynamic constants $K^T_{1,Ox}$ and $K^T_{2,Ox}$ are tabulated below, as well as those values reported in the literature.

TABLE 22. FIRST AND SECOND THERMODYNAMIC ACID DISSOCIATION CONSTANTS OF 8-HYDROXYQUINOLINE AND ITS METHYL HOMOLOGUES AT 25°C (Present Work).

REAGENT	$pK^T_{1,Ox}$	$pK^T_{2,Ox}$
8-Hydroxyquinoline	5.00± 0.02	10.24± 0.02
2-Methyl-8-hydroxyquinoline	5.64± 0.01	10.64± 0.01
5-Methyl-8-hydroxyquinoline	5.15± 0.01	10.64± 0.01
7-Methyl-8-hydroxyquinoline	5.07± 0.03	10.66± 0.02

TABLE 23. FIRST AND SECOND ACID DISSOCIATION CONSTANTS OF 8-HYDROXYQUINOLINE AND ITS METHYLHOMOLOGUES (Literature Values).

T = temperature (°C)
I = ionic strength
→ 0 extrapolated to zero ionic strength

REAGENT	T/°C	I	$pK_{1,Ox}$	$pK_{2,Ox}$	Ref.
8-Hydroxyquinoline	20	0	5.01	9.90	[12,13]
	25	→ 0		9.81	[14]
	20	→ 0	5.02		[14]
	25	→ 0	4.91	9.81	[14]
	20	0.01	5.13	9.89	[15]
	25	0.1$NaClO_4$		9.66	[16]
	25	0.085	5.01	9.86	[17]
	25	0.5NaCl	4.91	9.81	[18]
	25	0.1$NaClO_4$		9.70	[19]
	25	0.1$NaClO_4$	4.92	9.23	[20]
	16	0.1	5.17	9.87	[21]
	20	0.1	5.14	9.74	[22]
	25	0.1 (KNO_3)	4.95	9.63	[23]
2-Methyl-8-hydroxyquinoline	25	→ 0	5.61	10.16	[18]
	25	→ 0	5.61	10.16	[24]

No values have been reported for 5-methyl-8-hydroxyquinoline and 7-methyl-8-hydroxyquinoline in aqueous solutions.

B.2. DISCUSSION

In order to investigate the complexes formed between iron(III) and derivatives of 8-hydroxyquinoline, reliable values for the dissociation constants of these reagents were required. The values reported for these constants by earlier workers are not in good agreement, and inter-comparison of these values is difficult since ionic strength and temperature are frequently not specified (see Table 23). It was therefore necessary to repeat these determinations, and also to determine those constants for which no literature values exist.

The values obtained spectrophotometrically are in good agreement with predictions based on the inductive effect of the methyl group which should increase the basicity of the N atom and decrease the acidity due to the OH group. The expected trend of increase in $pK^{T}_{1,Ox}$ and $pK^{T}_{2,Ox}$ values on methyl substitution is definitely observed. It was, however, perturbing, that the value obtained now for $pK^{T}_{2,Ox}$ of 8-hydroxyquinoline differed by as much as 0.3 units from the value $pK^{T}_{2,Ox} = 9.90$ obtained by the careful work of Näsänen [12] and others [13,14]. The $pK^{T}_{1,Ox}$ value, however, is in very good agreement with $pK^{T}_{1,Ox} = 5.01$ obtained by the same authors. Similarly, the value found for $pK^{T}_{2,Ox}$ of 2-methyl-8-hydroxyquinoline is also higher than that obtained by Näsänen and others [12,13,14], while pK^{T}_{Ox} is consistent with their value $pK^{T}_{1,Ox} = 5.61$. Since the same procedure was followed for the determination of pK^{T}_{Ox} and $pK^{T}_{2,Ox}$, it is surprising that there should be good agreement between values for the first dissociation constants, and poor agreement between values for the second. Because of these large discrepancies, various tests were performed to establish possible sources of error.

The calibration of the wavelength and absorbance scale of the spectrophotometer was checked by measuring the absorbance of a known concentration of highly pure potassium chromate in 0.05*M* potassium hydroxide. From this value, the molar extinction coefficient was evaluated at the absorbance maximum, 371 nm, and found to be 4826 $m^2 \cdot mol^{-1}$, comparing favourably with the value of 4815 $m^2\ mol^{-1}$ quoted at 375 nm by Gillam, Stern and Timmons [25]. In addition, pH measurements on the pH M64 research pH meter were compared by obtaining readings of the same buffer solutions on a second pH meter. These readings were found to be consistent. Measurements were also carried out with a different glass electrode to make sure that this was not faulty.

Since no instrumental reasons were found to throw doubt on the validity of the present measurements of $pK^{T}_{2,Ox}$ there seems no reason for rejecting these and they have been adopted in the calculation of formation constants of the complexes of oxines with iron(III). At the same time it must be admitted that no explanation can be put forward for the lower values obtained by earlier workers.

B.3. EXPERIMENTAL

Solutions of 8-hydroxyquinoline and its methyl-substituted derivatives ($\sim 10^{-3}M$) were prepared by dissolving an accurately weighed amount of each reagent in a fixed volume of ethanol. Spectra were then measured for each reagent in acidic, neutral and alkaline media. Acetic acid-sodium acetate buffers were used to cover the low pH range and borax buffers to cover the higher range. To obtain readings at very high and very low pH, *M* and 0.1*M* sodium hydroxide and hydrochloric acid were used.

The ionic strength of 10 ml of each buffer mixture after dilution to a total volume of 20 ml was calculated, and the addition of the appropriate volume of standard sodium perchlorate solution was used to adjust the ionic strength to 0.1 mole ℓ^{-1}. All reagents were of AnalaR quality and glass distilled water was used throughout. The solutions were kept in a water bath at 25°C until use and the mounting block of the spectrophotometer was also thermostated at 25°C.

The required amount of each buffer (10 ml) was pipetted into a 20 ml volumetric flask, to which was added the appropriate amount of sodium perchlorate (0.5*M*). A constant volume (2 ml) of 8-hydroxyquinoline was pipetted into each flask, and the volume made up to 20 ml with distilled water. The blank was prepared by diluting 2 ml ethanol in 20 ml water. The absorbance of each solution was measured in a 1 cm cell at a fixed wavelength, that of maximum absorbance, followed by measurement of the pH. The pH meter was standardised against buffers of pH 7.00 and pH 4.01 and 25°C for the low pH range and against buffers of pH 7.00 and pH 9.18 at 25°C for the higher range. The standardisation procedure was performed before each experiment. An identical procedure was followed to obtain pK^B values for the 2-, 5- and 7-methyl homologues. The experimental data are summarized below and plots of absorbance against pH are given in Figures 12 and 13.

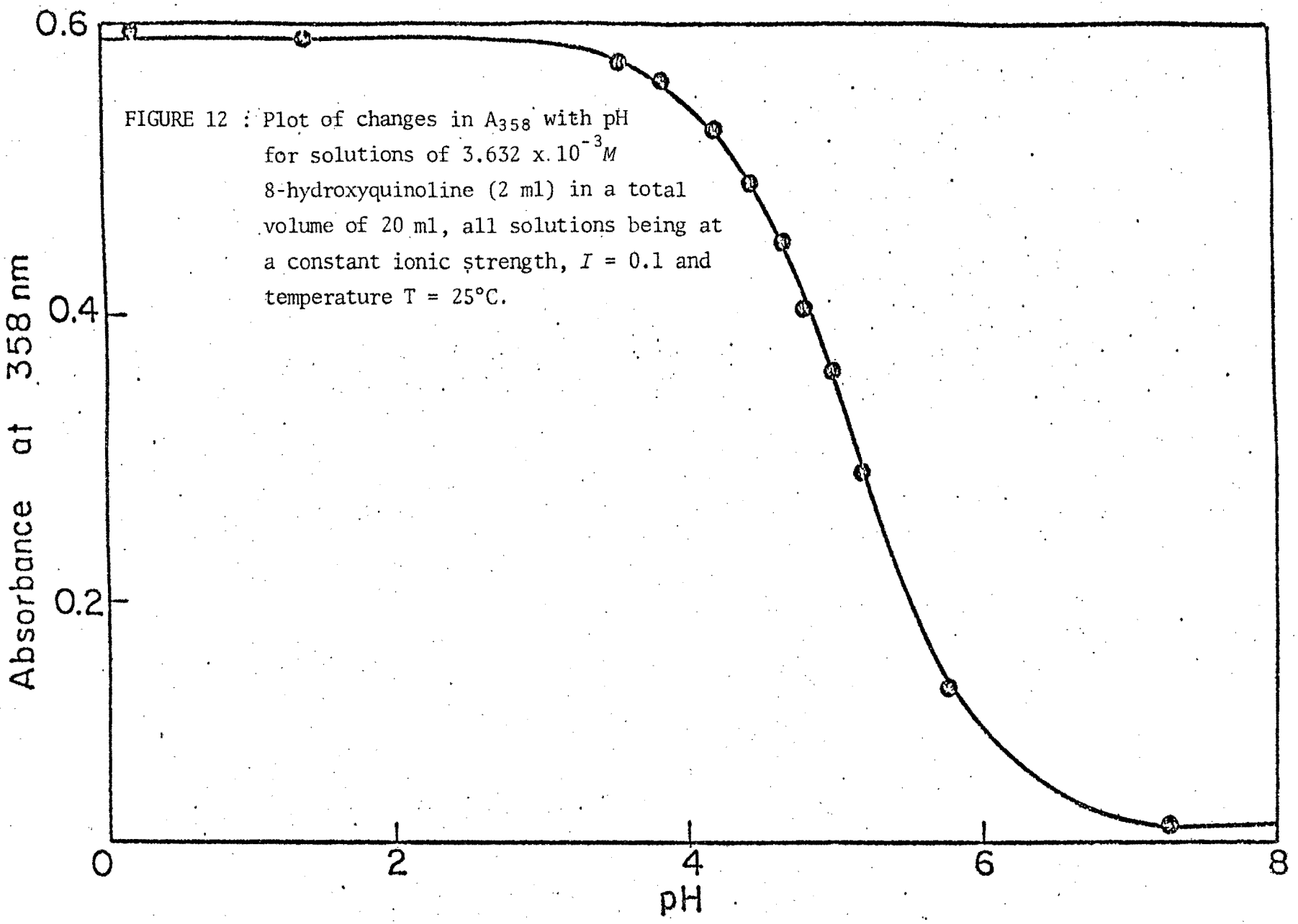


FIGURE 12 : Plot of changes in A_{358} with pH for solutions of $3.632 \times 10^{-3} M$ 8-hydroxyquinoline (2 ml) in a total volume of 20 ml, all solutions being at a constant ionic strength, I = 0.1 and temperature T = 25°C.

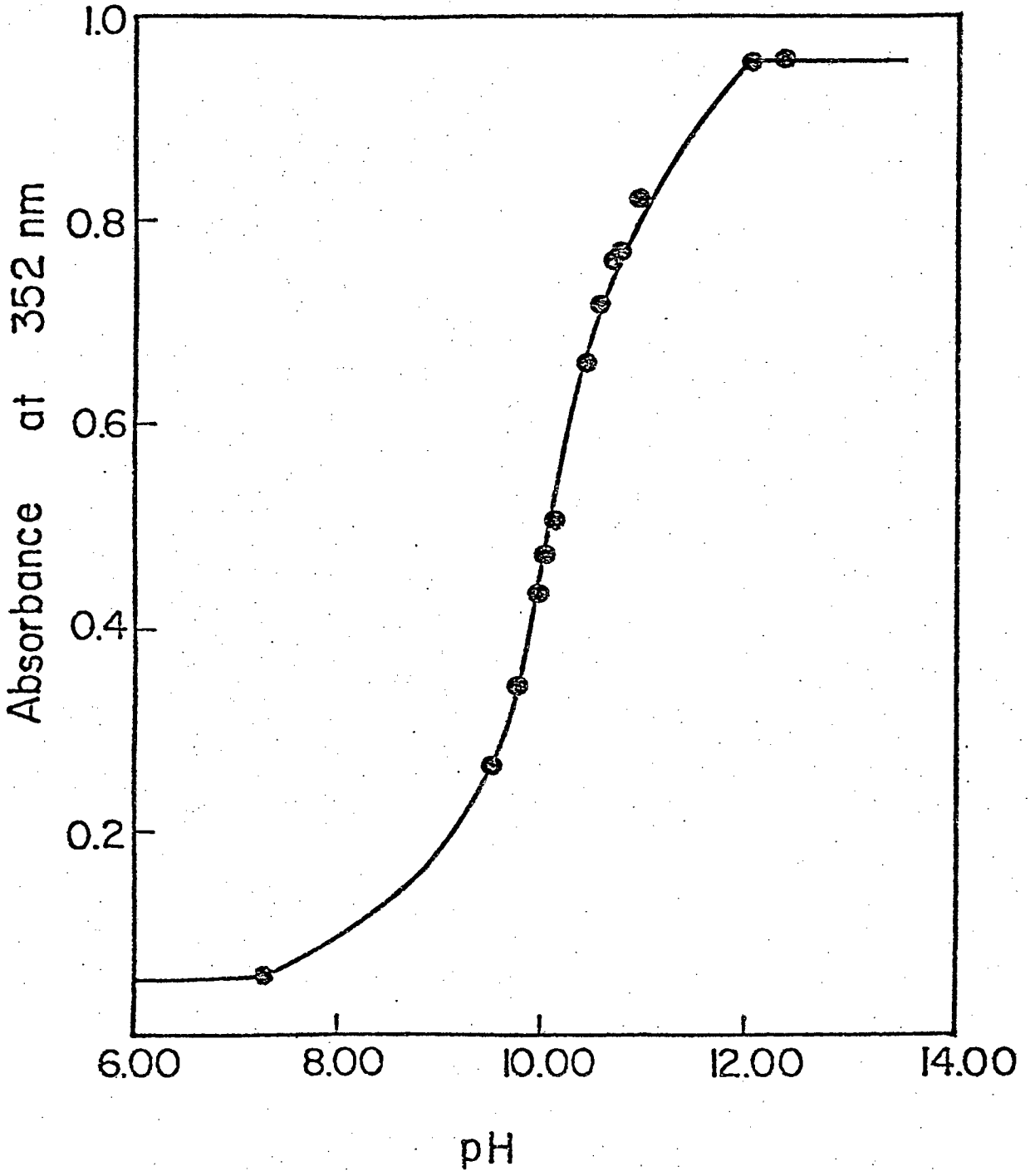


FIGURE 13 : Plot of changes in A_{352} with pH for solutions of $3.632 \times 10^{-3} M$ 8-hydroxyquinoline (2 ml) in a total volume of 20 ml, all solutions being at a constant ionic strength, I = 0.1 and temperature T = 25°C

TABLE 24. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_1^B OF 8-HYDROXYQUINOLINE AT 25°C

Concentration of 8-hydroxyquinoline = 3.632×10^{-3} mole ℓ^{-1}
Ionic strength I = 0.1 mole ℓ^{-1}
λ_{max} = 358 nm

A_{358}	pH	pK_1^B
0.596	0.22	
0.588	1.41	
0.573	3.56	(5.01)
0.560	3.85	5.06
0.527	4.19	5.06
0.492	4.43	5.08
0.451	4.62	5.08
0.405	4.81	5.09
0.360	4.98	5.11
0.290	5.18	5.09
0.140	5.79	5.11
0.045	7.26	Mean 5.09 ± 0.02

pK_1^B calculated using Equation (14) with $\varepsilon_{HOx} = 124$ and

$\varepsilon_{H_2Ox} = 1630$ m^2 mol^{-1} at 358 nm.

TABLE 25. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_1^B OF 2-METHYL-8-HYDROXYQUINOLINE AT 25°C

Concentration of 2-methyl-8-hydroxyquinoline = 7.566×10^{-3} moles ℓ^{-1}

Ionic strength I = 0.1 moles ℓ^{-1}

λ_{max}

A_{353}	pH	pK_1^B
1.231	0.29	
1.229	1.20	
1.217	3.83	5.66
1.204	4.17	5.73
1.179	4.38	5.66
1.152	4.55	(5.65)
1.114	4.78	(5.69)
1.066	4.97	5.73
0.987	5.17	5.72
0.871	5.42	5.73
0.641	5.79	5.73
0.132	7.31	
		Mean 5.73 ± 0.01

pK_1^B calculated using Equation (14) with ε_{HOx} = 174 and

ε_{H_2Ox} = 1630 m^2 mol^{-1} at 354 nm

TABLE 26. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_1^B OF 5-METHYL-8-HYDROXYQUINOLINE AT 25°C

Concentration of 5-methyl-8-hydroxyquinoline = 3.509×10^{-3} moles ℓ^{-1}
Ionic Strength I = 0.1 moles ℓ^{-1}
λ_{max} = 382 nm

A_{382}	pH	pK_1^B	
0.617	0.17		
0.616	1.18		
0.596	3.80		
0.591	3.94		
0.571	4.14	(5.21)	
0.546	4.35	(5.20)	
0.515	4.57	5.24	
0.474	4.76	5.24	Mean
0.423	4.94	5.23	5.24 ± 0.01
0.366	5.14	5.25	
0.282	5.38	5.23	
0.169	5.75	(5.19)	
0.046	7.28		

pK_1^B calculated using Equation (14) with $\varepsilon_{HOx} = 131$ and

$\varepsilon_{H_2Ox} = 1755$ m^2 mol^{-1} at 382 nm.

TABLE 27. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_1^B OF 7-METHYL-8-HYDROXYQUINOLINE AT 25°C

Concentration of 7-methyl-8-hydroxyquinoline = 3.585×10^{-3} moles ℓ^{-1}
Ionic Strength I = 0.1 moles ℓ^{-1}
λ_{max}

A_{355}	pH	pK_1^B	
0.662	0.10		
0.663	0.14		
0.629	3.53		
0.619	3.82		
0.598	4.18	(5.03)	
0.570	4.42	(5.09)	
0.541	4.61	5.13	Mean
0.500	4.79	5.14	5.16 ± 0.03
0.398	5.17	5.17	
0.374	5.28	5.20	
0.241	5.78	5.18	
0.136	7.29		

pK_1^B calculated using Equation (14) with $\varepsilon_{HOx} = 379$ and

$\varepsilon_{H_2Ox} = 1850\ m^2\ mol^{-1}$ at 355 nm

TABLE 28. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_2^B OF 8-HYDROXYQUINOLINE AT 25°C

Concentration of 8-hydroxyquinoline = 3.632×10^{-2} moles ℓ^{-1}

Ionic Strength I = 0.1 moles ℓ^{-1}

λ_{max}

A_{352}	pH	pK_2^B	
0.058	7.26		
0.264	9.49	10.01	
0.344	9.73	10.06	
0.435	9.94	10.08	
0.508	10.11	10.11	
0.469	10.03	(10.10)	Mean
0.658	10.44	10.13	10.15 ± 0.02
0.715	10.58	10.14	
0.745	10.67	10.16	
0.776	10.76	10.16	
0.823	10.93	10.17	
0.955	13.05		
0.955	13.31		

pK_2^B calculated using Equation (15) with ϵ_{HOx} = 160 and

ϵ_{Ox} = 2630 m^2 mol^{-1} at 352 nm

TABLE 29. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_2^B OF 2-METHYL-8-HYDROXYQUINOLINE AT 25°C

Concentration of 2-methyl-8-hydroxyquinoline = 7.566×10^{-3} moles ℓ^{-1}

Ionic Strength I = 0.1 moles ℓ^{-1}

λ_{max} = 353 nm

A_{353}	pH	pK_2^B	
0.134	7.24		
0.257	9.43	(10.58)	
0.343	9.65	10.55	
0.456	9.87	10.55	
0.566	10.03	10.55	Mean 10.55 ± 0.01
0.640	10.11	10.54	
0.866	10.35	10.54	
0.960	10.44	10.54	
1.067	10.55	10.55	
1.122	10.58	(10.52)	
1.246	10.68	10.51	
2.036	12.88		
1.948	13.29		

pK_2^B calculated using Equation (15) with ε_{HOx} = 177 and

ε_{Ox} = 2630 m^2 mol^{-1} at 353 nm

TABLE 30. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_2^B OF 5-METHYL-8-HYDROXYQUINOLINE AT 25°C

Concentration of 5-methyl-8-hydroxyquinoline = 3.535×10^{-3} moles ℓ^{-1}
Ionic Strength I = 0.1 moles ℓ^{-1}
λ_{max} = 370 nm

A_{370}	pH	pK_2^B	
0.094	7.35		
0.195	9.55		
0.249	9.76		
0.329	9.97		
0.403	10.15	(10.50)	
0.415	10.23	10.56	
0.555	10.48	10.55	
0.618	10.58	10.54	Mean 10.55 ± 0.01
0.686	10.71	10.55	
0.700	10.74	10.55	
0.760	10.87	(10.57)	
1.085	13.16		
1.102	13.45		

pK_2^B Calculated using Equation (15) with ε_{HOx} = 266 and

ε_{Ox} = 3095 m^2 mol^{-1} at 370 nm.

TABLE 31. ABSORBANCE AND pH MEASUREMENTS FOR THE DETERMINATION OF pK_2^B OF 7-METHYL-8-HYDROXYQUINOLINE AT 25°C

Concentration of 7-methyl-8-hydroxyquinoline = 3.585×10^{-3} moles ℓ^{-1}
Ionic Strength I = 0.1 moles ℓ^{-1}
λ_{max} = 372 nm

A_{372}	pH	pK_2^B	
0.043	7.35		
0.088	9.47		
0.137	9.70		
0.194	9.91		
0.250	10.10		
0.279	10.20	10.56	
0.367	10.44	10.58	
0.427	10.57	10.57	Mean 10.57 ± 0.02
0.465	10.68	10.60	
0.498	10.72	10.56	
0.551	10.84	10.55	
0.811	13.01		
0.818	13.36		

pK_2^B calculated using Equation (15) with ε_{HOx} = 120 and

ε_{Ox} = 2270 m^2 mol^{-1} at 372 nm.

CHAPTER VI

THERMODYNAMIC FORMATION CONSTANTS K^T OF COMPLEXES OF IRON(III) AND METHYL-SUBSTITUTED 8-HYDROXYQUINOLINES

CHAPTER VI

THERMODYNAMIC FORMATION CONSTANTS K^T OF COMPLEXES OF IRON(III) AND METHYL-SUBSTITUTED 8-HYDROXYQUINOLINES

If the linear molar (decadic) absorption coefficient, ε, of a 1:1 complex, FeL^{2+} could be obtained, then the concentration of this species could be deduced from the measured absorbance, A of any solution containing it, from the familiar Beer's Law relationship.

$$C = A/\varepsilon\ell \qquad (16)$$

In this expression ℓ = length of the absorption cell used.
Knowing the concentration of the species FeL^{2+} and the total amounts of iron and ligand present, it would be a simple matter to calculate the thermodynamic formation constant, K^T for the complex from equation (1).

$$Fe^{3+} + L^- \rightleftarrows FeL^{2+} \qquad (17)$$

In the case of 8-hydroxyquinoline and its derivatives (here we will replace HL by HOx) the ferric complex is not very stable so that the reaction represented by equation (17) cannot be made to go completely to the right and the value of ε cannot be computed directly since the value of $[FeOx]^{2+}$ will not be available. It was, therefore, necessary to calculate values of the thermodynamic stability constant, K^T_{FeOx}, (as defined in equation (1)) by making use of the expression (18), the derivation of which is given in the Appendix (page 71).

$$(K^T)^{-1} = \frac{\{C-(A/\varepsilon\ell)\}\{\varepsilon f_1 f_3 K_{Ox}^T b - (A f_1 f_3 K_{Ox}^T/\ell)\}}{\{Q f_2 (aH^+)\ A/\ell\}} \qquad (18)$$

where $c = [Fe]_{tot}$ = sum of the molar concentrations of ferric iron in all its forms in the solution

$b = [L]_{tot}$ = total concentration of 5-methyloxine [HL]

A = measured absorbance

ε = molar absorption coefficient for the complex $FeOx^{2+}$

ℓ = length of the cell

f_n = activity coefficient of an n-valent ion

$K_{Ox}^T = K_{1,Ox}^T K_{2,Ox}^T$ where $K_{1,Ox}^T$ and $K_{2,Ox}^T$ are the first and second thermodynamic dissociation constants for the acid

$$Q = 1 + 0.0028 f_3/f_2(aH^+)$$

It can be seen from equation (4) that if the molar absorption coefficient ε for the complex were known, as well as the two thermodynamic dissociation constants for the methyl-substituted oxines, it would be possible to calculate K^T from the absorbance measurements and the known concentrations, c and b.

A series of calculations of c, b and of Q were made for each of the 43 data points (a,pH). The complete set of data is given in Table 33. (Full experimental details are given later). The values of the activity

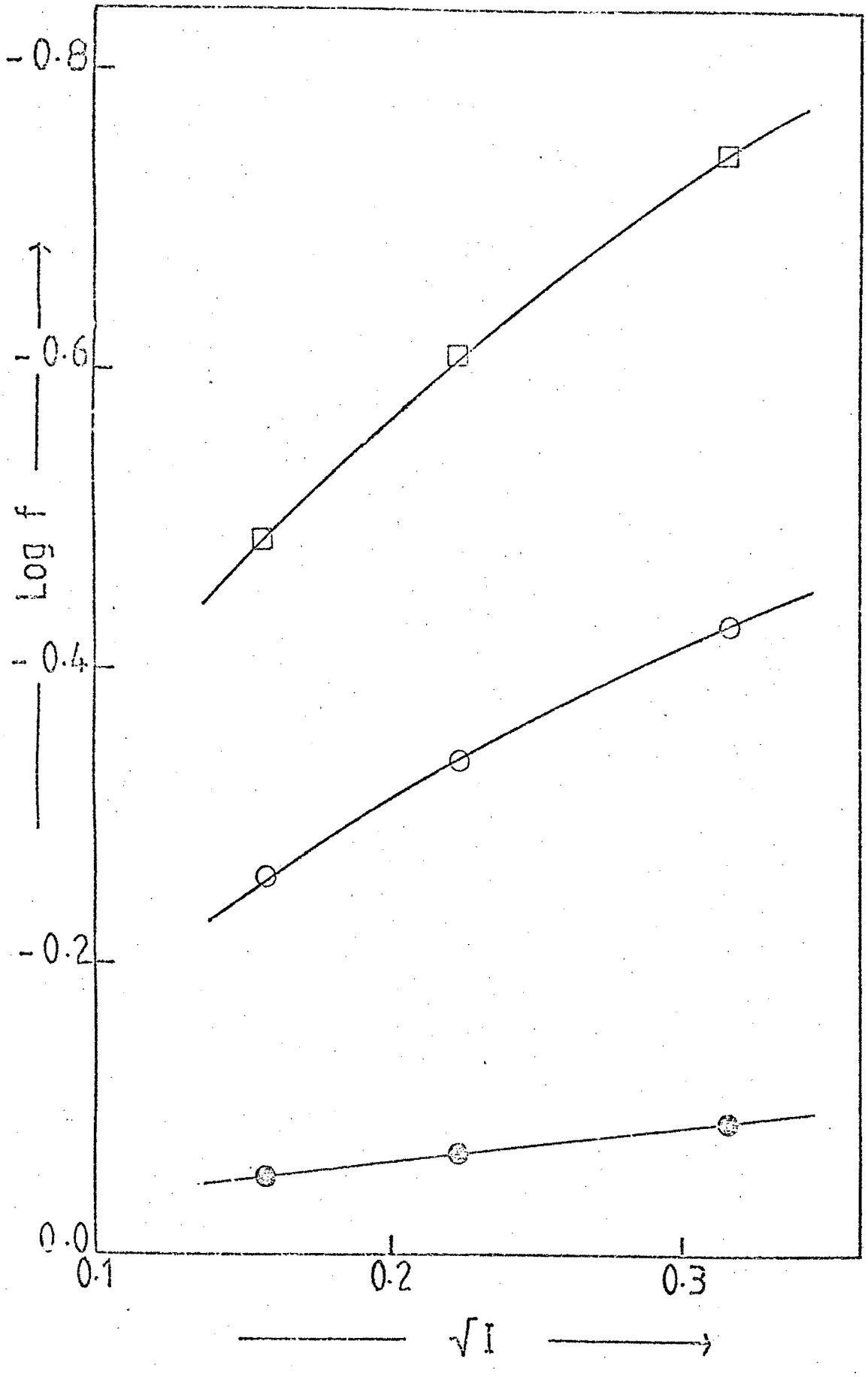


FIGURE 7 : Plot of log f against √I using data given by Kielland.

coefficient for an ionic strength I = 0.1M were interpolated from a plot of log f against $\sqrt{I}$ shown in Figure 7, using data given by Kielland [9] (see Table). The values f = 0.81, f_2 = 0.37 and f_3 = 0.18 were adopted.

TABLE. SELECTED DATA GIVEN BY KIELLAND USED IN DETERMINATION OF ACTIVITY COEFFICIENTS f_n

	Values of the activity coefficient, f.		
ION	I=0.025	0.860	0.1
H^+	0.880	0.860	0.830
NH_4^+	0.850	0.800	0.750
ClO_3^-	0.855	0.810	0.760
Fe^{3+}	0.325	0.245	0.180
L^-	0.875	0.845	0.810
L^{2+}	0.550	0.455	0.370

I = Ionic strength; f = activity coefficient; L^- = uni-negative organic ion; L^{2+} = di-positive organic ion.

THE MOLAR ABSORPTION COEFFICIENT, ε, OF THE COMPLEXES

It was not possible to determine the molar absorption coefficient of the complexes from their Job curves because of the difficulty of drawing tangents to the curves through the points x = o and x = 1 since they are so rounded. Rough estimates of ε for 5-methyl-8-hydroxyquinoline were calculated for the molar ratios at the maxima of these curves using the following expression, the derivation of which is given in the Appendix (equation A10).

$$cb\varepsilon^2\{Q^*A^*(aH^+{}^*)^2 - QA(aH^+)^2\}\ell^2 - (b + c)AA^*\varepsilon\{Q^*(aH^+{}^*)^2 - Q(aH^+)^2\}\ell$$

$$+ \{A^2Q^*A^*(aH^+)^2 - A^{*2}QA(aH^+)^2\} = 0 \qquad (19)$$

where A, Q, (aH^+) and A*, Q*, $(aH^+{}^*)$ represent two sets of values for corresponding experimental data.

Using equation (19) and the two most widely different values of A, pH and Q for each mole ratio, calculation gives the values of ε tabulated below.

TABLE 32 : CALCULATED ABSORPTION COEFFICIENTS, ε, FOR DIFFERENT RATIOS, x OF $[Fe^{3+}]/\{[Fe^{3+}] + [HOx]\}$

x	$\varepsilon/m^2\ mol^{-1}$
0.4	131.8
0.5	134.7
0.6	107.9

EXPERIMENTAL

Preparation of Solutions

(a) Stock Ferric Perchlorate Solution. (Ferric perchlorate (9.8777 g) was dissolved in 0.1153*M* perchloric acid (200 ml). This was standardized against EDTA solution, freshly prepared by weight from Anala R reagent. The appropriate portion of this solution was diluted with 0.1153*M* $HClO_4$ to prepare the 8.0422×10^{-4}*M* working solution.

The exact strength of the perchloric acid was determined by titration against 0.1*N* sodium carbonate.

(b) Stock Solutions of 8-Hydroxyquinoline and its Methyl-Substituted Derivatives. These solutions ($\sim 10^{-4}$*M*) were prepared by dissolving an accurately weighed amount of each reagent in a fixed volume of 0.1153*M* $HClO_4$.

DETERMINATION OF K^T

As preliminary experiments, absorption spectra of the complexes of each ligand in turn with ferric ion were measured. From these spectra were obtained the maximum wavelength of absorption, λ_{max} of each metal-ligand complex. Other preliminary experiments included the plotting of graphs indicating changes of absorbance with time. From these it was concluded that for all the complexes except the 2-methyl one, maximum colour was attained at approximately 20 minutes after addition of ammonia. Consequently absorbance readings for these complexes were taken 20 minutes after mixing. In the case of the complex of 2-methyloxine and Fe(III), a similar plot (see Fig.15) showed immediate signs of colour fading. Hence all measurements for this complex were taken as soon as

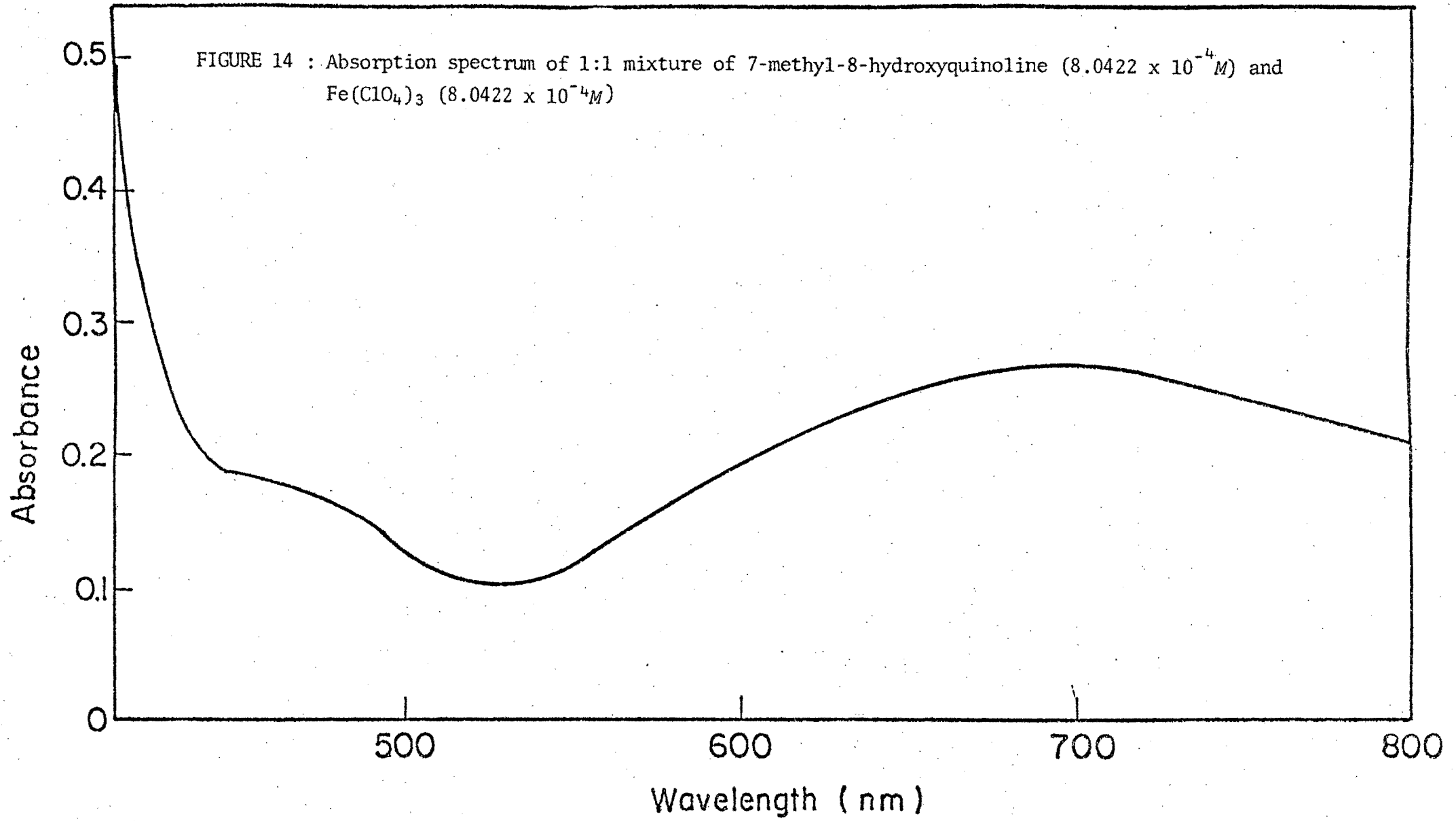


FIGURE 14 : Absorption spectrum of 1:1 mixture of 7-methyl-8-hydroxyquinoline ($8.0422 \times 10^{-4} M$) and $Fe(ClO_4)_3$ ($8.0422 \times 10^{-4} M$)

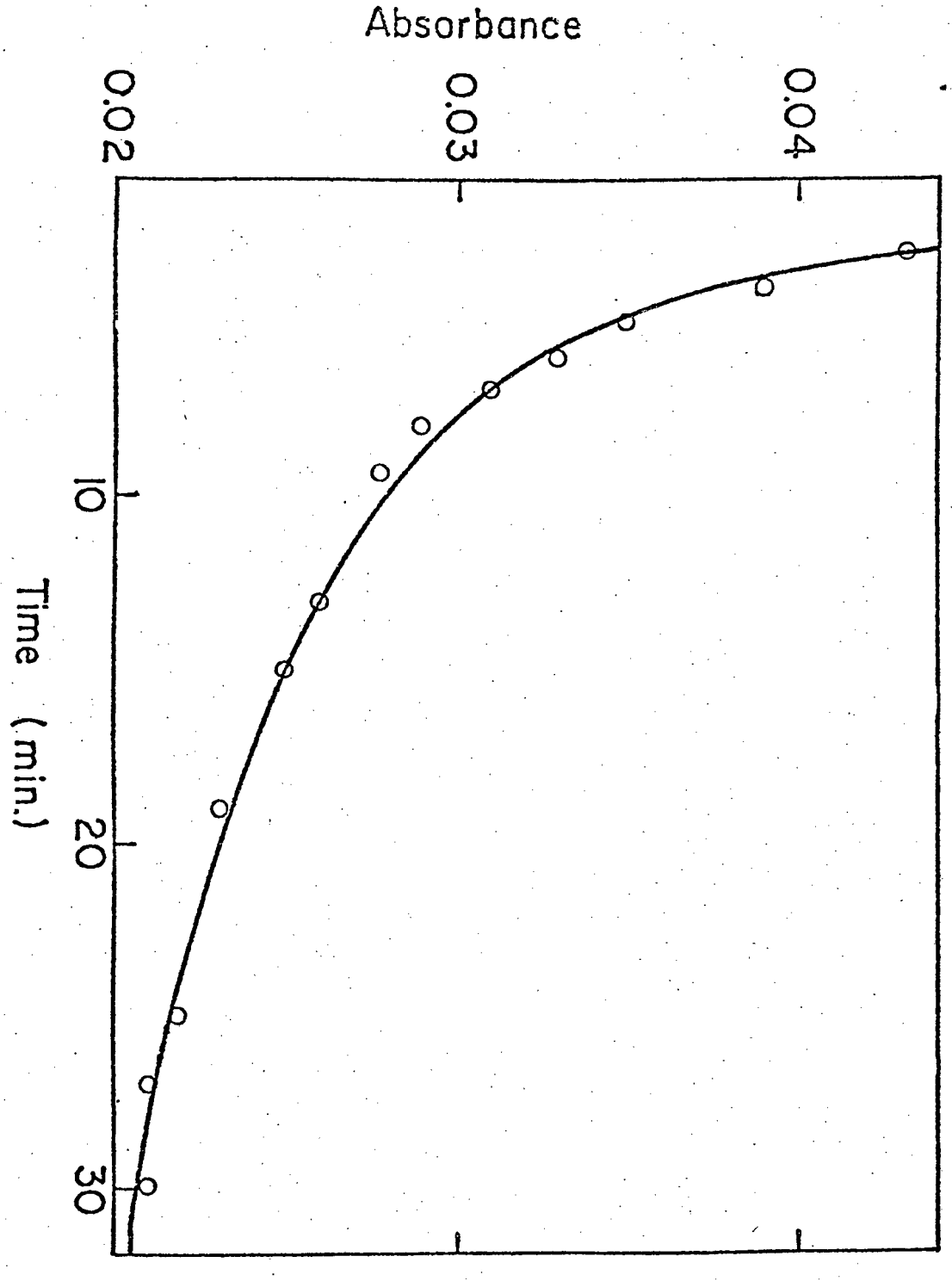


FIGURE 15 : Plot of change in absorbance with time of 1:1 mixture of 2-methyl-8-hydroxyquinoline and $Fe(ClO_4)_3$

possible after the addition of the ammonia.

For each ligand, three solutions were prepared, containing different ratios of $[Fe^{3+}]/([Fe^{3+}] + [HOx])$. Calculations were performed to determine the ionic strength of 20 ml of each solution in a total volume of 25 ml, taking into consideration all the ions present. The addition of the appropriate amount of sodium perchlorate was used to adjust the ionic strength of each sample to 0.1 mol ℓ^{-1}. For each ratio of ligand to iron, a number of absorbance measurements were made at the maximum wavelength of absorption and gradually increasing alkalinities adjusted by adding increasingly small amounts of dilute ammonia. The required amount of each solution (20 ml) was pipetted into a 25 ml volumetric flask. To this was added a small volume of dilute ammonia and the volume made up to 25 ml with distilled water. All absorbance measurements were taken in a 4 cm quartz cell and were immediately followed by pH readings.

TABLE 33 : SUMMARY OF DATA USED IN CALCULATIONS

N = experiment number ; c = total concentration of Fe(III); b = total concentration of oxine (or of a methyl-substituted oxine; Q (see text).

REAGENT	Number of experiment	c/mol dm^{-3}	b/mol dm^{-3}	Q
8-Hydroxyquinoline	1	3.217×10^{-4}	3.728×10^{-4}	1.11
	2	3.217×10^{-4}	3.728×10^{-4}	1.12
	3	3.217×10^{-4}	3.728×10^{-4}	1.17
	4	3.217×10^{-4}	3.728×10^{-4}	1.18
	5	3.217×10^{-4}	3.728×10^{-4}	1.23
	6	3.217×10^{-4}	3.728×10^{-4}	1.25
	7	3.217×10^{-4}	3.728×10^{-4}	1.27
	8	3.860×10^{-4}	2.982×10^{-4}	1.15
	9	3.860×10^{-4}	2.982×10^{-4}	1.17
	10	3.860×10^{-4}	2.982×10^{-4}	1.18
	11	3.860×10^{-4}	2.982×10^{-4}	1.22
	12	3.860×10^{-4}	2.982×10^{-4}	1.24
2-methyl-8-hydroxy-quinoline	13	3.217×10^{-4}	6.872×10^{-4}	1.29
	14	3.217×10^{-4}	6.872×10^{-4}	1.36
	15	3.217×10^{-4}	6.872×10^{-4}	1.40
	16	3.217×10^{-4}	6.872×10^{-4}	1.53
	17	3.217×10^{-4}	6.872×10^{-4}	1.57
	18	3.860×10^{-4}	5.498×10^{-4}	1.31
	19	3.860×10^{-4}	5.498×10^{-4}	1.32
	20	3.860×10^{-4}	5.498×10^{-4}	1.38
	21	3.860×10^{-4}	5.498×10^{-4}	1.50
	22	3.860×10^{-4}	5.498×10^{-4}	1.51
	23	3.860×10^{-4}	5.498×10^{-4}	1.64

REAGENT	Number of experiment	c/mol ℓ^{-1}	b/mol ℓ^{-1}	Q
5-Methyl-8-hydroxy-quinoline	24	2.574×10^{-4}	3.799×10^{-4}	1.10
	25	2.574×10^{-4}	3.799×10^{-4}	1.10
	26	2.574×10^{-4}	3.799×10^{-4}	1.17
	27	2.574×10^{-4}	3.799×10^{-4}	1.52
	28	2.574×10^{-4}	3.799×10^{-4}	2.49
	29	3.217×10^{-4}	3.166×10^{-4}	1.12
	30	3.217×10^{-4}	3.166×10^{-4}	1.16
	31	3.217×10^{-4}	3.166×10^{-4}	1.26
7-Methyl-8-hydroxy-quinoline	32	3.217×10^{-4}	3.217×10^{-4}	1.09
	33	3.217×10^{-4}	3.217×10^{-4}	1.11
	34	3.217×10^{-4}	3.217×10^{-4}	1.13
	35	3.217×10^{-4}	3.217×10^{-4}	1.14
	36	3.217×10^{-4}	3.217×10^{-4}	1.17
	37	3.217×10^{-4}	3.217×10^{-4}	1.22
	38	2.574×10^{-4}	3.860×10^{-4}	1.09
	39	2.574×10^{-4}	3.860×10^{-4}	1.11
	40	2.574×10^{-4}	3.860×10^{-4}	1.13
	41	2.574×10^{-4}	3.860×10^{-4}	1.15
	42	2.574×10^{-4}	3.860×10^{-4}	1.17
	43	2.574×10^{-4}	3.860×10^{-4}	1.20

CHAPTER VII

CALCULATION OF VALUES OF K^T FOR THE FORMATION OF IRON COMPLEXES

CALCULATION OF VALUES OF K^T FOR THE FORMATION OF IRON COMPLEXES, $FeOx^{2+}$

All the data are now available for calculating the thermodynamic formation constants of the species $FeOx^{2+}$ from the above spectrophotometric measurements by employing all the data points (A,pH). These calculations were performed for three slightly different assumed values of the linear decadic absorption coefficient, ε. In each case the standard deviation, s, of the set of measurements was calculated and the value of ε to be used in the later calculations was selected from that which gave the best precision for pK^T.

TABLE 34. THERMODYNAMIC FORMATION CONSTANTS OBTAINED BY CALCULATION USING EQUATION 18

K^T = thermodynamic formation constant for the formation of $FeOx^{2+}$.
s = standard deviation

REAGENT	$\varepsilon/m^2\ mol^{-1}$	$p(K^T)^{-1}$ s	$K^T \times 10^{14}$
8-Hydroxyquinoline	100.0	15.06 ± 0.11	11.5
	120.0	14.93 ± 0.07	8.5
	150.0	14.79 ± 0.08	6.2
			$K^T \times 10^{13}$
2-Methyl-8-hydroxy-	120.0	13.7 ± 0.12	5.5
quinoline	150.0	13.88 ± 0.13	7.6
	180.0	13.76 ± 0.15	5.8
			$K^T \times 10^{15}$
5-Methyl-8-hydroxy-	120.0	15.61 ± 0.14	4.1
quinoline	150.0	15.46 ± 0.09	2.9
	180.0	15.31 ± 0.26	2.0
			$K^T \times 10^{15}$
7-Methyl-8-hydroxy-	120.0	15.69 ± 0.07	4.9
quinoline	150.0	15.56 ± 0.07	3.6
	180.0	15.45 ± 0.09	2.8

The ε values which gave the smallest standard deviation were slightly higher than those calculated previously (see Table 32).
This is scarcely surprising in view of the fact that the reaction does not go to completion and calculation based on experimental results will give values of ε which are lower than the true one.

Each of the following Tables refers to the experimental results for a particular mole-ratio of each ligand.

TABLE 35. EXPERIMENTAL RESULTS FOR COMPLEX OF IRON(III) WITH 8-HYDROXY-QUINOLINE

10 ml of HOx($9.319 \times 10^{-4} M$)
10 ml of Fe^{3+} solution ($8.0422 \times 10^{-4} M$)

A_{645}	pH
0.149	1.91
0.183	1.95
0.280	2.09
0.306	2.12
0.419	2.23
0.454	2.26
0.469	2.29

8 ml of HOx($9.319 \times 10^{-4} M$)
12 ml of Fe^{3+} solution ($8.0422 \times 10^{-4} M$)

A_{645}	pH
0.214	2.03
0.257	2.10
0.294	2.13
0.358	2.20
0.400	2.24

TABLE 36. EXPERIMENTAL RESULTS FOR COMPLEX OF IRON(III) WITH 2-METHYL 8-HYDROXYQUINOLINE

10 ml of HOx ($1.718 \times 10^{-2} M$)
10 ml of Fe^{3+} solution

A_{640}	pH
0.193	2.33
0.244	2.42
0.284	2.47
0.377	2.59
0.411	2.62

8 ml of HOx
12 ml of Fe^{3+} solution (8.0422×10^{-4}M)

A_{640}	pH
0.202	2.36
0.211	2.37
0.248	2.44
0.333	2.56
0.353	2.57
0.451	2.67

TABLE 37. EXPERIMENTAL RESULTS FOR COMPLEX OF IRON(III) WITH 5-METHYL-8-HYDROXYQUINOLINE

10 ml of HOx
10 ml of Fe^{3+} solution

A_{670}	pH
0.177	1.95
0.264	2.06
0.460	2.28

12 ml of HOx
8 ml of Fe^{+} solution

A_{670}	pH
0.109	1.86
0.122	1.88
0.240	2.09
0.766	2.58
1.269	3.04

TABLE 38. EXPERIMENTAL RESULTS FOR COMPLEX OF IRON(III) WITH 7-METHYL-8-HYDROXYQUINOLINE

10 ml of HOx
10 ml of Fe^{3+} solution

A_{670}	pH
0.129	1.80
0.191	1.91
0.260	1.99
0.270	2.00
0.355	2.10
0.456	2.21

12 ml of HOx
8 ml of Fe^{3+} solution

A_{670}	pH
0.132	1.81
0.181	1.91
0.225	1.99
0.284	2.04
0.329	2.09
0.393	2.16

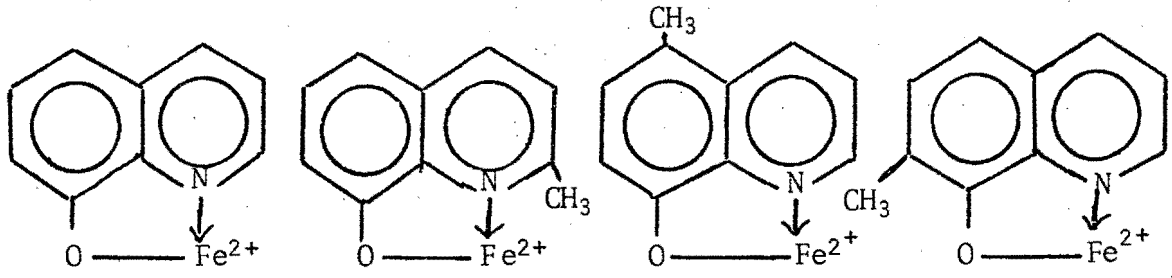
CHAPTER VIII

DISCUSSION

CHAPTER V111

DISCUSSION

The values obtained for the thermodynamic formation constants, K^T show quite definitely that the complexes *3* and *4* are somewhat stronger than *1*.



1 $K^T = 8.5 \times 10^{14}$ *2* $K^T = 5.5 \times 10^{14}$ *3* $K^T = 2.9 \times 10^{15}$ *4* $K^T = 3.6 \times 10^{15}$

This fact, when considered in conjunction with the values obtained for the thermodynamic acid dissociation constants of the parent oxines bears out the prediction that, ignoring steric factors, the complex becomes stronger the more basic the ligand. Since the effect of a methyl group in making electrons more available on the nitrogen atom of a quinoline ring is likely to be similar whether the methyl group is in the 2-, 5- or 7- positions, it is reasonable to suppose that the lesser stability of the complex can be accounted for on a steric basis. Thus ligands with bulky substituents adjacent to one of the donor atoms form much less stable metal-ligand complexes. This, having indeed been observed in the lower value of K^T for this complex, is confirmed by the apparent lack of reaction between 2-methyl 8-hydroxyquinoline and aluminium [3]. From the above results it is also evident that the 7-substituent does not produce steric hindrance to chelate formation as

is observed in the case of the 2-substituent. Although the above formulae are written as if the metal atom were unsolvated it will be realised that the iron will be in octahedral coordination with the O- and N- atoms of the chelating ligand and four water molecules. Models show that a 7-substituent will not approach within Van der Waal radii of the solvated cation whereas any 2-substituent will interfere sterically with the primary water coordinated to it. This effect has been thoroughly investigated and is supported by many measurements of stability constants of *e.g.* substituent oxines and cations such as Mg^{2+}, Zn^{2+}, UO_2^{2+} [27].

CHAPTER 1X

APPENDIX

1. Derivation of the relationship giving K^T for the complex of iron(III) and derivatives of 8-hydroxyquinoline.

In the following derivation of the equation relating K^T with experimentally determinable variables the ligand will be represented as L^- for the sake of generality and to simplify the typing.

We have from Beer's law

$$A = \varepsilon c\ell = \varepsilon[FeL^{2+}]\ell \qquad (A1)$$

and $$(K^T)^{-1} = f_3[Fe^{3+}]f_1[L^-]/f_2[FeL^{2+}] \qquad (A2)$$

where f_n is the activity coefficient of an n-valent ion

let b = the total concentration of oxine (or of one of its methyl-substituted homologues

$$= [H_2L^+] + [HL] + [L^-] + [FeL^{2+}]$$

since we have shown that iron(III) is present as a 1:1 complex.

When the pH is low as in the actual experiments the terms [HL] and $[L^-]$ are very small compared with $[H_2L^+]$ and we can invite

$$b = [H_2L^+] + [FeL^{2+}]$$

Now $[H_2L^+] = (aH^+)^2[L^-]K^T_{Ox}$

where $K^T_{Ox} = K^T_{1,Ox} \cdot K^T_{2,Ox} =$

$$= \frac{(aH^+)[HL]f_o}{[H_2L^+]f_1} \cdot \frac{(aH^+)[L^-]f_1}{[HL]f_o} = 1.62 \times 10^{-16}$$

for example, in the case of 5-methyl-8-hydroxyquinoline (see page 40).

Therefore $[FeL^{2+}] = b - (aH^+)^2[L^-]K_{Ox}^T$ (A3)

Eliminating $[L^-]$ from equations (A2) and (A3)

$$[FeL^+] = b - \frac{(aH^+)^2(K^T)^{-1}f_2[FeL^{2+}]}{f_1f_3[Fe^{3+}]K_{Ox}^T}$$

$$\text{whence } [FeL^{2+}] = \frac{bf_1f_3[Fe^{3+}]K_{Ox}^T}{f_1f_3[Fe^{3+}]K_{Ox}^T + f_2(K^T)^{-1}(aH^+)^2} \quad (A4)$$

and from equation (A1)

$$\frac{A}{\ell} = \frac{\varepsilon f_1f_3K_{Ox}^T[Fe^{3+}]b}{f_1f_3K_{Ox}^T[Fe^{3+}] + f_2(K^T)^{-1}(aH^+)^2} \quad (A5)$$

Over the pH range used in the experiments the species $FeOH^{2+}$ is the only hydrolysed form of iron(III) present in significant amounts so that

c = total molar concentration of iron(III) in all forms

$$= [Fe^{3+}] + [FeOH^{2+}] + [FeL^{2+}]$$

and taking $(aFeOH^{2+})(aH^{+})/(aFe^{3+}) = 2.8 \times 10^{-3}$ [26]

we find $$c = [Fe^{3+}] + 0.0028\, f_3[Fe^{3+}]/f_2(aH^{+}) + \frac{A}{\varepsilon \ell} \qquad (A6)$$

Hence $[Fe^{3+}] = \{c - (A/\varepsilon\ell)\}/Q$

where $$Q = 1 + \{0.0028 f_3/f_2(aH^{+})\} \qquad (A7)$$

Substituting (A7) into (A5)

$$\frac{A}{\varepsilon \ell} = \frac{\varepsilon f_1 f_3 K_{Ox}^{T} b\{c - (A/\varepsilon\ell)\}}{f_1 f_3 K_{Ox}^{T}\{c - (A/\varepsilon\ell)\} + f_2 (K^{T})^{-1}(aH^{+})^2 Q}$$

so that the desired expression becomes

$$(K^{T})^{-1} = \frac{\{c-(A/\varepsilon\ell)\}\{\varepsilon f_1 f_3 K_{Ox}^{T} b - (A f_1 f_3 K_{Ox}^{T}/\ell)\}}{\{f_2 (aH^{+})^2 QA/\ell\}} \qquad (A8)$$

2. Derivation of a relationship giving an approximate value for the molar absorption coefficient, ε, of the complex.

Expression (A8) may be rearranged as follows:

$$(K^T)^{-1} = \frac{\{c\varepsilon - (A/\ell)\}\{b\varepsilon-(A/\ell)\}}{Q(aH^+)^2(A/\ell)} \cdot \frac{f_1 f_3 K^T_{Ox}}{f_2\varepsilon} \qquad \text{(A9)}$$

from which it follows that the first term on the right hand side will be constant in solutions of the same ionic strength. If we now consider two solutions where the total concentration c and b are identical but the pH varies (so that (aH^+), A and Q have the values (aH^{+*}), A^* and Q*) we can write

$$\frac{\{c\varepsilon-(A/\ell)\}\{b\varepsilon-(A/\ell)\}}{Q(aH^+)^2(A/\ell)} = \frac{\{c\varepsilon-(A^*/\ell)\}\{b\varepsilon-(A^*/\ell)\}}{Q^*(aH^{+*})^2(A^*/\ell)}$$

or $\{c\varepsilon-(A/\ell)\}\{b\varepsilon-(A/\ell)\}Q^*A^*(aH^{+*})^2$

$$= \{c\varepsilon-(A^*/\ell)\}\{b\varepsilon-(A^*/\ell)\}QA(aH^+)^2$$

which can be expanded and rearranged in the form

$$bc\ell^2[Q^*A^*(aH^{+*})^2-QA(aH^+)^2]\varepsilon^2$$
$$-(b+c)\ell AA^*[Q^*(aH^{+*})^2-Q(aH^+)^2]\varepsilon$$
$$+ AA^*[AQ^*(aH^{+*})^2-A^*Q(aH^+)^2]$$
$$= 0 \qquad \text{(A10)}$$

which is a quadratic in ε independent of K^T and f_n.

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