THE SOLVENT EXTRACTION OF METAL CHELATES

by

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Thesis presented for the degree of
Doctor of Philosophy
of the University of London

July 1966

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Abstracts

A mathematical formula describing the efficiency of extraction of metals as chelates, from aqueous into organic phase was derived. The formula

$$E = \frac{1}{1 + q[H^{+}]^{m}}$$

which resembles other existing extractability formulae in its final approximation, is, however, original in derivation. Verification of the formula with simple metal oxinates and the possibility of its extension to systems in which hydrolysis of the metal takes place or involve other competing ligands (masking agents) have been investigated.

Enhancement of the selectivity and sensitivity of the 8-hydroxyquinaldine by substitution of **aryl** groups in the 2-position of the pyridine ring of the 8-hydroxyquinoline nucleus has already been investigated by some workers in the field with no success. The possibility of increasing selectivity and sensitivity of this organic reagent has been attempted by substitution of bulky alkyl groups of both powerful inductive and steric effects in the 2-position. Different methods of organic synthesis were examined for the synthesis of

2-ethyl-, 2-*iso*propyl- and 2-*t*.butyl-8-quinolinols.

Synthesis of the first two derivatives, 2-ethyl- and 2-*iso*propyl-8-quinolinols, in reasonable yields has been achieved by application of a suitable method. Preparation of the third derivative, 2-*t*.butyl-8-quinolinol, has been shown out to be possible.

The physical and chemical properties of these two derivatives which included ultraviolet, Infrared, X-ray, sensitivity and selectivity and solvent extraction, etc. have been examined thoroughly and general analytically useful data is presented.

Sensitivity has been shown to be improved, especially with the 2-*iso*propyl derivative, but the apparent selectivity has not improved. A tentative explanation of the increase in sensitivity of the reagents in terms of steric and solubility effects is presented. Application of the new derivatives in the analysis of metals indicate the suitability of the highly substituted derivative, 2-*iso*propyl-, for the analysis by solvent extraction separation followed by spectrophotometry, of aluminium in its alloys where the unsubstituted reagent fails.

To Fathia

Acknowledgements

The author wishes to express his gratitude to his supervisor Dr. D. A. Pantony for his continued interest and guidance throughout the course of this work; also to the United States Air Force for a maintenance bursary; and to his colleagues at the Imperial College for valuable discussions and help.

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CHAPTER ONE

GENERAL INTRODUCTION

Historical Survey

Solvent extraction (liquid-liquid extraction) of metal chelate complexes has, for a long time now, been recognised as a powerful method in separation, but it has not achieved a great advance until recently. This technique enjoys a favoured position among other separation methods because of its ease, simplicity, speed and wide scope. By utilizing apparatus no more sophisticated than a separating funnel, requiring but several minutes to perform, extraction procedures offer much to the analyst. Added to these advantages are cleanliness and the fact that the method does not involve contaminations, such as coprecipitations.

The principle of solvent extraction is the partition or distribution of a solute between two immiscible solvents. This principle has, from the earliest times in technology, been applied in the preparation of perfumes, essential oils, drugs, dyestuffs, etc. However, its application to inorganic problems was not made until 1842, when it was first foreshadowed by Peligot's discovery that uranium (VI) could be extracted with ether from nitric acid(1) and by Skey's proposals (1867) for the separation of cobalt from nickel, gold from platinium and iron from alkaline earths, aluminium, chromium, and manganese and also platinum and nickel, by exploiting the different solubilities of their thiocyanates in ether(2).

Up to forty years ago only the solvent extraction of ferric chloride(3) and gallium trichloride(4) had made impact on general analytical practice. The introduction of the versatile organic reagent (dithizone) by Fischer in 1925 marked a new stage in the solvent extraction and quantitative determination of a considerable number of metal ions(5).

The discovery of other types of chelating agents, e.g. thenoyltrifluoroacetone (TTA), cupferron, dimethylglyoxime, 8-hydroxyquinoline etc., which soon followed, promoted the application of this technique further in the analysis of ores and industrial products.

Basic Concepts

Similar to chromatography, ion exchange, precipitation from homogeneous solution, the principle of separation by solvent extraction is phase distribution (movement of matter across phase boundaries). The phase rule, as defined by Gibbs is;

$$P + F = C + 2$$

where P is the number of phases (in this case 2), F the number of degrees of freedom and C the number of components (1). Solvent extraction is limited to two immiscible solvents with one solute distributed between them which has, therefore, one degree of freedom at constant temperature and pressure. This means that by fixing the activity of the solute in one phase, a_1, the solute activity in the other phase, a_2, remains constant. This relationship was the basis of Nernst partition isotherm(7) which is in turn based on Berthelot and Jungfleish experiments(6). The thermodynamic concept of Nernst law is

$$K_D = \frac{a_2}{a_1} = \frac{\gamma_2 m_2}{\gamma_1 m_1}$$

where K_D represents the metal distribution coefficient, m, the solute concentration in molality, and γ, the molal activity coefficient.

Application of the distribution law to inorganic systems has been attempted in 1941 by Kolthoff and Sandell(8), who laid down the first quantitative description of the extraction process of a metal chelate zinc dithizonate. A full theoretical treatment was presented later by Irving(9), then by Connick and McVey(10), Furman et al.(11), Dyressen(12), Stary(13), Ringbom (14), Morrison and Freiser(15), Schweitzer(16), Oosting(17) and several other authors.

Definitions

Definitions of terms of similar superficial appearance and which are frequently used in this thesis are as follows:

Distribution or Partition Coefficient

A constant ratio exists between the activities of a particular species of solute in one phase and that of the same species in the second phase in equilibrium with it. This is a thermodynamic quantity unaltered by changing chemical conditions although changes of physical conditions, such as temperature bring about changes in it. In most of the work described in this thesis ratios of concentrations can replace those of activities.

Extraction Coefficient or Distribution Ratio

The stoichiometric ratio between the total concentrations of the solute species in the organic phase and that in the aqueous phase.

Extractability

The ratio between the total concentrations of the solute species in the organic phase and that in both organic plus aqueous phases.

Extraction Equilibria

Unlike the phenomenon of liquid-liquid extraction of ion association complexes, which is frequently selective and for which the physical-chemical interpretations are intrinsically complicated, the systems of metal chelate complexes behave as if they were thermodynamically ideal. The reason for this simplicity is attributed to the fact that the partition is of molecular rather than ionic species, the two solvents are highly immiscible and the concentration of the solute is usually low.

The latter restriction arises in two ways. First there is the limited solubility of the organic reagent and still smaller solubility of the metal chelate in the aqueous phase and even in the organic solvent (0.01 M is considered an upper limit). In the second place procedures involving metal chelates are generally used for the solvent extraction of microgram quantities of metals. Concentrations of all the solutes are therfore in the dilute, ideal,solution range even allowing for residues of solvents, buffering agents, etc.

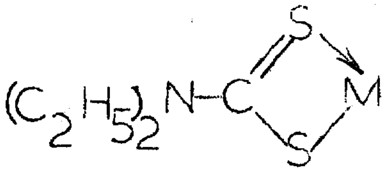
The factors of low concentration and high partition coefficients of, especially, the chelating agent tend to slow down the attainment of equilibration; but achievement of the latter can be approached by the forward and back reactions, i.e. either extraction into the organic phase from a mixture of free metal ions and chelating agent or reversing a previously prepared solution of the metal chelate into the organic solvent. Equilibrium may also be shifted by employing other factors such as excess organic reagent or pH conditiohs which have proved experimentally to affect the equilibrium. The factors influencing equilibria are to be shown to have theoretical basis later.

Solubility - Extraction of Metal Chelates

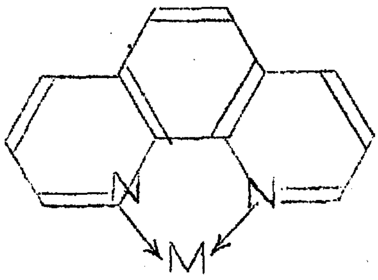
Extraction depends vitally on the formation of extractable complex. Simple metal salts are insoluble in non-polar solvents. This is attributed to their highly ionic nature, as they are strong electrolytes with a large solubility in aqueous media, in which the charged metal ions are co-ordinately bonded to the water of solvation, and to the low dielectric constant of the organic solvents.

Extraction of the metal is promoted by neutralisation of the metal-ion charge, i.e. dehydrating it totally or partially, and by increasing its size through the formation of large neutral molecules with a suitable organic reagent.

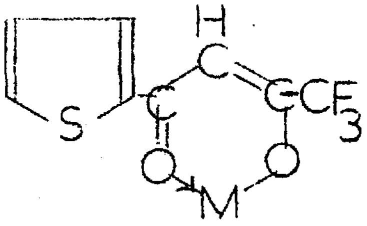
Organic reagents possessing such polyfunctional groups as -OH, -SH, -NH, =O, =S, =N, are capable of replacing the co-ordinated water molecules by occupying two or more positions of the co-ordination sphere of the metal ion to form a cyclic compound. The functional groups of the base must be so situated in the molecule that they permit the formation of a stable ring, four, five and six membered ring, of which the five-membered is most important. For example, the metal chelates of the following reagents:



diethyldithiocarbamate



phenanthroline



thenoyltrifluoroacetone

Formation of the metal chelates follows the **Lewis** electronic theory, which relates covalent-co-ordinate bond formation to acid-base reactions. The metallic cation is electron pair deficient, and may be considered as a polybasic acid capable of reacting with basic entities (electron donors), the number of which is limited by the co-ordination number, x, of the metal.

Stability of the metal chelates produced, according to the same theory, is determined by factors related to the "basicity" of the co-ordinating ligand, e.g. the basic strength of the functional groups; those related to the acidity of the metal such as cationic charge concentration (ionic potential), electronegativity, oxidation state of the metal, available bonding orbitals, the location of these orbitals; and finally special factors related to the configuration of the resultant complex, e.g. the size and number of chelate rings formed.

As the metal in these metal complexes has become part of the organic structure (quasi-organic) and is more or less buried inside the molecule, metal chelates are, therefore, only slightly soluble in water but dissolve readily in organic solvents which they resemble electronically.

The transfer of a metal cation into its organic chelate dissolved in an organic solvent is complex and is shown schematically below:

$$\begin{tikzcd}
M(OH)^{m-1} \arrow[r, shift left, "S_1"] & OH^- + {} \arrow[l, shift left] & M^{n+} + {} & R^{n-} \arrow[r, shift left, "K_c"] & MR_{\frac{m}{n}} \arrow[l, shift left] \arrow[r, shift left, "P_c"] & MR_{\frac{m}{n}}\ (org.) \arrow[l, shift left] \\
 & & + & + & & \\
 & & L^- \arrow[d, shift left, "B_1"] & nH^+ \arrow[d, shift left, "K_R^{\,a}"] & & \\
 & & ML^{m-1} \arrow[u, shift left] & RH_n \arrow[u, shift left] \arrow[d, shift left, "P_R"] & + H_2O \arrow[r, shift left, "K_R^{\,b}"] & H_{n+1}R^+ + OH^- \arrow[l, shift left] \\
 & & & RH_n\ (org.) \arrow[u, shift left] & &
\end{tikzcd}$$

From these relationships it can be seen that the extractability of a metal is dependent upon the following factors: dissociation constant of the metal chelate, K_c; the dissociation constant of the organic reagent, K_R; the partition coefficient of the metal chelate, P_c; the partition coefficient of the organic reagent, P_R; the dissociation constant of the metal hydroxy complex, S_1, the dissociation constant of the metal complex formed with a secondary complexing agent, B_1; also upon

the metal ion M^{m+}
the metal ion concentration
the chelating agent, RH_n
the chelating agent concentration
the pH
the presence of a complexing agent anion in the aqueous phase, OH^- and L^-
the complexing agent concentration
the presence of an adduct-forming substance in the organic phase
the adduct-forming agent concentration
the organic solvent
the temperature
the stability constant of the metal chelate
the equilibrium time and other kinetic factors,

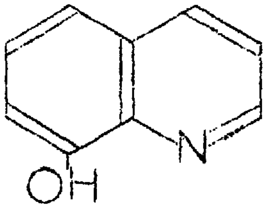
Extraction of the metal with a given organic reagent and organic solvent is especially greatly influenced by the concentration of the organic reagent. The higher the RH_n in the organic phase is, the higher the distribution ratioand the metal chelate formation and the extraction curve is shifted to the acid side, permitting extraction from more acidic solutions. Provided the reagent concentration (and certain other factors) is maintained constant, the distribution of the metal is a function of the hydrogen ion concentration alone. Thus the lower the pH is, the less efficient is the process of metal chelate formation and consequently its distribution.

The extraction of the metal is diminished also in the presence of certain secondary complexing agents. Owing to the production of the non-extractable ionic complexes in the aqueous phase.

By treating the above relationships quantitatively, a number of solvent extraction equilibria have been described for metal chelates.

Details concerning the qualitative pattern of the reactions involved in the metal chelate extraction; description of these reactions mathematically; the approximations encountered, and finally the investigation of the validity of the formula with typical di- and tervalent metal-8-hydroxyquinoline-water-chloroform systems are to be submitted in Chap. II of the thesis.

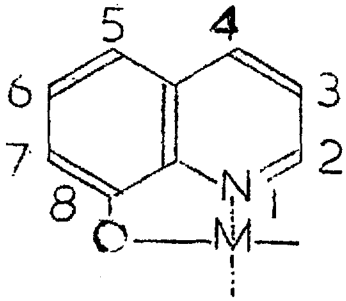
8-Hydroxyquinoline as a Chelating Agent



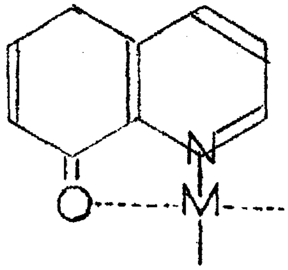
It is obvious that during the last 60 years 8-hydroxyquinoline, 8-quinolinol, "oxine", has proved itself to be a most versatile organic reagent. This is due to its ability to chelate with a wide variety of metals forming insoluble compounds. In many cases the metallic complexes have a stoichiometric composition and may be weighed directly to give the amount of metal.

The fact that different metallic complexes precipitate from solution at different pH's has been utilized for the separation of metals, and the discovery that certain metallic complexes are soluble in organic solvents forming highly coloured solutions, the intensity of which, with few reservations, is proportional to the amount of metal present, has led to the introduction of colorimetric techniques applied to the determination of trace metals in solution.

In oxine, the hydroxy group is so located with respect to the nitrogen atom of the quinoline nucleus that a stable five membered rings are formed with metals. By virtue of its structure two properties are exhibited, namely the phenolic and that of a quinone. As a consequence metals which react with the reagent, forming inner Complex Compounds, may do in two ways: the metal atoms may be bound co-ordinately to the heterocyclic nitrogen atom or to the oxygen atom; in either case a five membered ring is formed.



phenol



quinone

The same holds for the derivatives, with substituents in the 3, 4, 5, 6 or 7 positions since these all contain the same reactive grouping as the parent compound.

8-hydroxyquinoline Derivatives

8-hydroxyquinoline is very "unselective" in its action. It is known to form chelates with well over 50 metals, whereas certain derivatives, with substituents in either the pyridine or the benzene ring, are more "selective", and chelate under the same conditions with slightly fewer metals.

Thus, aluminium forms a stable 3:1 stoichiometric complex with 8-hydroxyquinoline which permits its determination by gravimetric, volumetric and absorptiometric procedures. Several substituted oxines behave similarly, but 2-methyl-8-hydroxyquinoline (8-hydroxyquinaldine) displays a remarkable difference. It was found by Merritt and Walker(18) that while a considerable number of metal ions is reactive with 8-hydroxyquinaldine, the latter would not give a precipitate under any conditions with aluminium. They attributed increased selectivity to increase of size compared with that of 8-hydroxyquinoline, and the difficulty in grouping larger molecules around a small ion. The close proximity of the methyl group to the reactive grouping causes steric hindrance, and the atomic radius of the aluminium is such that it is prevented from entering and forming the complex.

The steric nature of the failure of 8-hydroxyquinaldine to react with aluminium was supported by the observation that 2-phenyl and 2-styryl substituted 8-hydroxyquinoline derivatives would not react with aluminium, while the isomeric compounds with substituents in the 3- and 4-positions would react(20).

Now although the steric hindrance could be the explanation for the case above, however, it does not apply in all cases of non-chelation, as derivatives with substituents in position 5 are known which appear to be more selective in their action, e.g. 5-nitroso-8-hydroxyquinoline will not chelate with tervalent aluminium, gallium, and indium or magnesium under the same conditions in which chelation occurs with the parent compouhd. Increased selectivity cannot here be ascribed to steric hindrance, but rather to the action of nitroso group in the para position to the hydroxy group in increasing the acidity of the chelating function (the plenolic group) with the resultant formation of weaker metallic complexes(19).

The above behaviour of aluminium towards a 2-methyl-8-hydroxyquinoline has been utilized to work out a specific determination of aluminium in binary mixtures, using 8-hydroxyquinaldine to remove the second constituent by solvent extraction and then determining aluminium with 8-hydroxyquinoline by a spectrophotometric technique. The extension of the procedure to complex mixtures where aluminium is a minor constituent has not been wholey successful. Use of secondary complexing agents has improved the method but results have no great advantage over those obtained from existing procedures.

In an attempt to increase the selectivity of the method, preparation of a number of sensitive 8-hydroxyquinoline derivatives substituted in the 2-position with bulky alkyl groups; namely 2-ethyl-, 2-isopropyl- and 2-tert-butyl-, were investigated.

Also the issue of attributing the failure of aluminium to react with a 2-methyl and other 2-substituted 8-hydroxyquinoline, to steric hindrance or to the inductive effect caused by the 2-substituents remains open. It was therefore highly desirable to investigate the problem and attempt to present a clear structural explanation. The introduction of bulky alkyl groups both more inductive and voluminous than the methyl group into the 2-position of the pyridine ring of the 8-hydroxyquinoline nucleus, could clarify the issue either way. Little could be gained from qualitative experiments but quantitative differences between the new reagents should point to the correct mechanism. The results of these investigations are described in Chap. V of this thesis.

CHAPTER TWO

DERIVATIONS OF EXTRACTION EQUILIBRIA RELATIONSHIPS

Quantitative Treatment of Metal Chelates Extraction Equilibria

By consideration of the behaviour of metal chelate as that of a thermodynamically ideal system, and of the concurrent equilibria involved in the extraction process as those of the formation of an uncharged co-ordination complexes in the aqueous phase and the distribution of this extractable chelated species between the two immiscible phases according to the law of distribution(7), a number of quantitative relationships have been elucidated(8, 10, 11, 13, 15, 16, 17, 21), and others.

Here, a formula describing efficiency of extraction of metal chelates from aqueous into organic phases, formed according to the following reaction,

$$nM^{m+} + mRH_n \rightleftharpoons M_nR_m + mnH^+$$

$$\text{or} \quad M^{m+} + \frac{m}{n} RH_n \rightleftharpoons MR_{\frac{m}{n}} + mH^+ \qquad (1)$$

and by taking into account the same considerations, is derived. The final form of the new formula, but not the derivation, which is original, resembles other existing formulae in relating extraction efficiency of the metal to the hydrogen ion concentration raised to the power of the cationic ion charge (valency).

$$E = \frac{1}{1 + q\,[H^+]^m} \qquad (2)$$

During the solvent extraction of a metal ion M^{m+} with a weakly acidic chelating reagent HR, such as 8-hydroxyquinoline and a non-miscible solvent, the following reactions have to be considered:
(Note): unless otherwise indicated, concentrations of any species are those in aqueous phase. No activity corrections are included in these considerations.

1. The reagent dissociates to give the active chelating anion.

$$RH_n \rightleftharpoons R^{n-} + nH^+ \qquad (3)$$

The reagent dissociation is determined by a dissociation constant.

$$K_{R1} = \frac{[R^{n-}]\,[H^+]^n}{[RH_n]} \qquad (4)$$

2. It will be recalled that many organic reagents possess a basic nitrogen atom. Therefore, in the presence of protons the organic reagent can accept these:

$$RH_n + H_2O \rightleftharpoons RH^+_{n+1} + OH^- \qquad (5)$$

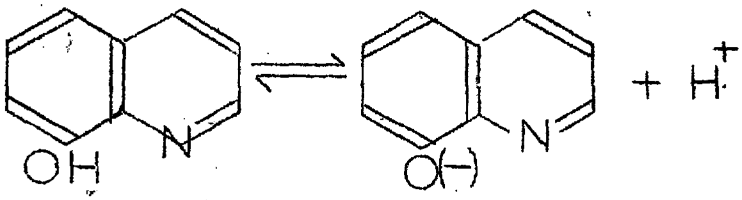
Such dissociation of the reagent is described by a dissociation constant.

$$K_{R2} = \frac{[RH^{+}_{n+1}]\,[OH^{-}]}{[RH_{n}]} \tag{6}$$

and

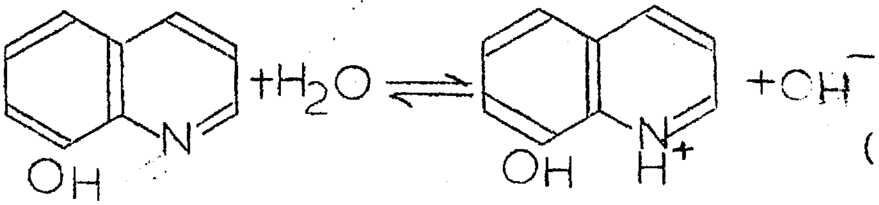
$$K_{RH^{+}} = \frac{[RH_{n}]\,[H^{+}]}{[RH^{+}_{n+1}]}$$

As an example of 1 and 2, 8-hydroxyquinoline dissociation occurs in the following two ways$^{(22)}$



(7)

OX OX^{-}



(8).

OX OX H^{+}

but only the species OX can be extracted into an organic solvent of low dielectric constant.

3. The undissociated organic reagent is extracted by the organic solvent.

$$[RH_n] \rightleftharpoons [RH_n]_{org} \qquad (9)$$

Distribution of the organic reagent between the two immiscible phases is determined by the partition coefficient:

$$P_R = \frac{[RH_n]_{org}}{[RH_n]} \qquad (10)$$

4. The metal ion reacts with the reagent anion to form the metal chelate

$$M^{m+} + \frac{m}{n} R^{n-} \rightleftharpoons MR_{\frac{m}{n}} \qquad (11)$$

The chelate formation is determined by the dissociation constant

$$K_c = \frac{[M^{m+}]\,[R^{n-}]^{\frac{m}{n}}}{[MR_{\frac{m}{n}}]} \qquad (12)$$

The chelate formation may occur stepwise according to the finding of Calvin(23). (For the sake of simplicity n is considered 1.)

$$M^{m+} + R^- \rightleftharpoons MR^{m-1} \qquad K_1 = \frac{[M^{m+}]\,[R^-]}{[MR^{m-1}]}$$

$$MR^+_{m-1} + R^- \rightleftharpoons MR_m \qquad K_m = \frac{[MR_{m-1}]\,[R^-]}{[MR_m]}$$

The overall dissociation constants K_i is the product $K_1K_2K_3 - - - - K_m$.

5. The metal chelate formed is extracted by the immiscible organic solvent.

$$[MR_{\frac{m}{n}}] \rightleftharpoons [MR_{\frac{m}{n}}]_{org} \qquad (13)$$

Distribution of the metal chelate between the two immiscible phases is determined by the partition coefficient.

$$P_c = \frac{[MR_{\frac{m}{n}}]_{org}}{[MR_{\frac{m}{n}}]} \qquad (14)$$

6. The metal ion can be fixed by other competing ions beside the organic reagent anion, e.g. hydroxyl or masking agents anionic groupings:

$$M^{m+} + OH^- \rightleftharpoons M(OH)^{m-1} \; \ldots \text{ etc.} \qquad (15)$$

$$M^{m+} + L^- \rightleftharpoons ML^{m-1} \; \ldots \text{ etc.} \qquad (16)$$

Such reactions are determined by the successive dissociation constants:

$$S_1 = \frac{[M^{m+}]\ [OH^-]}{[M(OH)^{(m-1)+}]} \quad \ldots \text{ etc.} \qquad (17)$$

$$B_1 = \frac{[M^{m+}]\ [L^-]}{[ML^{(m-1)+}]} \quad \ldots \text{ etc.} \qquad (18)$$

Mathematical Derivation of Extractability and Extraction Efficiency

Consider the metal ion, M^{m+}, extracted by the organic solvent, is in the form of chelate and such that no free metal ions or organic reagent anions, R^{n-}, $RH^{(n-1)}$ can be extracted by the organic solvent, then

$$[M^{m+}]_{org} = [R^{n-}]_{org} = RH^{(n-1)} \text{ , etc.} = 0$$

The total organic reagent, T_R, is therefore,

$$T_R = \frac{m}{n} [MR_{\frac{m}{n}}]_{org} \cdot Vorg + \frac{m}{n} [MR_{\frac{m}{n}}]_{aq} \cdot Vaq + [RH_n]_{org} \cdot Vorg$$
$$+ [RH_n]_{aq} \cdot Vaq + [R^{n-}]_{aq} \cdot Vaq + [RH_{n+1}]_{aq} \cdot vaq \quad (19.1)$$

where Vorg and Vaq represent the volumes in litres of the organic and aqueous phases respectively, while the values between square brackets refer to concentrations in $g.Litre^{-1}$.

By substituting appropriate values from eqs. 14 and 10,

$$T_R = \frac{m}{n}\,[MR_{\frac{m}{n}}]_{aq}\ \text{Vorg}\ P_c + \frac{m}{n}\,[MR_{\frac{m}{n}}]_{aq}.\text{Vaq} + [RH_n]_{aq}.\text{Vorg}\ P_R$$

$$+ [RH_n]_{aq}.\text{Vaq} + [R^{n-}]_{aq}.\text{Vaq} + [RH_{n+1}]_{aq}.\text{Vaq} \qquad (19.2)$$

By considering P_c Vorg + Vaq $= \alpha$ (19.3)

and substituting values from eqs. 4 and 6 (Note: unless otherwise indicated, dissociation of the reagent is that of K_{R1}).

$$T_R = \frac{m}{n}\,[MR_{\frac{m}{n}}]_{aq}\ \alpha + \frac{[R^{n-}]\ [H^+]^n}{K_R}\ \text{Vorg}\ P_R + \frac{[R^{n-}]\ [H^+]^n}{K_R}\ \text{Vaq}$$

$$+ [R^{n-}]_{aq}\ \text{Vaq} + \frac{[R^{n-}]\ [H^+]^{n+1}}{K_R K_{RH^+}}\ \text{Vaq} \qquad (19.4)$$

By considering P_R Vorg + Vaq $= \gamma$ (19.5)

and rearranging

$$T_R = \frac{m}{n}\,[MR_{\frac{m}{n}}]_{aq}\ \alpha + [R^{n-}]\ \left(\frac{[H^+]^n}{K_R}.\gamma + \frac{[H^+]^{n+1}}{K_R K_{RH^+}}.\text{Vaq}+\text{Vaq}\right) \qquad (19.6)$$

putting $\dfrac{[H^+]^n}{K_R}.\gamma + \dfrac{[H^+]^{n+1}}{K_R K_{RH^+}}\ \text{Vaq} + \text{Vaq} = \beta$ (19.7)

$$\therefore\ T_R = \frac{m}{n}\,[MR_{\frac{m}{n}}]_{aq}\ \alpha + [R^{n-}]\ \beta \qquad (19.8)$$

Following a similar treatment for the total metal, T_M,

$$T_M = [MR_{\frac{m}{n}}]_{org}\ Vorg + [MR_{\frac{m}{n}}]_{aq}\ Vaq + [M^{m+}]_{aq}\ Vaq \quad (20.1)$$

By substitution from eq. 14

$$T_M = [MR_{\frac{m}{n}}]_{aq}\ Vorg\ P_c + [MR_{\frac{m}{n}}]_{aq}\ Vaq + [M^{m+}]_{aq}\ Vaq \quad (20.2)$$

and by further substitutions of the value

P_c Vorg + Vaq = α from eq. 19.3 and that of $[M^{m+}]_{aq}$ from eq. 12

$$T_M = [MR_{\frac{m}{n}}]_{aq}\ \left(\alpha + \frac{K_c\ Vaq}{[R^{n-}]^{\frac{m}{n}}}\right) \quad (20.3)$$

From eqs. 19.8 and 20.3

$$[MR_{\frac{m}{n}}]_{aq} = \frac{T_R - \beta[R^{n-}]_{aq}}{\alpha .\ \frac{m}{n}} = \frac{T_M}{\alpha + \frac{K_c\ Vaq}{[R^{n-}]^{\frac{m}{n}}}} \quad (21.1)$$

$$\therefore\ \alpha .\frac{m}{n}\ T_M = \alpha\ T_R - \alpha\beta\ [R^{n-}]_{aq} + \frac{T_R K_c Vaq}{[R^{n-}]^{\frac{m}{n}}} - \frac{\beta K_c Vaq}{[R^{n-}]^{\frac{m}{n}-1}} \quad (21.2)$$

$$\therefore \quad \alpha . \frac{m}{n} T_M \, [R^{n-}]^{\frac{m}{n}} - \alpha T_R \, [R^{n-}]^{\frac{m}{n}} + \alpha\beta \, [R^{n-}]^{\frac{m}{n}+1} +$$

$$\beta \, K_c \, Vaq \, [R^{n-}] - T_R K_c Vaq = 0 \tag{21.3}$$

$$0 = - \alpha\beta \, [R^{n-}]_{aq}^{\frac{m}{n}+1} + \alpha \, (T_R - \tfrac{m}{n} T_M) \, [R^{n-}]^{\frac{m}{n}} -$$

$$\beta \, K_c \, Vaq \, [R^{n-}] + T_R K_c Vaq \tag{21.4}$$

From the earlier definition of extractability as the ratio between the total quantity of metal in the organic phase and that in both organic plus aqueous phases, and by assuming that only one metal chelate species exists in both phases of the simple metal chelate systems treated,

$$\therefore \quad E = \frac{[MR_m]_{org} \, Vorg}{T_M} \tag{22.1}$$

By substitution of the appropriate values from eqs. 14 and 20.3

$$E = \frac{[MR_m]_{aq} \, P_c \, Vorg}{[MR_m]_{aq} \left(\alpha + \dfrac{K_c Vaq}{[R^{n-}]^{\frac{m}{n}}}\right)} \tag{22.2}$$

$$= \frac{P_c \ Vorg}{\alpha + \frac{K_c \ Vaq}{[R^{n-}]^{\frac{m}{n}}}} \qquad (22.3)$$

On substituting the value of R^{n-} from eq. 21.4 which corresponds to the approximate value obtained when considering β and K_c in the third term very small in reasonably acid solution and T_R and Vaq of the last term to be small too, compared with unity,

$$- \alpha\beta \ [R^{n-}]_{aq} + \alpha \ (T_R - \frac{m \ T_M}{n}) = 0 \qquad (21.5)$$

$$\therefore \ [R^{n-}]_{aq} = \frac{T_R - \frac{m \ T_M}{n}}{\beta} = \frac{nT_R - mT_M}{n \ \beta} \qquad (21.6)$$

Extractability becomes,

$$E = \frac{P_c \ Vorg}{\alpha + \frac{K_c Vaq \ n^{\frac{m}{n}} \ \beta^{\frac{m}{n}}}{(nT_R - mT_M)^{\frac{m}{n}}}} \qquad (22.4)$$

$$= \frac{Vorg \ P_c \ (nT_R - mT_M)^{\frac{m}{n}}}{\alpha(nT_R - mT_M)^{\frac{m}{n}} + K_c \ Vaq \ n^{\frac{m}{n}} \ \beta^{\frac{m}{n}}} \qquad (22.5)$$

By putting the value $\beta = \frac{[H^+]^n}{K_R}.Y + \frac{[H^+]^{n+1}}{K_R K_{RH^+}} Vaq + Vaq$

from eq. 19.7

$$E = \frac{\text{Vorg}\ P_c(nT_R - mT_M)^{\frac{m}{n}}}{\alpha(nT_R-mT_M)^{\frac{m}{n}} + K_c\text{Vaq}\ n^{\frac{m}{n}}\left[\frac{[H^+]^n}{K_R}.Y + \frac{[H^+]^{n+1}}{K_RK_{RH^+}}\text{Vaq}+\text{Vaq}\right]^{\frac{m}{n}}} \qquad (22.6)$$

By substitution of the value $P_c\text{Vorg} + \text{Vaq} = \alpha$ from eq. 19.3 and the value of y from eq. 19.5

$$E = \frac{\text{Vorg}\ P_c(nT_R-mT_M)^{\frac{m}{n}}}{(P_c\text{Vorg}+\text{Vaq})(nT_R-mT_M)^{\frac{m}{n}} + K_c\text{Vaq}n^{\frac{m}{n}}\left[\frac{[H^+]^n}{K_R}(P_R\text{Vorg}+\text{Vaq}) + \frac{[H^+]^{n+1}}{K_RK_{RH^+}}\text{Vaq}+\text{Vaq}\right]^{\frac{m}{n}}} \qquad (22.7)$$

By considering $P_c\text{Vorg} \gg \text{Vaq} \ll \frac{[H^+]^N}{K_R}(P_R\ \text{Vorg})$ at pH's lower than 8 and $n = 1$ and rearranging the equation

$$E = \frac{\text{Vorg}\ P_c(nT_R-mT_M)^{\frac{m}{n}}}{P_c\text{Vorg}(nT_R-mT_M)^{\frac{m}{n}}+K_c\text{Vaq}n^{\frac{m}{n}}\left[\frac{[H^+]^n}{K_R}(P_R\text{Vorg}+\frac{[H^+]}{K_{RH^+}}\text{Vaq}\right]^{\frac{m}{n}}} \qquad (22.8)$$

If $n > 1$ then this only holds for more acid solutions

~pH 4. By dividing the numerator and denominator by $\mathrm{Vorg}\ P_c(nT_R-mT_M)^{\frac{m}{n}}$

$$E = \frac{1}{1 + \frac{K_c\ \mathrm{Vaq}}{P_c\ \mathrm{Vorg}} \left(\frac{n}{nT_R-mT_M}\right)^{\frac{m}{n}} \left[\frac{[H^+]^n}{K_R}\left(P_R\ \mathrm{Vorg} + \frac{[H^+]}{K_{RH^+}}\ \mathrm{Vaq}\right)\right]^{\frac{m}{n}}} \tag{22.9}$$

or

$$E = \frac{1}{1 + \frac{K_c\ \mathrm{Vaq}}{P_c\ \mathrm{Vorg}} \left[\frac{1}{K_R}\ \left(\frac{n}{nT_R-mT_M}\right)\left(P_R\ \mathrm{Vorg} + \frac{[H^+]}{K_{RH^+}}\ \mathrm{Vaq}\right)\right]^{\frac{m}{n}}[H^+]^m} \tag{23.1}$$

Various reasonable approximations can be made: for example, experimentally $nT_R > mT_M$ and it may be assumed that the volume of solvents do not exceed a ratio of 10:1 while P_c is very large (i.e. $\gg$ 1000) then,

$$E = \frac{1}{1 + \frac{K_c\ \mathrm{Vaq}}{P_c\ \mathrm{Vorg}} \left(\frac{\mathrm{Vorg}\ P_R}{K_R T_R} + \frac{[H^+]}{K_R T_R K_{RH^+}}\mathrm{Vaq}\right)^{\frac{m}{n}}\ [H^+]^m} \tag{23.2}$$

and for a given system the equation may be reduced to

$$E = \frac{1}{1 + q\,[H^+]^m} \qquad (2)$$

However, above pH 8, protonated oxine species are not to be expected in the system, therefore, the value $\frac{[H^+]^{n+1}}{K_R K_{RH^+}}Vaq$ in eq. 19.7 is to be ignored; and eq. 22.7 become

$$E = \frac{Vorg\ P_c(nT_R-mT_M)^{\frac{m}{n}}}{(P_cVorg+Vaq)(nT_R-mT_M)^{\frac{m}{n}} + K_cVaqn^{\frac{m}{n}}\left\{\frac{[H^+]^n}{K_R}(P_RVorg+Vaq)+Vaq\right\}^{\frac{m}{n}}}$$

(24.1)

By considering $P_cVorg \gg Vaq$ in the first term and on dividing the numerator and demominator by Vorg $P_c(nT_R-mT_M)^{\frac{m}{n}}$

$$E = \frac{1}{1 + \frac{K_cVaq}{P_c\ Vorg}\left(\frac{n}{nT_R-mT_M}\right)^{\frac{m}{n}}\left\{\frac{[H^+]^n}{K_R}(P_RVorg+Vaq) + Vaq\right\}^{\frac{m}{n}}}$$

(24.2)

By making similar approximations to those of eq. 23.1

i.e. considering $nT_R > mT_M$, the volume of solvents do not exceed of a ratio 10:1 and $P_c \gg 1000$ and rearranging the equation,

$$E = \frac{1}{1 + \frac{K_c\ Vaq}{P_c\ Vorg}\left\{\frac{P_R\ Vorg+Vaq}{K_R T_R} + \frac{Vaq}{T_R}\right\}^{\frac{m}{n}} [H^+]^m} \qquad (24.3)$$

Here, the small values of Vaq and $\frac{Vaq}{T_R}$ inside the big brackets may be neglected also, on a further approximation

$$E = \frac{1}{1 + \frac{K_c\ Vaq}{P_c\ Vorg}\left\{\frac{P_R\ Vorg}{K_R\ T_R}\right\}^{\frac{m}{n}} [H^+]^m} \qquad (24.4)$$

and for a given system the equation can also be reduced to

$$E = \frac{1}{1 + Z\ [H^+]^m} \qquad (2)$$

Derivation of Coefficient of Extraction,

Extractability from eq. 2:

$$E = \frac{1}{1 + q\,[H^+]^m} \qquad (2)$$

which is, in turn, equal to the ratio between the total quantity of metal in the organic phase and that in both organic plus aqueous phases, i.e.

$$E = \frac{[RM]_{org}}{[RM_{org}] + [RM]_{aq}} \qquad (25.1)$$

and assuming that only the fully co-ordinated metal chelate species exists in both aqueous and organic phases.

Therefore,

$$\frac{1}{E} = 1 + \frac{[RM]_{aq}}{[RM]_{org}} \qquad (25.2)$$

However, the ratio $\frac{[RM]_{org}}{[RM]_{aq}}$ is equal to the coefficient of extraction (from the earlier definition)

$$\therefore \quad \frac{1}{E} = 1 + \frac{1}{\theta} \qquad (25.3)$$

or $\frac{1}{\Theta} = \frac{1}{E} - 1$

On substituting the value of E from eq. 2

$$\frac{1}{\Theta} = 1 + q\,[H^+]^m - 1 \qquad (25.4)$$

$$\therefore\ \frac{1}{\Theta} = q\,[H^+]^m$$

and the logarithmic form of the equation

$$\log \Theta = -\log q - m \log [H^+] \qquad (25.5)$$

which is $\log \Theta = -\log q + mpH \qquad (25.6)$

By representing log q equal to constant K, $p\Theta = k - mpH$. (25.7)

It can be seen that eqs. 23.2 and 24.4 have highlighted the relationships between the extractability of a metal with a given reagent and organic solvent, and the properties of the solvent and metal chelate system; K_c , K_R, K_{RH}, P_c, P_R and of the variables T_R and $[H^+]$ which are subject to the experimental variation for a given system.

Effect of pH

Extractability of the metal is shown by the previous equations to be a function of pH of the aqueous phase and the total amount of the organic reagent. Due to limitations to be stated later, it is seldom possible to change the concentration of reagent more than 10- or 100- fold. The hydrogen ion concentration can, however, be varied over a range of more than 14 powers of 10. Therefore by maintaining the reagent concentration constant, and provided equilibrium has been attained, the extractability becomes almost a function of pH alone (eq. 2). According to eq. 2, theoretical prediction of the extractability of metal is possible for every value of pH, if q is known. The extraction curves plotted from extractability vs. pH are expected a series of symmetrical sigmoid curves similar to those obtained by Irving et al.(9) based on the application of a similar formula. The steepness of the curves should bear the same relation with the metal ion charge, i.e. increase with increasing valency. This is obvious from eq. 25.7, whereby the increase one unit in the pH will increase the coefficient of extraction tenfold in the case of univalent metal ions, but 100-, 1,000- and 10,000-fold for divalent tervalent and tetravalent metal ions respectively.

Influence of the Concentration of the Organic Reagent

It may be noted from eqs. 23.2, 24.4 that the higher the total reagent, T_R, the higher the yield of the active chelating anion resulting from the reagent dissociation and the higher the extractability and the extraction curve is shifted to the acid side, permitting extraction from more acidic solutions. The use of high concentrations of the organic reagent is thus advantageous especially for the extraction of metals which are easily hydrolysed. Practical considerations often limit the permissible variation in the magnitude of the latter parameter. The upper limit is set by the solubility of the reagent in the organic solvent used, which is often small; the lower limit is given by the formation of non-extractable hydroxycomplexes. Besides, large excess of the reagent affects the spectrophotometric measurements of the metal chelates extracts particularly those which have absorption maxima close to that of the chelating agents. As a consequence, the total concentration of reagent is practically bound to certain limits and rarely does the ratio of these exceed 10:1, which, for a bidentate reagent-bearing two anionic basic groups, and bivalent ion, corresponds to an equivalent pH change of one.

Influence of K_R and P_R and the Association with K_c and P_c

It becomes evident from the same equations that the higher the P_R/K_R ratio, the lower is the extractability of the metal, and the extraction curve is shifted towards the alkaline side. The influence of the ratio K_c/P_c, however, is more complicated. This is due to the strong correlations existing between K_c and K_R, on one hand, and P_c and P_R on the other. The variation of the logarithms of the formation constants of the co-ordination compounds of Cu^{2+}, Ni^{2+}, Ba^{2+} with structurally similar β-diketones has been found to be, at least empirically, an essentially linear function of the negative logarithms of the dissociation constants of the β-diketones(53). The partition coefficients of metal chelates of a particular metal, bear a linear relationship with the partition coefficients of the different chelating agents applied in the extraction, thehigher the partition of the organic reagent, the higher expected the active chelating anion and the complex formation equilibrium is shifted to the right.

Influence of the Immiscible Solvents

The volume of immiscible phases affect extraction. Eq. **24.4** shows that the volume of organic phase is of subordinate effect compared with that of the aqueous phase. For example, if m/n = 1, then the Vorg term disappears. Therefore, the greater the bulk of the aqueous phase is, the lower the distribution of the metal.

However, the structure of the organic solvent still influences the distribution of both reagent and metal chelate since it affects P_R and P_c.

Calculation of Extractability, E

Verifications of the formulae were made as follows:

Initially, simple metal-chelating reagent-water-chloroform systems which do not involve additional complexes, hydrolysing or masking agents and the metal chelates of which are of high partition coefficients were chosen for such investigations. They are those of cupric and ferric oxinates which are typical examples of simple di- and ter-valent metal chelates. Monovalent metal chelates such as silver oxinate has not been considered in these investigations because of its low partition coefficient and to which the approximation formulae are inapplicable.

For a full treatment, the constants K_c, K_R, P_R and

P_c of the above two metal chelate systems have to be known.

Many data regarding the dissociation constants of the oxine(24) and metal oxinates(25) have already been published.

Although the partition coefficient of oxine between chloroform and water has been reported by different workers(24), the values, however, were contradicting; log P_R ranged from 2.3 to 2.81. Determination of this constant was, therefore, necessary. It was made according to the extractability formula:

$$E = \frac{1}{1 + \frac{Vaq}{P_R\ Vorg}\left(1 + \frac{K_1}{[H^+]} + \frac{[H^+]}{K_2}\right)}$$

from the known experimental values of E at 22°, Vaq, Vorg, $[H^+]$ and the well known dissociation constants of the reagent: $K_1 = 10^{-9.66}$ and $K_2 = 10^{-5.0}$ (54).

An average value is obtained from 6 to 8 determinations. Here, seven partition coefficient determinations gave values ranged between 2.38 and 2.52, with an average of 2.48. This value is satisfactory and it agrees closely with the figure given by Moeller et al.(55), 2.55.

Regarding the partition coefficients of the cupric and ferric oxinates, no reference was available. This necessitated their determination experimentally. Measurements of the two partition coefficients of the metal chelates under investigation between water and chloroform phases, by existing partition coefficient methods(26, 27), produced unsatisfactory results. Partition coefficients according to Sandall et al. method(26) was made from separate metal chelate solubility measurements in aqueous and organic phases. The objections to this method are:

a. The solubility of themetal chelate in water was made at pH's 0.75-2.00 and 6. Experimentally the solubility figure obtained at the lower pH range was high, hence the partition coefficient is low.

b. Also, the equilibrium time ranged between 30-120 minutes was considered insufficient to bring about equilibration. This is expected from the ratio between the large bulk of the water solvent and the negligably small quantity of the solute, its poor 'wetting' qualities, and the slowness of attainment of equilibrium.

Partition coefficient measurement made according to Hoste et al. method(27) by equilibrating an aqueous solution of the metal with an organic phase containing excess reagent, at a non-specified pH resulted in low partition values. Measurements of the solubility of the metal chelate in the aqueous phase which was made by back extraction into an organic solvent produced a high result. This erroneous result may be attributed to the fact that the aqueous phase after equilibration was still saturated with the metal chelate, and the attempts to separate completely the organic solvent by centrifuging the aqueous phase were impractical.

Determination of the Partition Coefficients of Metal Oxinates

A. Solubility of the Metal Oxinate in Chloroform

The measurement which is based on Geiger and Sandell method(26) is made by equilibrating 20-30 mg. of the anhydrous metal oxinate for 24 hours with 2 mls. of chloroform, using continuous mechanical shaking. After filtration through a sintered glass disc, the absorption of the filtrate suitably diluted with chloroform was determined at the respective wavelength of maximum absorption in a high precision spectrophotometer (Hilger Uvispec H700). Solubility measurements thus produced were of good agreement. An average value in g.mole.litre^{-1} was obtained from 6 to 8 experiments.

B. Solubility of the Metal Oxinate in Water

It is determined by equilibrating about 0.2 g. of the anhydrous metal oxinate with 1 litre of double distilled water of a neutral pH (6 ± 1) for 24 hours, again with vigorous mechanical shaking, and then back-extracting the metal oxinate from 500 ml. of the filtered aqueous phase by shaking with chloroform. After suitable dilution with shloroform, optical density of the chloroform extract is determined at a proper wavelength and the reading is compared with a standard graph produced from metal oxinate of known concentrations vs. optical density measurements. The metal chelates studied were virtually non-ionised, even bearing in mind the effect of hydrogen ion concentration (10^{-7} M) in the aqueous solution. This is evident from potentiometric studies of the ionic copper in the aqueous filtrate, obtained after equilibration with copper oxinate at pH 6. The procedure was that an equilibrium was established between the metal chelate and cu-electrode, and the potential difference was measured with the aid of Dynacap pH meter and a saturated calomel-electrode.

This electrode system is sensitive to copper ion concentrations of the order of 10^{-4} M. With the copper oxinate solution investigated, no reproducible potentials were obtained and hence it was concluded that the free metal ion concentration was much less than 10^{-4} M.

C. Partition coefficient

$$= \frac{\text{solubility (g.mole.litre}^{-1}\text{) in CHCl}_3}{\text{solubility (g.mole.litre}^{-1}\text{) in H}_2\text{O}}$$

Table I. Solubility and partition coefficient values of metal oxinates.

Metal oxinate	Solubility in chloroform g.mole.litre^{-1}	Solubility in water g.mole.litre^{-1}	Partition Coefficient
$Cu(OX)_2$	$3.45 \cdot 10^{-3}$	$7.50 \cdot 10^{-8}$	$4.6 \cdot 10^{4}$
$Fe(OX)_3$	$2.07 \cdot 10^{-2}$	$1.67 \cdot 10^{-6}$	$1.2 \cdot 10^{4}$
$Ni(OX)_2$	$5.02 \cdot 10^{-2}$	$1.31 \cdot 10^{-6}$	$3.8 \cdot 10^{4}$

Solubility measurements of metal oxinates in both water and chloroform solvents, obtained according to the above procedures were found satisfactory. The differences between results were within the acceptable limits, e.g. the values for copper oxinate solubility in water, obtained from eight determinations were ranging from $2.8 - 10^{-8}$ to $1.1 - 10^{-7}$ with an average value of $7.5 \cdot 10^{-8}$, while, the solubility of the same oxinate in chloroform, in six experiments gave values ranging from 3.36 to $3.52 \cdot 10^{-3}$ and an average of $3.45 \cdot 10^{-3}$.

Nevertheless, these experiments are open to some criticism for reasons given above, and because it is not necessarily valid to assume that the ratios of concentrations in saturated solutions in chloroform and water are identical with the partition coefficients. Indeed, such a method(65) for the reagent gives results a multiple 2.4 high compared with the rational indirect method. This discrepancy is likely to be enhanced in the case of the chelates. However, the approach gives results which are probably in the right order and in the absence of better data they are used in all subsequent calculations.

Extractability (Experimental)

The cation is extracted from water into chloroform phase as its 8-hydroxyquinolinate complex, by equilibration at different measured pH's, with oxine. At each pH value the optical density (absorption) of the organic phase is measured hence its extractability, and graphically related to the hydrogen ion concentration conveniently plotted as pH.

Reagents: All chemicals are of A.R. purity.

Extraction efficiency is defined as

$$E = \frac{\text{total quantity of metal in the organic phase}}{\text{total quantity of metal in both organic and aqueous phases}}$$

Because the Beer-Lambert Law is obeyed extremely exactly by the metal-8-hydroxyquinolinate complexes, therefore E can equally well be expressed in terms of absorption in the organic phase.

$$E = \frac{\text{measured optical density}}{\text{maximum optical density}}$$

In summary, therefore, the following parameters of equations 23.2 and 24.4 have been or can be obtained experimentally: E, P_c, Vaq, Vorg, T_R, P_R and $[H^+]$; while K_R and to some extent, K_c, are available in the literature.

Extractability (Theoretical)

This is calculated from the formulae, using the previously reported constants and the experimental values for Vaq, Vorg, T_R and $[H^+]$.

Checking the Validity of the Formula

The experimental extraction curves for Fe^{3+}, Cu^{2+} and Ni^{2+} oxinates were plotted from the corresponding extractability values, measured between the minimum ($\sim$ 1) and maximum ($\sim$ 4) pH values of extraction vs. the pH Figs. I and II. They are in the form of apparently sigmoid curves, the slopes of which depend mainly on the charge of the metal ion species present in the aqueous phase.

The theoretical curves should obviously be similar to the experimental and in good congruence with them.

However, the expected and found extractability curves, although agreeing generally with sigmoid shape and slope were found to be displaced by up to 0.5 pH unit.

Experimentally measured parameters such as E, Vaq, Vorg, T_R and $[H^+]$ were subject to minor errors only, values of K_R and K_{RH^+} appear to be acceptable, while P_R although quoted value is given as $10^{2.81}$ has been redetermined as 3.02×10^2. The two most doubtful parameters are undoubtedly those of K_c (published values) and P_c (own values). The criticism of evaluation of P_c has been given earlier in this thesis, and methods used for the determinations of K_c are inconsistent or are based on single unsubstantiated experiments.

In equation 22.8 or its approximation for low pH's (23.2) it therefore becomes useful to evaluate the ratio K_c/P_c from the accurately measured extractability values at different pH's in conjunction with other experimental parameters and the reasonably reliable values for P_R, K_R and K_{RH^+} , according to the following arrangement of the formula:

$$K_c/P_c = \frac{1 - E}{E\,\frac{Vaq}{Vorg}\left(\frac{P_R Vorg}{T_R K_R} + \frac{[H^+]}{K_R T_R K_{RH^+}}\,Vaq\right)^{\frac{m}{n}}\;[H^+]^m}$$

The following are the ratios K_c/P_c for the investigated metal oxinates determined accordingly. Each value is an average calculated from three extractability values located at different positions on the curve.

Metal Oxinate	K_c/P_c
Ferric oxinate	1.0×10^{-38}
Cupric oxinate	5.4×10^{-25}
Nickel oxinate	4.3×10^{-22}

The extractability equations are thus useful in two ways: first for the determination of the extractability of a metal at different pH's, provided accurate data regarding the other various parameters are available; and second for the determination of the stability constants of the metal chelates as seen above, i.e. from extractability values obtained from a graph plotted from experimentally determined extractability vs. pH, provided only one metal chelate species is formed in the aqueous phase, the partition of which is very accurately measured.

Example:

Determination of extractability of nickel as oxinate from aqueous into chloroform phase at pH 2.9, if the following are known:

The ratio K_c/P_c for $Ni(OX)_2$	4.3×10^{-22}
Volume of the aqueous phase	0.050 litre
Volume of the organic phase	0.025 litre
Partition of the oxine between water and chloroform	3×10^2
Dissociation constants of the oxine	K_R $10^{-9.66}$ and K_{RH^+} $10^{-5.0}$
Total reagent concentration (oxine)	1.72×10^{-3} M

$$E = \frac{1}{1 + \frac{K_c}{P_c}\frac{Vaq}{Vorg}\left(\frac{P_R Vorg}{K_R T_R} + \frac{[H^+]}{K_R T_R K_{RH^+}} \ Vaq\right)^{\frac{m}{n}} \ [H^+]^m}$$

$$= \frac{1}{1 + 4.3 \times 10^{-22} \times \frac{0.050}{0.025}\left(\frac{3.0\times10^{2}\times10^{-2}\times2.5}{10^{-9.66}\times1.72\times10^{-3}} + \frac{1.26\times10^{-3}\times5\times10^{-2}}{10^{-9.66}\times1.72\times10^{-3}\times10^{-5}}\right)^{\frac{2}{1}} [1.59 \times 10^{-6}]}$$

$= 0.36.$

Determination of the K_c/P_c Ratio of $Ni(OX)_2$

Experimental extractability at three pH values

E at pH 2.6 = 0.23

E at pH 2.9 = 0.55

E at pH 3.5 = 0.86

$$E = \frac{1}{1 + K_c/P_c \frac{Vaq}{Vorg} \left(\frac{P_R Vorg}{K_R T_R} + \frac{[H^+]}{K_R T_R K_{RH^+}} Vaq\right)^{\frac{m}{n}} [H^+]^m}$$

where			Reference
K_c/P_c	=	?	
E	=	0.23, 0.55, 0.86	Experimental
Vaq	=	0.050 litre	"
Vorg	=	0.025 litre	"
P_R	=	3 02	Own value
K_R	=	$10^{-9.66}$	(54)
K_{RH^+}	=	$10^{-5.0}$	(54)
T_R	=	1.72×10^{-3} M	Experimental
m	=	2	
n	=	1	
pH	=	2.6, 2.9, 3.5 respectively	Experimental

$$K_c/P_c = \frac{1 - E}{E.\frac{Vaq}{Vorg} \left(\frac{P_R Vorg}{K_R T_R} + \frac{[H^+]}{K_R T_R K_{RH^+}} Vaq\right)^{\frac{m}{n}} [H^+]^m}$$

K_c/P_c at pH 2.6

$[H^+] = 2.5 \times 10^{-3}$

$[H^+]^2 = 6.25 \times 10^{-6}$

$E = 0.23$

$$K_c/P_c = \frac{1 - 0.23}{0.23 \times \frac{0.050}{0.025}\left(\frac{3\ 02 \times 0.025}{10^{-9.66} \times 1.72 \times 10^{-3}} + \frac{2.5 \times 10^{-3} \times 5.0 \times 10^{-2}}{10^{-9.66} \times 1.72 \times 10^{-3} \times 10^{-5}}\right)^2}$$

$$\frac{}{6.25 \times 10^{-6}}$$

$$= \frac{0.77}{0.46\ (4.39 \times 10^{12.66} + 7.26 \times 10^{12.66})^2\ 6.25 \times 10^{-6}}$$

$$= \frac{0.77}{0.46 \times (1.17 \times 10^{13.66})^2\ \ 6.25 \times 10^{-6}}$$

$$= \frac{0.77}{0.46 \times 1.37 \times 10^{27.32} \times 6.25 \times 10^{-6}}$$

$$= 1.95 \times 10^{-22.32}$$

$$= 9.3 \times 10^{-23}$$

Similarly at pH 2.9, and E = 0.55, $K_c/P_c = 2.1 \times 10^{-22}$
and at pH 3.5, and E = 0.86, $K_c/P_c = 1.5 \times 10^{-21}$

$\therefore$ Mean value = 4.3×10^{-22}

Similar calculations for the copper oxinate give the following results:

pH	E	K_c/P_c
1.8	0.20	1.5×10^{-25}
2.1	0.50	5.0×10^{-25}
2.4	0.84	1.1×10^{-24}

Mean value: 5.4×10^{-25}

and for Ferric Oxinate:

pH	E	K_c/P_c
1.6	0.20	2.9×10^{-39}
1.75	0.45	6.5×10^{-39}
2.00	0.80	4.6×10^{-38}

Mean value: 1.0×10^{-38}

Bearing in mind that the experimental values of P_c remain substantially constant, these values of K_c/P_c follow the pattern of published values of K_c and if it may be temporarily assumed that the values of P_c are correct the K_c's can be evaluated as follows:

Element	K_c/P_c	P_c	K_c	Literature K_c	Reference
Ferric	1.0×10^{-38}	1.2×10^{4}	1.2×10^{-34}	$10^{-33.9}$	25
Cupric	5.4×10^{-25}	4.6×10^{4}	2.5×10^{-20}	$10^{-23.4}$	25
Nickel	4.3×10^{-22}	3.8×10^{4}	1.6×10^{-17}	$10^{-18.7}$	25

It appears, therefore, that dissociation constants evaluated from the solvent extraction work resemble closely the published data which have been largely determined electrochemically and it would appear that assumption with regard to the evaluation of P_c and the general validity of the extraction formulae is substantiated.

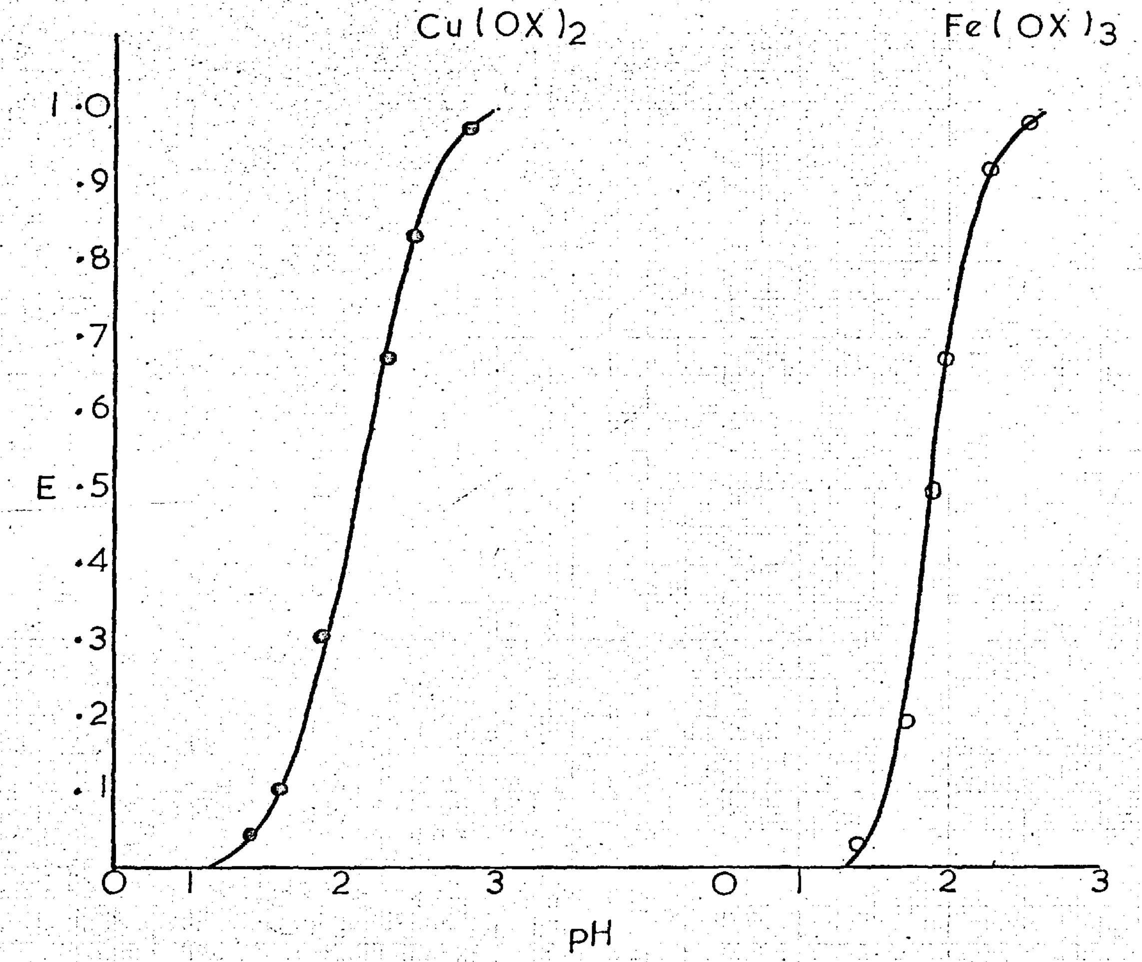


FIG. I EXTRACTABILITY OF METAL OXINATES

Influence of Competing Complexing Reactions

Equations 23.2 and 24.4 have two important limitations that have so far been neglected; the hydrolysis of the metal ion and the effect of masking agents. Extraction of the metal according to the previous equations could be achieved only if the following conditions are fulfilled.

a. The metal oxinate should be sparingly soluble in the aqueous phase so that its partition coefficient, P_c, has a large value. In this case the concentration of both charged and uncharged intermediate metal oxinate species (where $s = 1 \rightarrow m - 1$) in the aqueous phase could be neglected at the lower values of metal distribution. The validity of neglecting such concentrations has already been reported

during

the application of similar formulae$^{(56)}$ on similar systems.

b. The formation of hydroxy complexes $M(OH)_m$ can be neglected at the pH's investigated.

The above conditions are fulfilled for the extraction of Cu^{2+} and Fe^{3+} oxinates with chloroform, and therefore the experimental extraction curves did not differ substantially from the theoretical ones calculated according to eq. 23.2.

Effect of Hydrolysis on Extractability

However, if hydrolysis of metal ion has occurred in the aqueous phase, with the result of formation of hydroxycomplexes like $M(OH)^{(m-1)+}$, $M(OH)_2^{(m-2)+}$, ... etc. another equation which takes into consideration the combined effects of hydrolysis and complex formation with the chelating reagent has to be applied. The derivation of such an equation is as follows:

The total reagent, T_R, in the previous system is not likely to be effected on hydrolysis. Its value, therefore, remains as in eq. 19.8, i.e.

$$T_R = \alpha \frac{m}{n} [MR_{\frac{m}{n}}]_{aq} + \beta [R^{n-}]_{aq}$$

The total metal, T_M, on the other hand, will be greatly affected. An appreciable fraction of the metal in the aqueous phase should exist as metal hydroxycomplexes. With multivalent metals a considerable number of lower hydroxycomplexes could be produced.

Therefore, by neglecting in the organic phase any species other than the fully co-ordinated chelate $[MR_{\frac{m}{n}}]$, the total metal will be

$$T_M = [MR_{\frac{m}{n}}]_{org}.Vorg + [MR_{\frac{m}{n}}]_{aq}.Vaq + [M]_{aq}.Vaq + [M(OH)]_{aq}.Vaq + [M(OH)_2]_{aq}.Vaq \qquad (26.0)$$

By considering the dissociation constants of these metal hydroxycomplexes, and neglecting charges for convenience of presentation,

$$S_1 = \frac{[M]\ [OH]}{[M(OH)]}, \quad S_2 = \frac{[M]\ [OH]^2}{[M(OH)_2]} \quad \text{etc.} \qquad (26.1)$$

On substituting the values $[M(OH)]$ and $[M(OH)_2]$, from eq. 26.1 and the value $[MR_{\frac{m}{n}}]_{org}$ from eq. 14

$$T_M = [MR_{\frac{m}{n}}]_{aq}.P_c.Vorg + [MR_{\frac{m}{n}}]_{aq}.Vaq + [M]_{aq}.Vaq + \frac{[M]\ [OH]}{S_1}.Vaq + \frac{[M]\ [OH]^2}{S_2}.Vaq \qquad (26.2)$$

By putting $\frac{1}{S} = 1 + \frac{[OH]}{S_1} + \frac{[OH]^2}{S_2} + \ldots\ldots$ (26.3)

$$T_M = [MR_{\frac{m}{n}}]_{aq}.P_c.Vorg + [MR_{\frac{m}{n}}]_{aq}.Vaq + \frac{1}{S}.Vaq.[M]_{aq} \qquad (26.4)$$

By further substitution of the value $P_c.Vorg + Vaq = \alpha$ from eq. 19.3 and that of $[M]_{aq}$ from eq. 12 we find

$$T_M = \alpha\ [MR_{\frac{m}{n}}]_{aq} + \frac{K_c[MR_{\frac{m}{n}}]_{aq}.Vaq}{[R^{n-}]^{\frac{m}{n}}\ S} \qquad (26.5)$$

$$= [MR_{\frac{m}{n}}]_{aq} \left\{ \alpha + \frac{K_c\ Vaq}{[R^{n-}]^{\frac{m}{n}}\ S} \right\} \qquad (26.6)$$

But from eq. 21.1

$$[MR_{\frac{m}{n}}]_{aq} = \frac{T_R - \beta[R^{n-}]_{aq}}{\alpha\ \frac{m}{n}} = \frac{T_M}{\alpha + \frac{K_c\ Vaq}{[R^{n-}]_{aq}^{\frac{m}{n}}\ S}}$$

$$\therefore \frac{\alpha m T_M}{n} = \alpha T_R - \alpha\beta[R^{n-}]_{aq} + \frac{T_R K_c Vaq}{[R^{n-}]^{\frac{m}{n}} S} - \frac{\beta\ K_c\ Vaq}{[R^{n-}]^{(\frac{m}{n} - 1)} S} \qquad (27.1)$$

and

$$\frac{\alpha m T_M}{n}[R^{n-}]^{\frac{m}{n}} - \alpha\, T_R[R^{n-}]^{\frac{m}{n}} + \alpha\beta[R^{n-}]^{(\frac{m}{n} + 1)} - \frac{T_R K_c Vaq}{S} + \frac{\beta K_c Vaq[R^{n-}]}{S} = 0 \qquad (27.2)$$

$$\therefore\ \alpha\beta[R^{n-}]^{(\frac{m}{n} + 1)} + \alpha[R^{n-}]^{\frac{m}{n}} \left(\frac{m}{n} T_M - T_R\right) + \frac{T_R K_c Vaq}{S} + \frac{\beta K_c Vaq[R^{n-}]}{S} = 0 \qquad (27.3)$$

By assuming the third term of eq. 27.3 <1 and the fourth term $\ll 1$ in highly alkaline medium, the approximation of the equation becomes:

$$\alpha\beta[R^{n-}]^{(\frac{m}{n} + 1)} + \alpha[R^{n-}]^{\frac{m}{n}} \left(\frac{m}{n} T_M - T_R\right) = 0 \qquad (27.4)$$

$$\therefore\ [R^{n-}] = \frac{-\frac{m}{n}T_M + T_R}{\beta} \qquad (27.5)$$

$$= \frac{nT_R - mT_M}{n\,\beta} \qquad (27.6)$$

It is seen from eq. 27.6 that the value $[R^{n-}]$ has not been affected by the hydrolysis of the metal and it is equivalent to that of eq. 21,6.

Extractability of the metal, from the definition and from eq. 22.1

$$E = \frac{M_{org}\,V_{org}}{T_M}$$

since the metal in the organic phase is in the form of the fully co-ordinated chelate

$$\therefore \quad E = \frac{[MR_{\frac{m}{n}}]_{org}.V_{org}}{T_M}$$

but by substitution of appropriate values from eqs. 14 and 20.3

$$E = \frac{[MR_{\frac{m}{n}}]_{aq}.P_c.V_{org}}{[MR_{\frac{m}{n}}]\left\{\alpha + \dfrac{K_c\ V_{aq}}{[R^{n-}]^{\frac{m}{n}}\ S}\right\}} = \frac{P_c.V_{org}}{\alpha + \dfrac{K_c\ V_{aq}}{[R^{n-}]^{\frac{m}{n}}.S}} \qquad (28.1)$$

On substituting the value of $[R^{n-}]$ from eq. 27.6

$$E = \frac{P_c.V_{org}}{\alpha + \dfrac{K_c\ V_{aq}\ n^{\frac{m}{n}}\ \beta^{\frac{m}{n}}}{(n\ T_R - mT_M)^{\frac{m}{n}}.S}} \qquad (28.2)$$

$$= \frac{P_c.Vorg.S.\ (nT_R - mT_M)^{\frac{m}{n}}}{\alpha(nT_R - mT_M)^{\frac{m}{n}}.S + K_c\ Vaq\ n^{\frac{m}{n}}\ \beta^{\frac{m}{n}}} \qquad (28.3)$$

but by substitution of the appropriate values of α from eq. 19.3 and that of β in alkaline medium from eq. 19.7 i.e. by ignoring $\frac{[H^+]^{n+1}}{K_R K_{RH^+}}$ Vaq in the latter value (reference eq. 24.1)

$$E = \frac{P_c.Vorg.S.(nT_R - mT_M)^{\frac{m}{n}}}{(P_c Vorg + Vaq)(nT_R - mT_M)^{\frac{m}{n}}.S. + K_c Vaq n^{\frac{m}{n}}}$$

$$\overline{\left[\frac{[H^+]^n}{K_R}(P_R Vorg + Vaq) + Vaq\right]^{\frac{m}{n}}}$$

$$(28.4)$$

By considering $P_c Vorg \gg Vaq$ at pH's where a complete hydrolysis of the metal has not yet taken place, and on dividing the numerator and denominator by $P_c VorgS(nT_R - mT_M)^{\frac{m}{n}}$

$$E = \frac{1}{1 + \frac{K_c Vaq}{P_c VorgS}\left(\frac{n}{nT_R - mT_M}\right)^{\frac{m}{n}}\left\{\frac{[H^+]^n}{K_R}(P_R Vorg + Vaq) + Vaq\right\}^{\frac{m}{n}}} \qquad (28.5)$$

By making similar approximations to those of eqs. 23.1 and 24.2, i.e. considering $nT_R > mT_M$, the volume of solvents do not exceed of a ratio 10:1 and $P_c \gg 1000$ and rearranging the equation

$$E = \frac{1}{1 + \frac{K_c\ Vaq}{P_c VorgS}\left(\frac{P_R Vorg + Vaq}{K_R\ T_R} + \frac{Vaq}{T_R}\right)^{\frac{m}{n}}\ [H^+]^m} \qquad (28.6)$$

The values Vaq and $\frac{Vaq}{T_R}$ inside the big brackets may be neglected as they are small

$$E = \frac{1}{1 + \frac{K_c\ Vaq}{P_c VorgS}\ \left(\frac{P_R Vorg}{K_R T_R}\right)^{\frac{m}{n}}\ [H^+]^m} \qquad (28.7)$$

By putting the equivalent value of $\frac{1}{S}$ from eq. 26.3

$$E = \frac{1}{1 + \frac{K_c Vaq}{P_c Vorg}\left(1 + \frac{[OH]}{S_1} + \frac{[OH]^2}{S_2} + \ldots\right)\left(\frac{P_R Vorg}{K_R T_R}\right)^{\frac{m}{n}}\ [H^+]^m} \qquad (28.8)$$

It can be seen from eq. 28.8 and when hydroxy-complexes of the metal are produced in the aqueous phase, extractability tends to decrease according to the dissociation constants of the metal hydroxycomplexes and the concentration of the hydroxyl ions, Fig. II.

For the sake of compatibility the formula is written in terms of the hydrogen ion concentration as follows:

$$E = \frac{1}{1 + \frac{K_c Vaq}{P_c Vorg}\left(1 + \frac{K_w}{S_1[H^+]} + \frac{K_w^2}{S_2[H^+]^2} + \ldots\right)[H^+]^m\left(\frac{P_R \cdot Vorg}{K_R T_R}\right)^{\frac{m}{n}}} \qquad (28.9)$$

where K_w represents the hydrolysis constant of water

$K_w = [H^+][OH^-] = 10^{-14}$ at °C

When only the first hydrolysis step is considered as is likely to be in practice, the formula approximately becomes

$$E = \frac{1}{1 + \frac{Vaq K_w K_c [H^+]^{m-1}}{P_c Vorg S_1}\left(\frac{P_R Vorg}{K_R T_R}\right)^{\frac{m}{n}}} \qquad (29.1)$$

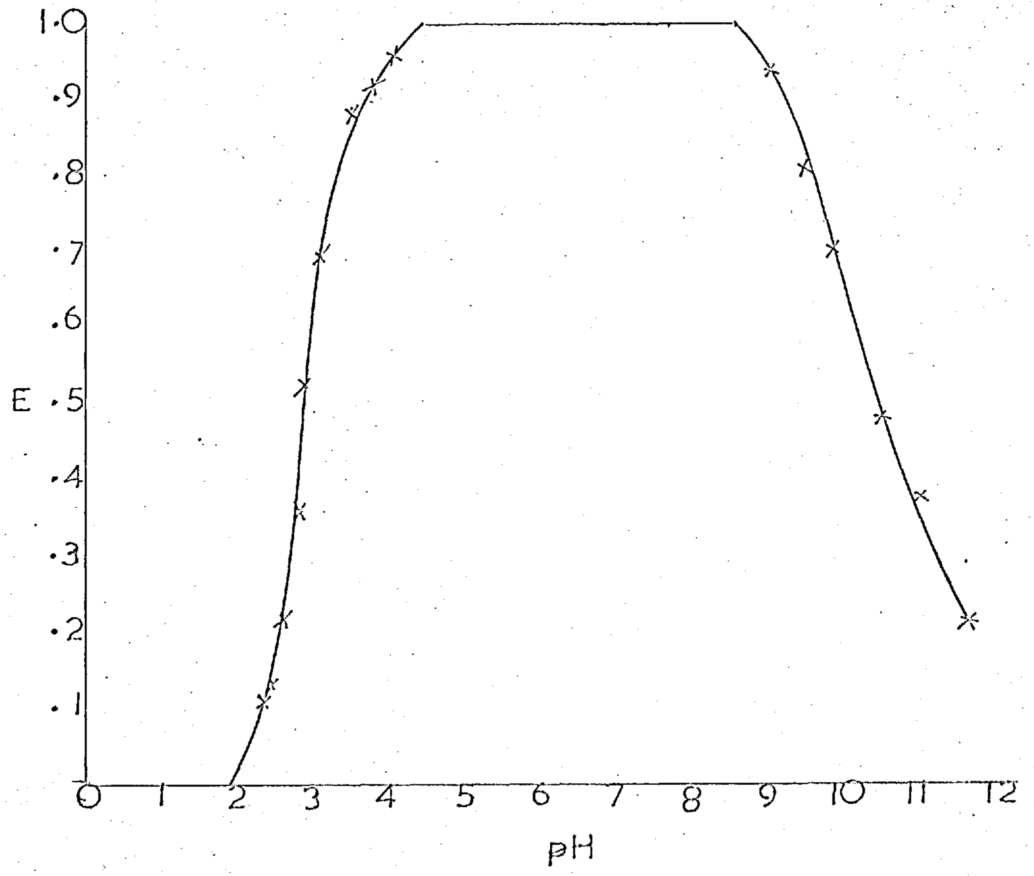


FIG.II, EFFECT OF HYDROLYSIS ON THE EXTRACTION OF Ni(OX)$_2$

which indicates that the extractability will be much less sensitive to pH variation. In fact, from equation 28.9, if the neutral hydroxide is formed (i.e. the mth hydrolysis is considered alone) then the extractability will be independent of changes of pH, as would be expected.

In an increasing number of extraction procedures for metal pairs that are difficult to separate, a supplementary 'masking' chelating agent can be introduced to improve spearation factor (the relation between the distribution ratios or extraction coefficients of the material of interest and the interference.

$$= \frac{(C_1)_o/(C_2)_o}{(C_1)_w/(C_2)_w} = \frac{(C_1)_o(C_1)_w}{(C_2)_o(C_2)_w} = \theta_1/\theta_2$$

where C_1 is the total concentration of component 1, in either the organic or water phases, and C_2 is the total concentration of component 2 in the same particular phases).

The masking agent forms an ionic non-extractable water soluble complex species with the metals in competition with the extracting agent. Oxalate, tartrate, nitrilotriacetic acid, and tetraethylenediamine-tetra-acetic acid, EDTA, are typical examples on such secondary complexing agents.

An extractability formula applied to systems which involve masking agents is described as follows:

Derivation of such formula is similar to that of eq. 28.8 described for hydrolysis systems, with the exception of replacing S with B_1 and [OH] with [L] throughout the steps of derivation. Where B represents the overall dissociation constants of the metal-complexing agents compounds. They are obtained from

$$B_1 = \frac{[M]\ [L]}{[M(L)]} \quad , \qquad B_2 = \frac{[M]\ [L]^2}{[M(L)_2]} \quad \ldots \text{ etc.}$$

(Note: if only a monoligand complex is formed, B_2 should not be considered).

By assuming that the hydrolysis is negligably small, (i.e. $B_i < S_i$) the new formula becomes

$$E = \frac{1}{1 + \frac{K_c V_{aq}}{P_c V_{org}}\left(1 + \frac{[L]}{B_1} + \frac{[L]^2}{B_2} + \ldots\right) [H^+]^m \left(\frac{P_R\ V_{org}}{K_R T_R}\right)^{\frac{m}{n}}}$$

(30.1)

From the above equation, it is evident that in the presence of a masking agent, the distribution ratio of a metal at various values of pH, is diminished according to the dissociation constants of the new metal complexes, and the equilibrium concentration of the masking agent. The lower the dissociation constant of the new complex the more alkaline is the solution required for the extraction of metal.

In the case of EDTA which forms only a monoligand complex and the equilibrium of which is affected by hydrogen ion concentration, Fig. III, the value of [L] is calculated from the total concentration of the complexing agent and from its dissociation constants as follows:

$$\phi = \frac{C_y}{[y^{4-}]} = \frac{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}{K_1K_2K_3K_4} \qquad (30.2)$$

where C_y = total concentration of free EDTA in all forms

K_i = successive ionization constants of EDTA.

The formula can be written:

$$E = \frac{1}{1 + \frac{Vaq\ C_yK_c}{Vorg P_c\phi\ B}\left(\frac{P_R Vorg}{K_R T_R}\right)^{\frac{m}{n}}[H^+]^m} \qquad (30.3)$$

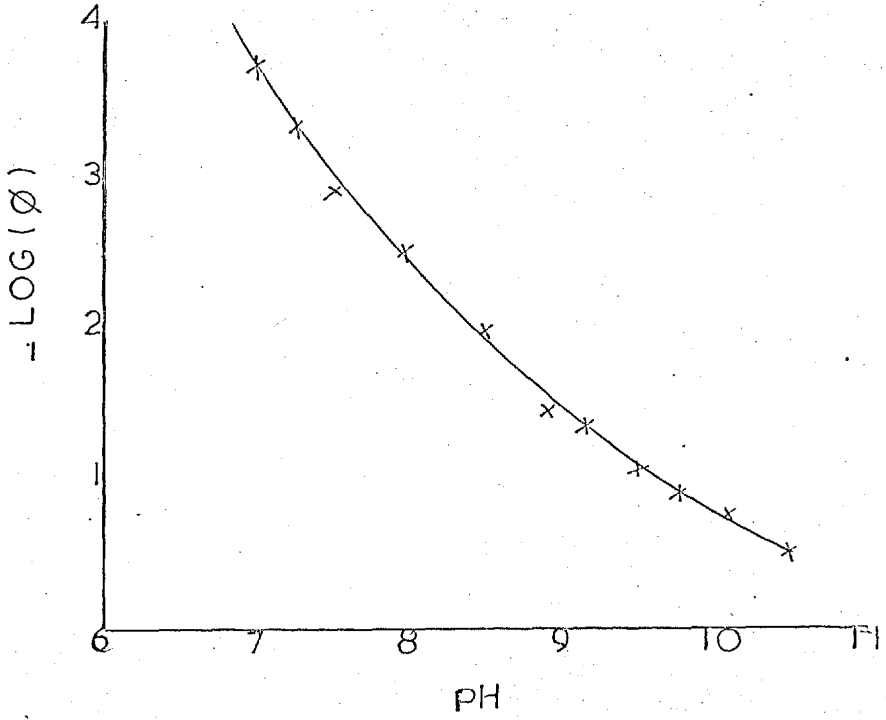


FIG. III, EFFECT OF PH ON THE EQUILIBRIUM CONCENTRATION OF THE EDTA ANION

Checking the Validity of the Equation

Verification of the equation was made with the same systems of Cu^{2+} and Fe^{3+} oxinates.

Experimental Extractability

The procedure of determining extractability is similar to the one applied to the simple metal-8-hydroxyquinolinate systems, with the exception of incorporating a complexing agent into the system. Thus, equilibration is made between 25 ml. of 1% W/V oxine solution in chloroform and 50 ml. of aqueous phase, containing the appropriate amount of metal, 5 ml. of IM sodium perchlorate, and 10 ml. of 0.05 M EDTA to give an ionic concentration of 0.01 M.

Theoretical Extractability

This is calculated from eqs. 30.1 and 30.3 using the previously reported constants and the experimental values for T_R, Vaq, Vorg and of $[H^+]$.

[L] is calculated from a plot of $-\log(\phi)$ vs. pH, using ϕ values evaluated at various pH's from the known EDTA ionization constants, pK_i = 10.26, 6.16, 2.67, 1.99$^{(25)}$.

Dissociation constants, B, of the ferric- and cupric-EDTA chelates are known - viz $10^{-25.1}$ and $10^{-18.9}$ respectively(28). Application of these to the formulae gave predicted extraction curves somewhat different from the experimental. Assuming that the formula for extraction in the presence of EDTA is correct (equation 30.3) then the quantity BP_c/K_c can be evaluated from the expression:

$$\frac{BP_c}{K_c} = \frac{E}{1-E} \cdot \frac{Vaq}{Vorg} \cdot \frac{C_Y}{\emptyset} \left(\frac{P_R Vorg}{K_R T_R} \right)^{\frac{m}{n}} [H^+]^m$$

For example, for ferric oxinate:

$E = 0.88$

$Vaq = 5 \times 10^{-2}$ litre

$Vorg = 2.5 \times 10^{-2}$ litre

$C_Y = 10^{-2}$ M

$\emptyset = 10^{0.39}$

$P_R = 3 \times 10^2$

$K_R = 10^{-9.66}$

$T_R = 1.72 \times 10^{-3}$ g.mole

$pH = 10.10$

$$\therefore \frac{BP_c}{K_c} = \frac{0.88}{0.12} \cdot \frac{5\text{x}10^{-2}}{2.5\text{x}10^{-2}} \cdot \frac{10^{-2}}{10^{0.39}} \left(\frac{3\text{x}10^2\text{x}2.5\text{x}10^{-2}}{10^{-9.66}\text{x}1.72\text{x}10^{-3}}\right)^3$$

$$(10^{-10.1})^3$$

$= 1.25 \times 10^{9.07}$ or 1.46×10^{9}

Similarly at pH 9.5 and 9.0
BP_c/K_c equal 4.9×10^{10} and 3.4×10^{11} respectively, giving a mean of 1.3×10^{10}.

For cupric the values were calculated to be 4.8×10^{7}, 3.6×10^{8} and 1.2×10^{8}, giving a mean of 1.7×10^{8} (Insufficient extraction data for nickel chelate can be obtained in the working pH range).

Assuming the calculated values of K_c/P_c are satisfactory the dissociation constants, B, of ferric and cupric metal EDTA complexes can be evaluated as 1.3×10^{-28} and 9.2×10^{-17} respectively.

These are somewhat different from those obtained electrochemically and given above. On the other hand, using the data of Stary(78) and the present equation (24.3), the value of B can be calculated as 5.7×10^{-33} for ferric and 7.0×10^{-20} for cupric.

The results are summarized in the following tables:

Calculated from own results

Element	BP_c/K_c	K_c/P_c	B	Literature B
Ferric	1.3×10^{10}	1×10^{-38}	1.3×10^{-28}	$10^{-25.1}$
Cupric	1.7×10^{8}	5.4×10^{-25}	9.2×10^{-17}	$10^{-18.9}$

Calculated from Stary's results

Element	BP_c/K_c	K_c/P_c	B	Literature B
Ferric	5.7×10^{5}	1×10^{-38}	5.7×10^{-33}	$10^{-25.1}$
Cupric	1.3×10^{5}	5.4×10^{-25}	7.0×10^{-20}	$10^{-18.9}$

Ignoring the ferric result of Stary, which is apparently wild, it appears that reasonable agreement is obtained in the determination of dissociation constants. With further refinement with regard to thermostatting and pH measurement the approach appears to be suitable for the determination of stability constants, and, in converse, for the prediction of extraction versus pH extraction curves.

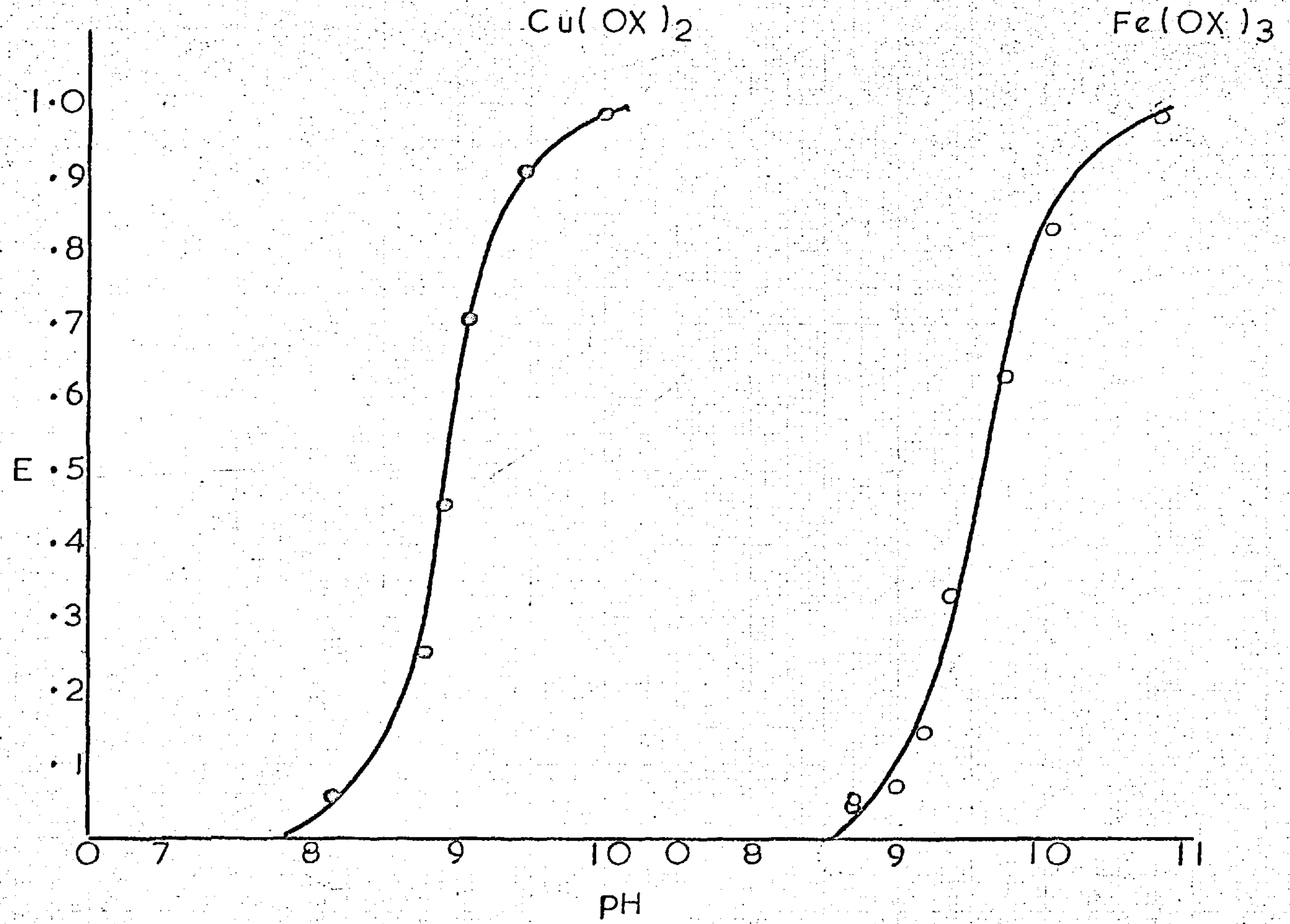


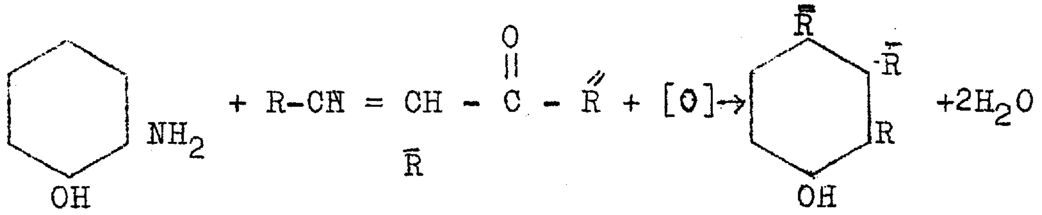
FIG IV EFFECT OF THE COMPLEXING AGENT EDTA ON THE EXTRACTION OF METAL OXINATES

CHAPTER THREE

DISCUSSION OF THE METHODS OF SYNTHESIS OF 2-ALKYL SUBSTITUTED 8-QUINOLINOLS

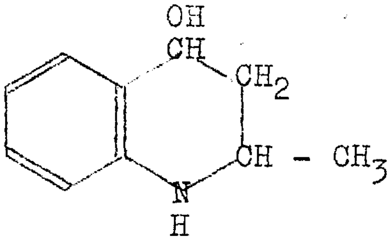
Synthesis of the 8-quinolinol homologues, substituted in the 2-position of the pyridine ring, with ethyl-, <u>iso</u>propyl- and <u>tert</u>-butyl- groups, as one of the principle objectives of the work, has been attempted by the application of very long organic processes, and rigorous schemes of reactions. The noteworthy discussions of the main methods used in the synthesis are presented as follows:

<u>The Doebner von Miller Synthesis</u>(29)



This reaction between aromatic amines and α : β-unsaturated carbonyl compounds has been the most widely used method of making 2-, 3-, and 4- methyl substituted quinolinols. The mechanism of this reaction is not clear: recent work(30) on the reaction between aniline and crotonaldehyde has shown that crotonylidineaniline ØN = CH - CH = CH - CH_3 is formed and that this undergoes rearrangement on heating with hydrochloric acid to give quinaldine;

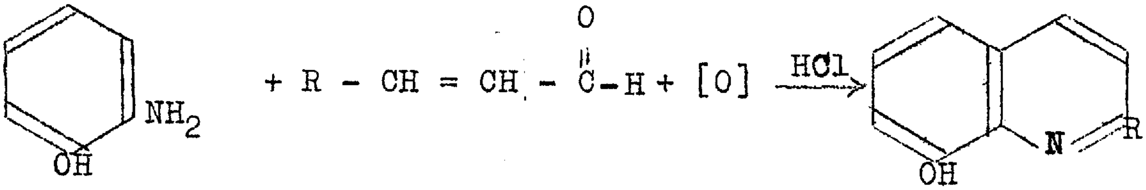
conversely, however, it has been shown(31) that an aldol base



is formed which gives quinaldine on heating.

The conditions that have been employed in this reaction and the closely related Skraup reaction(32) vary tremendously. Reaction times from ninety seconds(33) to many hours, oxidising agents ranging from ferric chloride(34) to p-nitrobenzene sulphonic acid(35), and catalysts from sodium iodide to zinc chloride(34); nitrocompounds instead of amines(36) have also been used.

In this work the experimental procedure generally consisted of making the necessary $\alpha:\beta$-unsaturated aldehyde (penten 2-al-1, 2-methyl penten-3-al-5, 2:2-dimethyl penten-3-al-5) by a scheme developed by Martin et al.(37), heating it in concentrated hydrochloric acid with *o*-aminophenol and *o*-nitrophenol for six hours, removing the o-nitrophenol by steam distillation from acid medium, and finally steam distilling or subliming the product after neutralization of the reaction mixture. The reactions between the three α : β-unsaturated aldehydes and o-aminophenol may be represented by the following equation,



o-amino-phenol α:β-unsaturated aldehyde *o*-nitro-phenol 2-alkyl-8-quinolinol

(where R = ethyl-, *iso*propyl- or *t*.butyl-group)

Although the synthesis leading to the preparation of the 2-alkyl substituted quinolin-8-ol derivatives gave reasonable yields, the condensation according to this method remains inefficient. Low yields are found in practice and may be ascribed to the following:

a. Although the Doebner von Miller balanced equation obviously requires an oxidising agent, no effective one was found. Picric acid, *o*-nitrophenol and arsenic pentoxide in phosphoric acid have been tried in this reaction(38, 18, 39). In the present work it was noted that o-nitrophenol can be recovered almost quantitatively by steam distillation from acid medium and after the Doebner von Miller reaction is over.

b. Most of α : β-unsaturated carbonyl compounds tend to polymerize under the rather strenuous conditions of the Doebner von Miller reaction. This was partially compensated for by using excess aldehyde. Also copolymerization with o-aminophenol to give bakelite type resins was always observed as a side reaction.

c. Commercial o-aminophenol is impure and even when purified by sublimation the substance turns dark again in a few days.

d. The product after steam distillation quickly discoloured and required numerous recrystallizations to give a permanently white-yellowish oxine derivative.

e. o-Aminophenol appears to be less active in Skraup type reactions(32) than most aromatic amines.

f. Absence of active catalysing agent. Hydrochloric acid has been used as the principle catalyst in this reaction.

The possibility of improving the yields from the Doebner von Miller reaction has been investigated. Such investigations were mixture of failure and success e.g. ferric salt has been employed as a condensing and oxidising agent in the reaction, and in conjunction with o-nitrophenol, but, resulted in oxidation breakdown of any oxine derivative during the isolation stages and consequently steam distillation of the latter from alkaline medium was not possible.

Dissociation of the ferric-2-alkyl-8-quinolinate, in order to set free the organic ligant, has been attempted by different ways, but no success has been achieved in this direction.

A.R. hydrochloric acid is not active enough as a catalysing agent. An attempt has been made to increase its potential by bubbling hydrochloric acid gas through the reaction system; no improved yield was noticed.

Steam distillation was not satisfactory as a means of isolation the 8-quinolinol derivatives, because they were not sufficiently volatile in steam: the isolation was partially successful by subliming the air-dried, very gummy precipitates, obtained on neutralising the reaction mixtures; vacuum steam distillation was a complete failure.

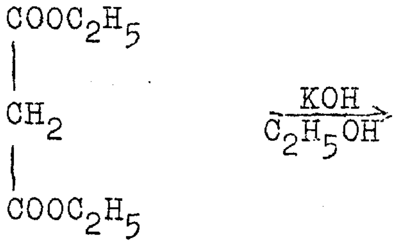
The Doebner von Miller reaction was totally unsuccessful in the preparation of 2-tert-butyl-8-quinolinol.

Attempts were made to synthesise the derivative according to this method from the reaction of o-aminophenol with 2:2-dimethyl penten-3-al-5, but the product, characterised by m.p. 67-68°, was identified as 8-hydroxyquinoline. This suggests the elimination of the bulky alkyl group from its position on the pyridine ring. This observation necessitated the search for milder conditions of condensation and isolation. Addition of or removing the oxidant; lowering or elevating the condensation temperatures; super-steam or vacuum distillation; sublimation, have all been tried but with no success noted.

Preparation of the α :β-unsaturated Aldehydes

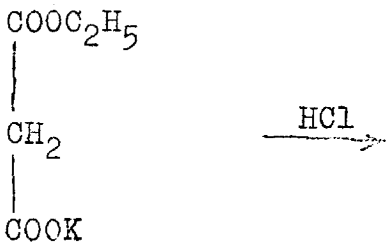
A. Martin, Schepartz and Daubert Method(37)

The general scheme of reaction may be outlined as follows:



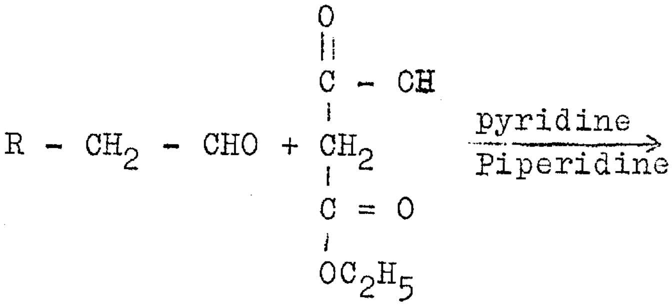
$$\begin{matrix} COOC_2H_5 \\ | \\ CH_2 \\ | \\ COOC_2H_5 \end{matrix} \quad \xrightarrow[C_2H_5OH]{KOH}$$

diethyl malonate



$$\begin{array}{l} COOC_2H_5 \\ | \\ CH_2 \\ | \\ COOK \end{array} \xrightarrow{HCl}$$

potassium ethyl malonate



$$R - CH_2 - CHO + \begin{array}{l} O \\ \| \\ C - CH \\ | \\ CH_2 \\ | \\ C = O \\ | \\ OC_2H_5 \end{array} \xrightarrow[\text{Piperidine}]{\text{pyridine}}$$

aliphatic aldehyde ethyl hydrogen malonate

$$R - CH_2 - CH = CH - COOC_2H_5 \xrightarrow[\text{lithium aluminium hydride}]{LiAlH_4}$$

α :β-unsaturated ester

$$LiAl(OC_2H_5)_2\ (OCH_2 - CH = CH - CH_2R)_2 \xrightarrow[H_2O]{H_2SO_4}$$

$$R - CH_2 - CH = CH - CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7}$$

α: β-unsaturated alcohol

$R - CH_2 - CH = CH - CHO$ α: β-unsaturated aldehyde

This scheme, which has been applied to the preparation of a number of α : β-unsaturated aldehydes of high degree of purity such as 2-heptenal and 2-nonenal(37) has been successfully used in the preparation of reasonable yields of penten-2-al-1 and 2-methyl-penten-3-al-5, both free of their saturated isomers. However, the method was unsuitable for the production of 2:2-dimethyl penten-3-al-5. This is also ascribed to the limitations of low yield. The α : β-unsaturated ester which is the main source for the desirable unsaturated aldehyde could not be prepared, except in a trace quantity, by Galats method of condensation(40) between ethyl hydrogen malonate and trimethyl acetaldehyde. This is to be expected from steric considerations and it appears that the presence of at least a single hydrogen atom on the α-carbon atom of the aliphatic aldehyde may be necessary for such condensations.

The yields at the different stages of the scheme have been reproduced and in some cases improved.

Total yields of the mono salt of ethyl hydrogen malonate and of ethyl hydrogen malonate, which were (82%) and (96%) respectively, have been reproduced.

The α:β-unsaturated esters were prepared according to the Galat method by heating a mixture of (1 mole) aliphatic aldehyde, (2 mole) half ester of diethyl malonate, (6 mole) dry pyridine and 1 ml. piperidine (catalyst), under reflux on a steam bath for six hours; cooling the mixture overnight and removing the pyridine and piperidine by fractional distillation in vacuo under nitrogen, produced 62% 1-ethyl 2-pentenoate and 52% 1-ethyl 2-en-4:4-dimethyl butyrate. Attempts to increase the yield yet further, through variation of conditions of reaction, e.g. the time and temperature of condensation, mole ratio of reactants, were not successful. Moreover, attempts of separation of the $\alpha : \beta$-unsaturated ester from pyridine after the convertion of the latter into its hydrochloride salt by hydrochloric acid treatment of the mixture, and thus cutting down the very long time required for fractionation (6 moles pyridine require 2 days of fractionation) were also unsuccessful. A considerable amount of the ester was lost during the successive extractions with hydrochloric acid.

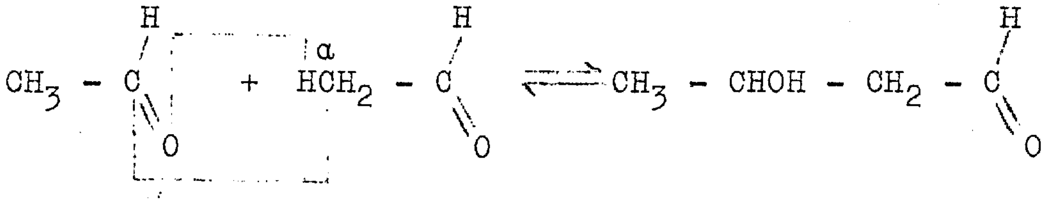
The yield of the crude $\alpha : \beta$-unsaturated alcohol, however, has been improved from 79 to 100% by applying 100% excess of the reducing agent (lithium aluminium hydride) during the process of reduction. Distillation of the crude alcohol under nitrogen through a helix-packed fractionating column, resulted in the loss of approximately 50% because of partial polymerization of the alcohol. Attempts to use the crude unsaturated alcohol in the dichromate-sulphuric acid oxidation to the corresponding aldehyde met with complete failure, and purification by vacuum distillation has been found to be indespensable.

The low yield of the unsaturated aldehyde $< 50\%$, produced from low-temperature oxidation of the pure unsaturated alcohol has not been improved by allowing more time for the oxidation process. On the contrary, it resulted in a further oxidation breakdown and polymerization. The use of a less concentrated oxidising agent solution was also not effective.

B. The Aldol Condensation

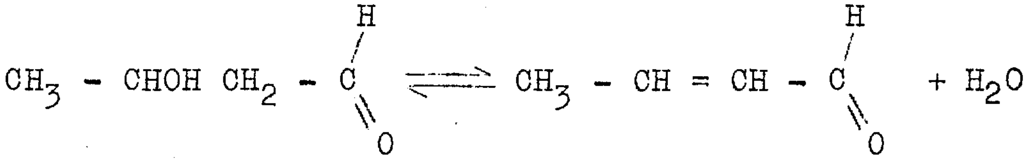
This is a general reaction exhibited by aldehydes and ketones having labile (usually α) hydrogen atoms(52). The hydrogen of one molecule of the carbonyl compound adds to the carbonyl group of another molecule of the same or different compound to form an aldol (hydroxy aldehyde) or a ketol (hydroxy ketone).

The first step of the condensation which is promoted by basic catalyst is easily reversible,



$$CH_3 - \overset{H}{\underset{O}{C}} + \overset{\alpha}{H}CH_2 - \overset{H}{\underset{O}{C}} \rightleftharpoons CH_3 - CHOH - CH_2 - \overset{H}{\underset{O}{C}}$$

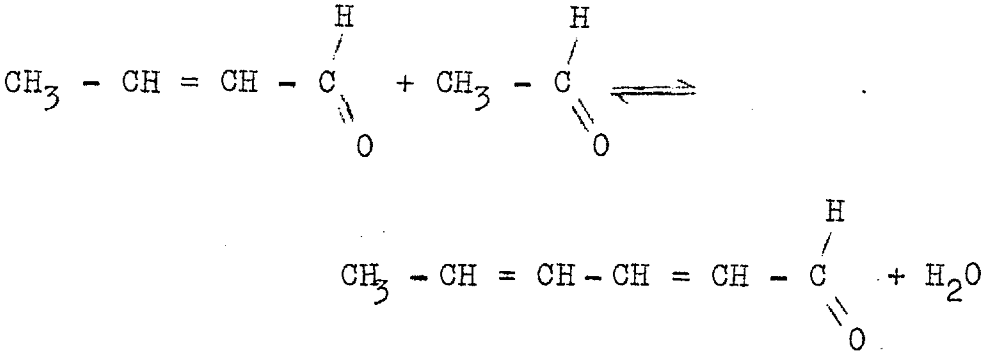
while the second step, loss of water, which is brought about by the same catalyst, is also, but less readily reversible.



$$CH_3 - CHOH\ CH_2 - \overset{H}{\underset{O}{C}} \rightleftharpoons CH_3 - CH = CH - \overset{H}{\underset{O}{C}} + H_2O$$

This reaction has been extensively used in the synthesis of unsaturated derivatives(41, 42, 43, 44, 49, 50, 51), mostly α-alkyl acrolein derivatives.

However, no information whatsoever regarding its application in the preparation of β-alkyl-acrolein derivatives, is provided in the literature. The reason for the general reluctance to apply this apparently simple method of condensation is that both reactants, and the products, contain α-hydrogen atoms and hence the reaction can be extensively polymeric in character and is difficult to stop at the desired stage. This is markedly different from condensations using ketones, or aromatic aldehydes which lack α-hydrogen atoms where the reaction is less complex. It can be expected, therefore, that a complex mixture, with highly polymeric or condensed resins and also side reaction products will eventually be produced, from which the desirable α : β-unsaturated aldehyde is not easily separable. This is demonstrated in view of the fact that the unsaturated aldehyde produced by the former reaction, reacts with another molecule of aldehyde,

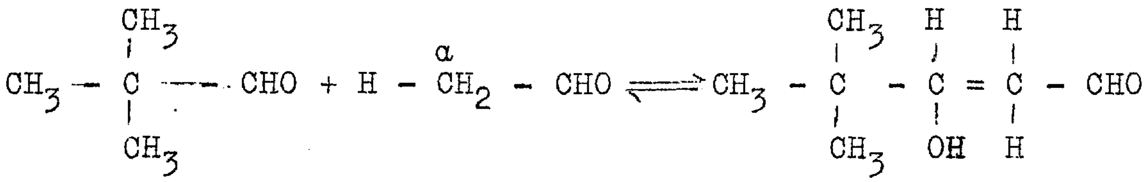


$$CH_3-CH=CH-C\begin{smallmatrix}H\\ /\\ \\ \backslash\backslash\\ O\end{smallmatrix} + CH_3-C\begin{smallmatrix}H\\ /\\ \\ \backslash\backslash\\ O\end{smallmatrix} \rightleftharpoons CH_3-CH=CH-CH=CH-C\begin{smallmatrix}H\\ /\\ \\ \backslash\backslash\\ O\end{smallmatrix} + H_2O$$

and polymerization of this type, which takes place in the presence of strong bases, leads eventually to aldehyde resins.

Moreover, when both aldehydes possess active α-hydrogen atoms, there is a high probability of the formation of both the symmetrical aldols and both the 'mixed' aldols in widely different proportions. The 'mixed' isomers would be almost impossible to separate by phsysical means.

Accordingly, and in view of the complex reactions expected, the aldol condensation reaction has been ruled out for the synthesis of (1) penten-2-al-1 from the condensation of acetaldehyde andpropion aldehyde and of (2) 2-methyl penten-3-al-5 from the reaction of aceteldehyde and isobutyraldehyde. However, the method appeared far more useful than the Martin et al. scheme in the synthesis of 2:2 dimethyl penten-3-al-5 from the reaction of trimethyl acetaldehyde*and acetaldehyde,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO + H-\overset{\alpha}{CH_2}-CHO \rightleftharpoons CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}-CHO$$

Here the self condensation of trimethyl acetaldehyde is impossible owing to the absence of the α-hydrogen atom, while it continues to be important for the acetaldehyde. This effect can be compensated by using excess of the acetaldehyde. The reaction mixture produced is less complex and separation of the desired unsaturated aldehyde from other ingredients is, in principle, possible by fractional distillation.

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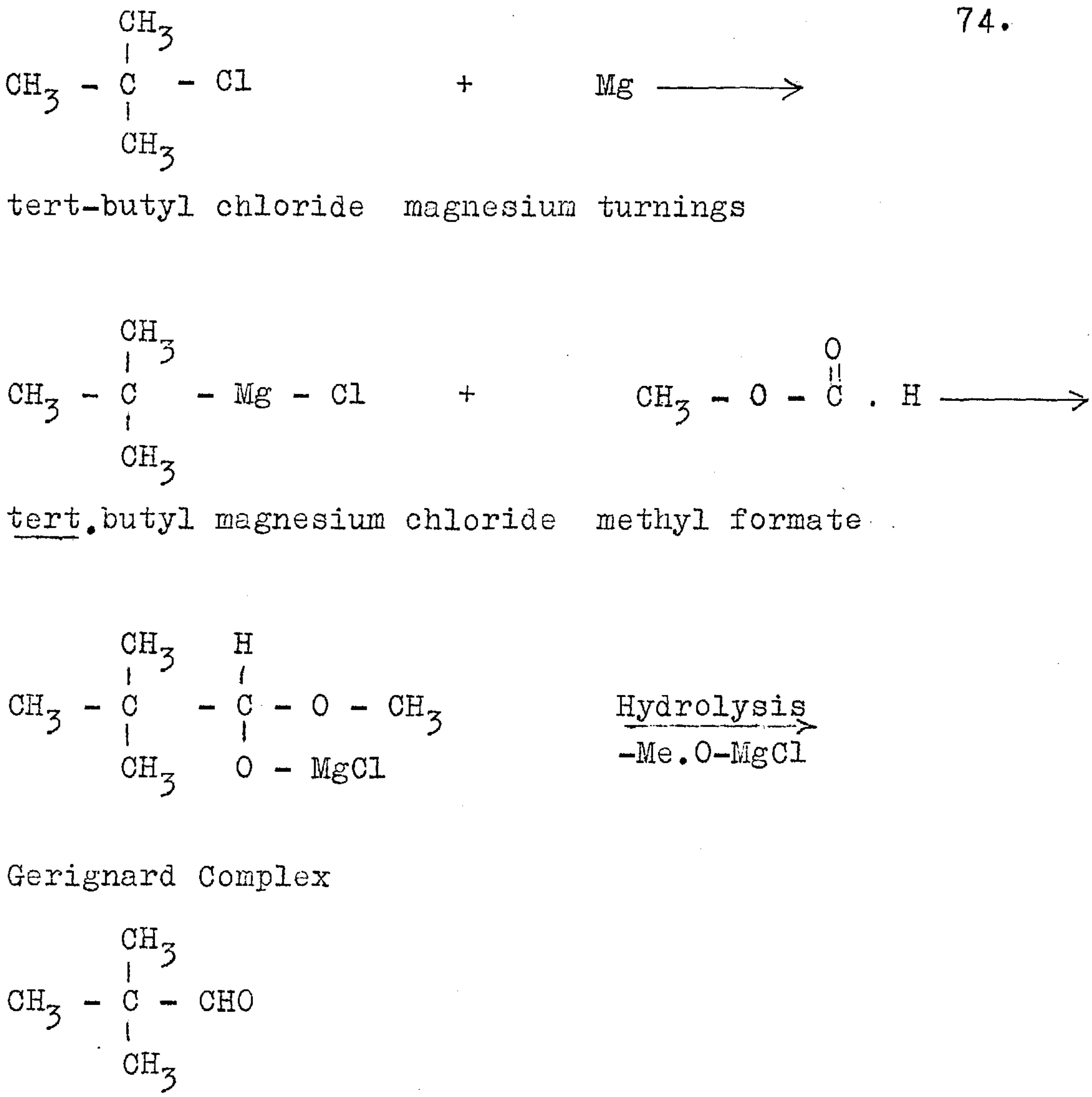
* Trimethyl acetaldyde is not available commercially. It was, therefore produced by a modification of Bouvault method(45), the outline of which is as follows



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl \quad + \quad Mg \longrightarrow$$

tert-butyl chloride magnesium turnings

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Mg-Cl \quad + \quad CH_3-O-\overset{O}{\overset{\|}{C}}.H \longrightarrow$$

tert.butyl magnesium chloride methyl formate

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{O-MgCl}{C}}-O-CH_3 \quad \xrightarrow[-Me.O-MgCl]{Hydrolysis}$$

Gerignard Complex

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHO$$

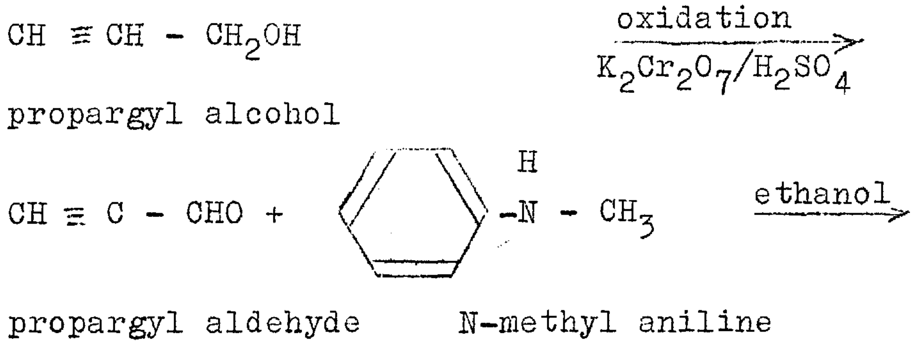
trimethyl acetaldehyde

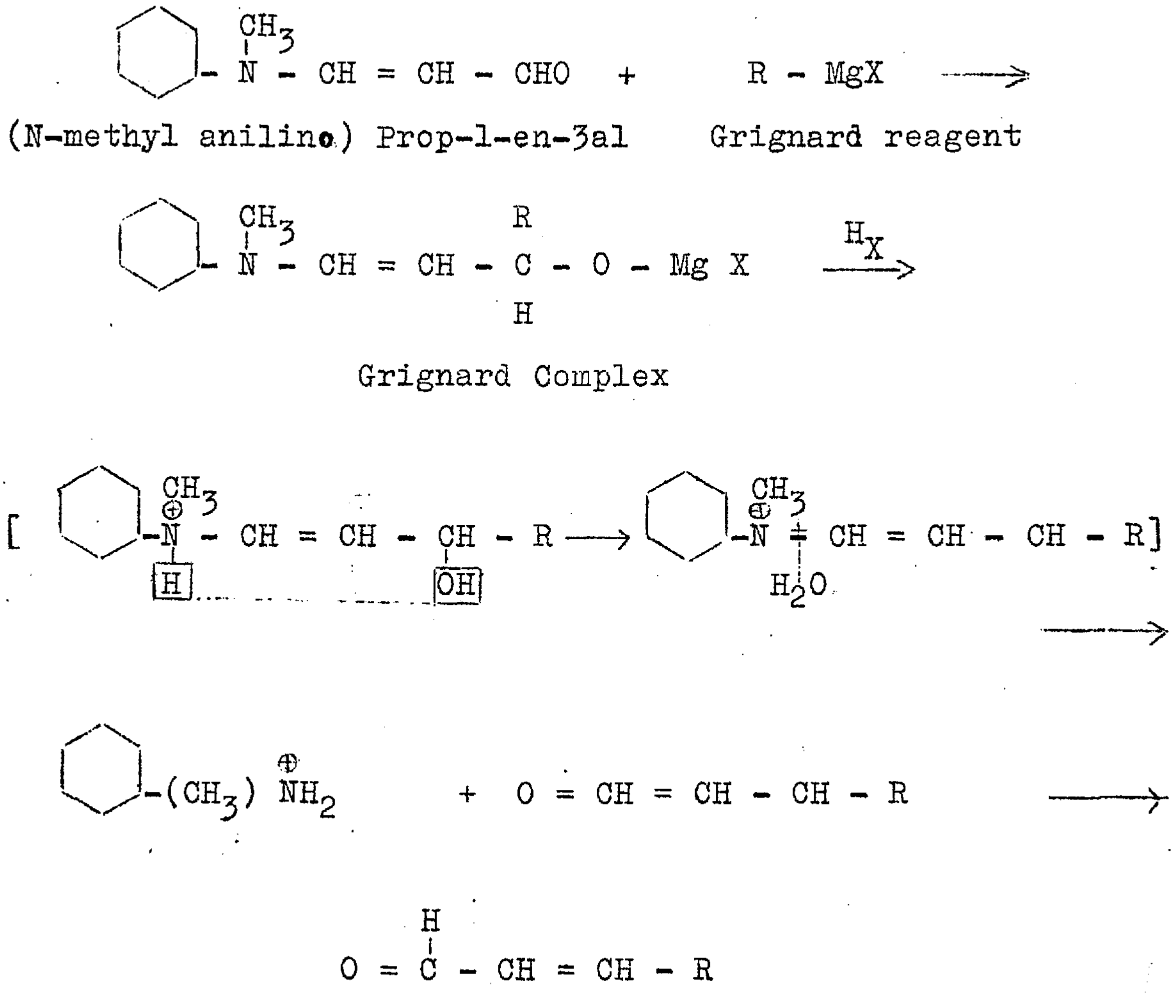
In this work the experimental procedure of aldol condensation, generally consisted of adding the acetaldehyde to a cooled, well stirred mixture of trimethyl acetaldehyde, ethanol and alkali and through which nitrogen gas was bubbling. After the mixture was allowed to stand overnight, the required $\alpha:\beta$-unsaturated aldehyde was separated by fractionation.

Some of the 2:2 dimethyl penten-3-al-5 has been prepared by this method, but owing to the inductive and steric effects, the rate of condensation between trimethyl acetaldehyde and acetaldehyde was extremely slow. In an attempt to improve the yield, factors which have been reported to influence the aldol condensation such as mole ratio of reactants, catalysts and catalyst concentration, temperature and diluents have been briefly studied with this particular system but results showed no appreciable improvement. It is clear that a general study of the kinetics of 'mixed' aldol condensations would be well worthwhile.

C. Jutz Method(16)

An apparently scheme of reactions is as follows:





(N-methyl anilino) Prop-1-en-3al

Grignard reagent

Grignard Complex

α:β-unsaturated aldehyde

where R = ethyl-, <u>iso</u>propyl- or <u>tert</u>-butyl-groups.

This method has been reported to be successful in the preparation of β-alkyl acrolein derivatives, and each stage of its scheme, with the exception of the second (which was unsepcified) is said to produce satisfactory yields.

The preparation of the propargyl aldehyde according to the method of Willie and Saffer(47) from the oxidation of the starting material, propargyl alcohol in the cold and under vacuo by concentrated chromic-sulphuric acid mixture was successfully carried out. But despite repeated attempts, variation of conditions etc., the condensation of propargyl aldehyde with N-methyl aniline in ethanol could hot be accomplished satisfactorily. The best yield obtained was 1% based on propargyl aldehyde and hence the method was abandoned.

CHAPTER FOUR

SYNTHESIS OF 2-ALKYL SUBSTITUTED 8-HYDROXYQUINOLINE DERIVATIVES

Synthesis of the Half-Ester, Ethyl Hydrogen Malonate

The synthesis is based on Breslow et al.(58) method described for β-keto esters of the type $RCOCH_2COOC_2H_5$, and which is in turn a modification of the small scale preparation of Marguery(59).

Procedure

In a five-litre three-necked flask equipped with a dropping funnel, reflux consenser and a mercury-sealed stirrer, were placed 400 g. (2.5 moles) of diethyl malonate (practical grade dried over drierite) and 1600 ml. of A.R. absolute ethanol. To this was added with stirring during 1 hour a solution of 140 g. of potassium hydroxide in 1600 ml. of A.R. ethanol. A white crystalline silky precipitate formed. After stirring for three hours and standing overnight the mixture was heated to boiling on a steam-bath and filtered hot, through a jacketed funnel, to remove dipotassium malonate. The monopotassium salt, which precipitated on cooling the filtrate, was filtered using a buchner funnel, washed with a small amount of ether and dried in vacuo. Concentration of the mother liquid to about 500 ml. yielded another crop of crystals.

The total yield of monopotassium salt of ethyl hydrogen malonate reported was 82%. The yield obtained 80%.

To a chilled solution of the potassium salt (106 g. ≡ 0.625 mole) in 60 ml. of water (immersed in an ice-bath) was added slowly with stirring 55 ml. of concentrated hydrochloric acid. The mixture was extracted three or four times with ether, the etherial extract dried over anhydrous sodium sulphate and the solvent distilled. The liquid residue of ethyl hydrogen malonate was dried in vacuo (2 mm.) at room temperature for 3 hours. Yields of 99% were repeatedly obtained.

Synthesis of the α:β-Unsaturated Esters

The method followed for the synthesis of the unsaturated esters - 1-ethyl 2-en-4:4-dimethyl butyrate, 1-ethyl 2-pentenoate and 1-ethyl 2-en 4:4-dimethyl pentenate (in small yield), was that of Calat(40).

Procedure

528 g. (4 moles) ethyl hydrogen malonate, 116 g. propion aldehyde; 144 g. isobutyraldehyde or 172 g. trimethyl acetaldehyde (2 moles), 2.4 ml. of piperidine and 950 g. (12 moles) of dry pyridine* were mixed together

and heated under reflux on steam bath for six hours, and allowed to stand at room temperature overnight. The pyridine was then distilled in vacuo under vacuum (using 20 inch, helix-packed, electrically heated fractionating column equipped with a total-reflux partial-take-off head and a manostat-controlled vacuum, but with a dry nitrogen leak). The unsaturated ester begins to distill after the complete removal of the pyridine, and the fractionation temperature and pressure remain constant to the end of the distillation.

The three unsaturated esters produced by this method were colourless compounds characterised with pleasant ester smell and infrared spectra of α:β-unsaturated esters.

Description	% Yield	B.P. (°C)
1-ethyl 2-pehtenoate	62	70-72/36 mm
1-ethyl 2-en--4:4-dimethyl butyrate	52	70-72/24 mm
1-ethyl 2-en-4:4-dimethyl pentenate	2	38-40/4 mm

Table II

Infrared absorption characteristics of an a:β-unsaturated ester.

	Wavelength (µ)	Wave No. cm^{-1}	Assignment
1.	5.83	1,715	α:β-unsaturated ester characteristic band ($C = O$ stretching)
2.	6.06	1,650	stretching $C = C$ frequency
3.	11.35	980	trans $\overset{H}{C} = \underset{H}{C}$ deformation
4.	14.1	710	Cis $\overset{H}{C} = \overset{H}{C}$ deformation
5.	3.35	2,980	$C - H$ unsaturated stretching
6.	7.63-8.50	1,310-1,180	$C - O$ stretching

Reduction of the α:β-Unsaturated Esters by Lithium Aluminium Hydride

The method applied here is that of Nystrom et al.(60) described originally for the reduction of aldehydes, ketones, esters, acid anhydrides and other organic compounds, with slight modification.

In general, the experimental procedure for effecting reduction by lithium aluminium hydride is substantially identical to those commonly employed in Grignard synthesis. Starting with $LiAlH_4$, the same precautions against the excess of moisture are taken, and following the usual Grignard technique the substance to be reduced, was added with stirring at a rate determined by the vigour of the reaction as indicated by the refluxing ether. The reaction results in precipitation of a complex alcoholate which may cause the mixture to thicken and may necessitate the addition of further quantities of ether. As in Grignard synthesis, the metal alcoholate is decomposed by hydrolysis and the product is isolated from the ether extract.

Procedure

A solution of 56 g. $LiAlH_4$ in 1800 ml. of sodium dried ether was placed in a 5 litre three-necked flask equipped with reflux condenser, dropping funnel and mechanical spark-proof stirrer, and protected from moisture until completion of the reaction by calcium chloride tubes attached to the openings. Through the dropping funnel, 200 g. of the unsaturated ester was introduced at a rate such as to produce gentle reflux. Ten minutes after the last addition and with combined stirring, water was added cautiously, drop by drop, cooling the flask if, during the exothermic decomposition of excess hydride, the refluxing became too vigorous. To the mixture 600 ml. of ice water was added, and to this then added 1800 ml. of 10% sulphuric acid.

After separation of the ether layer, the aqueous layer was extracted with two further 250 ml. portions of ether. The crude a:β-unsaturated alcohol after evaporation of the ether from the dried etherial extract gave 100% yields; but distillation of this product under nitrogen through the fractionating column resulted in about 50% of pure α:β-unsaturated alcohol. The latter alcohols are characterized from the infrared spectrum of α:β-unsaturated alcohol.

Description	Yield	B.P. (°C)
penten 2-ol-1	49	59-60/30 mm.
2-methyl penten-3-ol-5	48.5	68/37 mm.

Table III

Infrared absorption characteristics of an α:β-unsaturated alcohol.

	Wavelength (u)	Wave No. cm^{-1}	Assignment
1.	5.78	1,705	α:β-unsaturated alcohol characteristic band
2.	3.35	2,980	C - H of the CHO stretching
3.	3.00	3,330	O - H stretching (hydrogen bonded OH)

Low Temperature Oxidation of the α:β-Unsaturated Alcohols

Oxidation of penten-2-ol-1 and 2-methyl penten-3-ol-5 was performed according to the procedure of Delaby and Guillot-Allegre(61) described earlier for some α:β-unsaturated alcohols such as 2-heptenal and 2-nonenal(37).

Procedure

Into a long-necked 1-litre flask, a solution of 30 g. potassium dichromate and 30 g. of concentrated sulphuric acid in 270 ml. of water was introduced. The flask was cooled in ice to about 5°C (cooling below 5°C has the disadvantage of causing crystallization). At this moment, an emulsion of 10 g. olefinic alcohol and 10 g. of water was added in one lot. The mixture was stirred vigorously while keeping the flask in ice. There was a very rapid browning and heat evolution. Observation of the thermometer showed the temperature after having reached a maximum (about 20-24°C) begin to fall. The reaction was stopped at once by the addition of 100 ml. of diethyl ether while the stirring was continued. Duration of oxidation was only 2-3 minutes.

After separation of the ether layer, the brownish aqueous phase was re-extracted with two 50-ml. portions of diethyl ether. The brown etherial extract was washed with water, saturated solution of sodium bicarbonate and then with water again and dried over anhydrous sodium sulphate. 1 g. of hydroquinone was added as a stabilizer.

The liquid residue after the removal of ether was distilled in a fractionating column in vacuo and with a nitrogen leak.

The aldehydes produced were characterised from the infrared spectrum of an α:β-unsaturated aldehyde,

Description	% Yield	B.P. (°C)
penten-2-al-1	58.6	62-64/80 mm.
2-methyl penten-3-al-5	41.2	59-60/48 mm.

Table IV

Infrared absorption characteristics of an α:β-unsaturated aldehyde.

	Wavelength (μ)	Wave No. cm^{-1}	Assignment
1.	5.78-5.93	1,705-1,685	α:β-unsaturated aldehyde characteristic bands (C = O stretching)
2.	3.35	2,980	C - H of the CHO stretching and deformation
	with two weak shoulders		
	at 3.47	2,880	
	3.60	2,730	
3.	6.94-7.55	1,440-1,325	other vibrations

Synthesis of Trimethyl Acetaldehyde

Trimethyl acetaldehyde was prepared from the reaction of purified methyl formate and *t*.butyl magnesium chloride by a modification of the methods of Bouvault(45) and Campbell(62).

Purification of Methyl Formate

Commerically pure methyl formate b.p. 31-35° was purified according to the method described for the purification of ethyl formate(63). It consisted in allowing the methyl formate to stand for 1 hour with 15% of its weight of anhydrous potassium carbonate with occasional shaking; decanting the ester into a dry flask containing some anhydrous potassium carbonate and allowing it to stand over for a further hour, followed by filtration into a dry flask and distillation through the fractionating column protected from moisture until completion of distillation. The fraction b.p. 31-32°C was sufficiently pure for subsequent work.

Preparation of Grignard Reagent

t.Butyl-magnesium chloride was prepared from magnesium turnings and t,butyl chloride as follows: 120 g. of dry magnesium turnings and 900 ml. of sodium dried ether were placed in a 3-litre three-necked flask equipped with a dropping funnel, reflux condenser and a mercury-sealed stirrer and protected from the moisture until completion of the reaction by calcium chloride tubings attached to the openings. Few crystals of iodine and 6 ml. of t.butyl chloride were introduced into the flask without the stirrer running.

The reaction was initiated by warming the flask gently in a water bath. The water bath was removed when the reaction showed signs of proceeding, e.g. disappearance of the iodine colour and generation of heat shown by the rapid reflux of ether.

550 ml. of the t.butyl chloride in 850 ml. of sodium dried diethyl ether were then introduced at a rate such as to produce a gentle reflux. The complete addition of the alkyl halide took 1.5 hours per g.mole on the average.

Procedure

The Grignard reagent was filtered under an atmosphere of dry nitrogen and added dropwise to 600 ml. of purified methyl formate. The temperature of the reaction was kept below -40°C until the addition of the Grignard reagent was completed. The cooling mixture (solid carbon dioxide - ethanol) was removed, while the stirring was continued until the temperature of the reaction mixture reached room temperature. The white-coloured Grignard complex was transferred into a 5-litre beaker containing 1 kgm. crushed ice and hydrolysed using

500 ml. of 35% sulphuric acid. After separation of the etherial layer, the aqueous phase was extracted with two further portions of diethyl ether. The combined ether extract of the aldehyde was dried over anhydrous potassium carbonate. 2 g. of hydroquinone were added as stabiliser. Ether was removed by distillation through a fractionating column and the liquid residue was fractionated at ordinary atmospheric pressure, under a gentle stream of nitrogen.

Fractions of b.p. 67-74° were considered sufficiently pure for subsequent work. The gas chromatographic separation and subsequent infrared identification showed less than 10% impurity in the aldehyde. Yield 19% based on the Grignard reagent used.

Table V

Infrared absorption characteristics of an aliphatic saturated aldehyde.

	Wavelength (μ)	Wave No. cm^{-1}	Assignment
1.	5.75-5.81	1,740-1,720	aliphatic saturated aldehyde characteristic band (C=0 stretching)
2.	3.47-3.70 10.26-13.1	2,880-2,700 975-763	C-H of the CHO stretching and deformation
3.	6.77-7.33	1,485-1,370	other vibrations

Synthesis of the 2-Alkyl-8-Hydroxyquinoline Derivatives

The preparations of 2-ethyl, 2-*iso*propyl and the attempted 2-*tert*-butyl-8-hydroxyquinoline derivatives were made according to Merritt and Walker method(18), based on the Doebner von Miller(29) and the Skraup(32) reactions, described originally for the 8-hydroxyquinaldine.

Procedure

Into 500 ml. three-necked flask, equipped with a dropping funnel, reflux condenser and a mercury-sealed stirrer, 27.5 g. (0.25 mole), *o*-amino-phenol and 12.5 g. (0.09 mole) *o*-nitro-phenol, both dissolved in 75 g. concentrated hydrochloric acid, were introduced. The α:β-unsaturated aldehyde equivalent to (0.275 mole) was added with stirring and over a period of 20-30 minutes. The flask was heated in a water bath at 95-100°C for six hours and allowed to stand at room temperature overnight. The excess *o*-nitro-phenol was then removed by steam distillation from the acid solution and until the distillate was almost colourless. After cooling the flask to 30°C the reaction mixture was made almost neutral by the addition of 20% sodium hydroxide, and then almost alkaline to litmus, i.e. pH 7-8, by the addition of solid sodium carbonate.

Removal of the 7-alkyl-8-quinolinol derivative thus precipitated from the alkaline mixture, was made either by filtration through sintered glass crucible or by super-steam distillation.

The product obtained by filtration was purified by sublimation under vacuo (~ 5 mm. Hg). The sublimate of the 8-quinolinol derivative obtained mixed with o-amino-phenol was further purified by sauxlet extraction with petroleum ether (B.p. 40-60°). The pure derivative was crystallized afterwards from the petroleum ether extract after concentrating the liquid.

The product obtained by the super-steam distillation, on the other hand, turned dark red on exposure to air. A further purification was required. This was carried out by a second super-steam distillation from just alkaline (pH 7-8) medium, followed by recrystallization from low boiling petroleum ether.

The two new 8-quinolinol derivatives purified by the above procedures were mainly light yellow crystalline solids characterised by the following:

Description	(M.p.)	% Calculated			% found		
		C	H	N	C	H	N
2-ethyl-8-quinolinol	50-51	76	6.4	8.1	75.98	7.23	8.28
2-*iso*propyl-8-quinolinol	86-87	77	7	7.5	76.0	6.88	7.98

Aldol Condensation

Preparation of the β-*t*.butyl-acrolein (2:2-dimethyl-penten-3-al-5) was made by a modification of Kraft(64) method, from the reaction of trimethyl-acetaldehyde and acetaldehyde in presence of a basic catalyst, aqueous potassium hydroxide.

Procedure

To a mixture of 1.68 g. (0.03 mole) of potassium hydroxide, in 1.8 g. (0.1 mole) of water, 78 g. (1.7 moles) of ethanol and 22 g. (0.255 mole) of trimethyl acetaldehyde, placed in 250 ml. three-mecked flask, equipped with a dropping funnel, reflux condenser and a mercury-sealed stirrer, were added, while bubbling nitrogen gas gently through the solution, 70 g. (1.6 moles) of acetaldehyde, and over a period of three hours. The temperature of the reaction is kept below 35°C. The yellow mixture formed was allowed to stand at room temperature overnight, while the nitrogen gas bubbling was continued. The solution was acidified with glacial acetic acid and fractionated in vacuo under nitrogen using "a six-inch single surface helix-packed column in conjunction with a side condenser and Perkin intermediate receiver, as the fractionating device".

The yellow fraction b.p. 68-70 (50 mm.) was characterised, from the I.R. Spectrum of an α:β-unsaturated aldehyde (Table IV) as the desired product (yield 16%).

CHAPTER FIVE

PROPERTIES OF THE 2-ETHYL- AND 2-_ISO_-PROPYL-8-QUINOLINOLS

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the 2-ethyl- and the 2-isopropyl-8-quinolinols, from 225-400 mμ, which furnish additional information about their structures have been studied in acid, neutral and alkaline solvents. Fig. V is a typical example of these spectra. The spectra were recorded with aunicam ultravoilet spectrophotometer sp.800 with automatically adjusted slit width.

Reproducibility is judged by the agreement of duplicates within 1-2 mμ. Approximate obedience to Beer's law over the concentration range used (generally 0.000025M - .01M) was universal.

In the following tables absorption maxima are given in millimicrons (mμ); the figures in parantheses are the molecular extinction coefficients and I, II, III represent absorption maxima. Apart from the 8-hydroxyquinoline and 8-hydroxyquinaldine data which were recorded by Merritt et al.(22), other data are the authors work.

FIG.V ULTRAVIOLET SPECTRUM OF 2-ISO-PROPYL-8-QUINOLINOL IN CYLOHEXANE

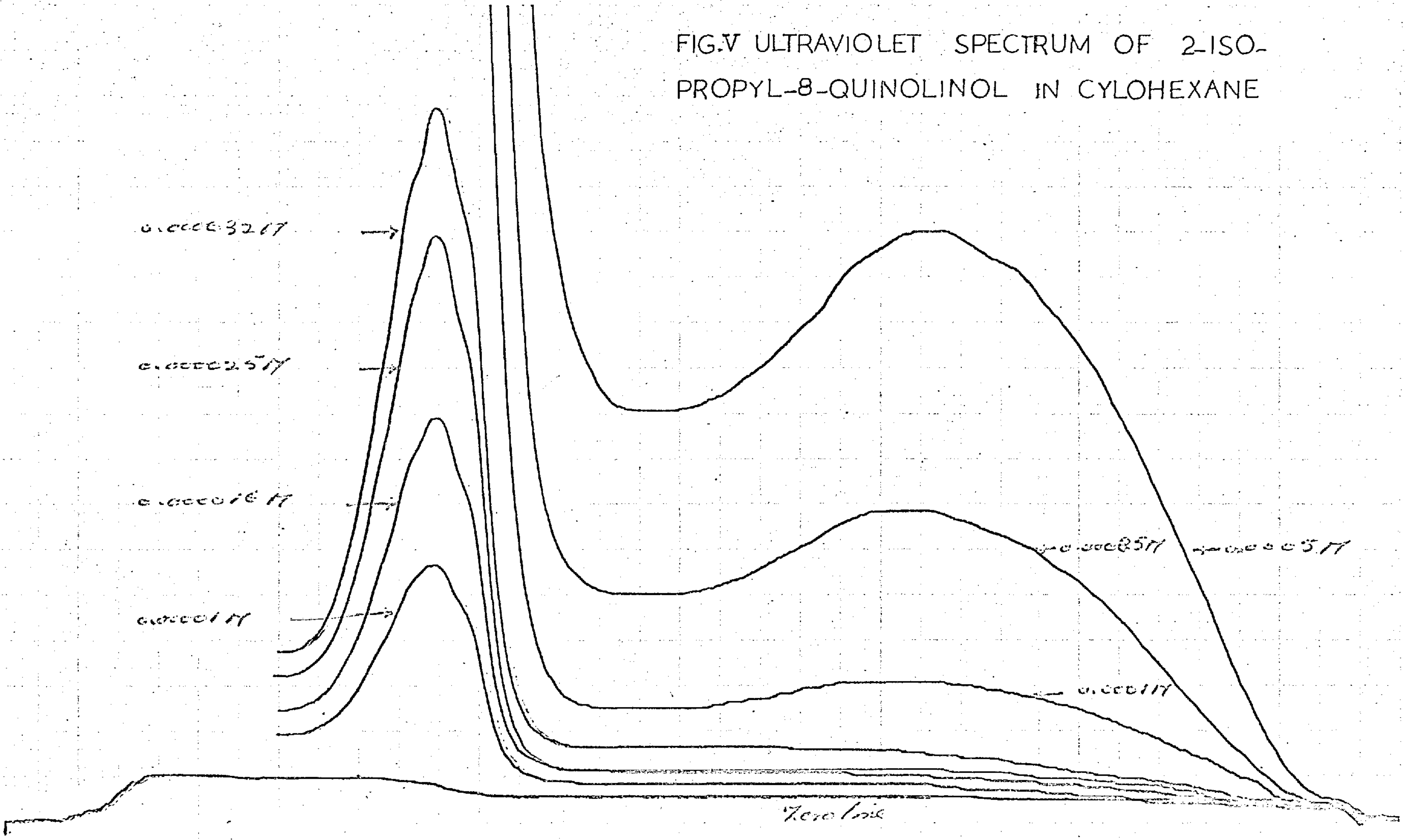


Table VI

U.V. absorption maxima of 8-quinolinols in neutral solvent

Compound	Neutral Solvent (Cyclohexane)	
	I	II
8-quinolinol	242 (42,000)	320 (2,400)
2-methyl-8-quinolinol	246 (43,000)	309 (2,900)
2-ethyl-8-quinolinol	245 (50,000)	305-8 (2,600)
2-isopropyl-8-quinolinol	245 (48,000)	304-7 (2,500)

Table VII

U.V. absorption maxima of 8-quinolinol in hydrochloric acid

Compound	0.1-3 N hydrochloric acid solution		
	I	II	III
8-quinolinol	250(40,000)	317-9(1,700)	358(1,700)
2-methyl-8-quinolinol	255(44,000)	320(3,100)	345(1,700)
2-ethyl-8-quinolinol	254(49,000)	317-8(3,500) 308-11(3,200)	330-43 (1,760)
2-isopropyl-8-quinolinol	254(49,000)	319(3,600) 309-12(3,300)	336-43 (1,900)

Table VIII

U.V. absorption maxima of 8-quinolinols in sodium hydroxide

Compound	0.1-1 N potassium hydroxide	
	I	II
8-quinolinol	253 (32,000)	345 (2,700)
2-methyl-8-quinolinol	255 (30,000)	335 (3,000)
2-ethyl-8-quinolinol	255 (35,000)	331-5 (3,000)
2-*iso*propyl-8-quinolinol	255 (34,000)	331-5 (3,100)

Interpretation of the Spectra

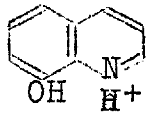
Measurements of the absorption maxima and the molecular extinction coefficients have two limitations:

1. The second area of maximum of absorption is rather broad compared with the first band, therefore the difference in wavelength of maximum absorption should not be considered significant unless they amount to at least 5 mμ.
2. The absolute precision of the molecular extinction coefficients is not better than ± 10%. This is due to the fact that the solutions used were prepared by weighing out quantities of the order of 1-2 mg. on an ordinary analytical balance.

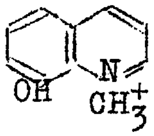
Interpretation of the spectra of the two 8-quinolinol derivatives studied were made either by comparison with the spectra of 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline, or with the spectra of closely related known compounds.

The spectra produced are all similar in shape to the absorption spectra of 8-quinolinol and 2-methyl-8-quinolinol. Some shifts in (maxima-II) of the two quinolinol derivatives, amounting to 10-15 mμ when compared with 8-quinolinol, are produced. These are bathochromic shifts, produced by the replacement of the hydrogen, on the 2-position of the pyridine ring of the 8-quinolinol nucleus, with ethyl or <u>iso</u>propyl groups. They are at slightly lower wavelength ranges than those of the 2-methyl-8-quinolinol. Evidence for the bathochromic shifts produced on replacing hydrogen in an aromatic ring by methyl group have been reported$^{(66,\ 67,\ 68)}$.

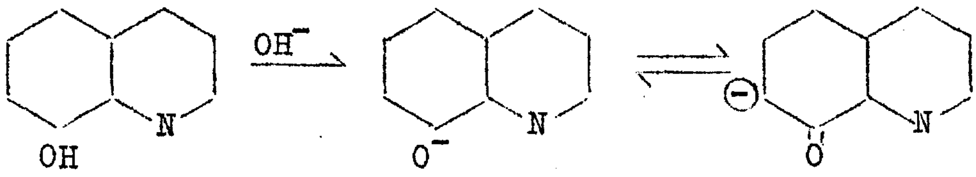
The spectra of the 2-ethyl- and 2-<u>iso</u>propyl-8-quinolinols in hydrochloric acid are considerably different from those observed in neutral or alkaline solutions, Table VII. This has been attributed, for 8-quinolinol, to a change of structure. Protonated oxine was claimed to have been formed; evident from the similarity of the spectra of oxine in acid solution and its diazomethane reaction product



which has been postulated to have the structure in acid solution and the dissimilarity in neutral solution, where the diazomethane product has the presumed structure(69).



A very pronounced bathochromic shift of the 2-ethyl and 2-isopropyl-8-quinolinols absorption bands, mounting to 10-15 mμ when compared with 8-quinolinols, are produced in alkaline medium, Table VIII. This is in accord with an empirical rule(70) in which it is stated that when ionization increases the tendency of a group to shift electrons into an aromatic ring a bathochromic shift occurs; ionization of the oxine takes place in alkaline medium to give the oxonium ion (structure II) which would readily allow shift of electrons to the benzene ring to give the quinone ion (structure III)(67).



I II III

Infrared Absorption Spectra

The infrared absorption spectra of the 8-quinolinols and derivatives from 2-15 μ, (5000-650 cm^{-1}), were automatically recorded with a Unicam infrared spectrophotometer sp.200, using the Nujol mull technique Fig. VI. The probable precision in assigning wavelengths is estimated to be ± 0.05 μ. The 8-quinolinol derivatives have no significant absorptions at the regions where total absorption of the Nujol mull occur * (3.4 u(2,970cm^{-1}), 6.83u(1,475cm^{-1}) and 7.25u(1,390cm^{-1})

Table IX

Infrared absorption maxima of 8-quinolinols in Nujol mull
(* Nujol mull absorption bands.)

8-quinolinol	2-methyl 8-quinolinol	2-ethyl 8-quinolinol	2-isopropyl- 8-quinolinol
2.93 (3,495)	2.93 (3,495)	2.93 (3,495)	2.93 (3,495)
*3.4 (2,970)	*3.4 (2,970)	*3.4 (2,970)	*3.4 (2,970)
6.35 (1,580)	6.2 (1,600)	6.2 (1,600)	6.2 (1,600)
6.65 (1,520)	6.35 (1,580)	6.35 (1,580)	6.35 (1,580)
*6.83 (1,475)	6.65 (1,520)	6.65 (1,520)	6.65 (1,520)
7.1 (1,410)	*6.83 (1,475)	*6.83 (1,475)	*6.83 (1,475)
*7.25 (1,390)	*7.25 (1,390)	7.1 (1,410)	*7.25 (1,390)
7.8 (1,290)	7.5 (1,340)	*7.25 (1,390)	7.5 (1,340)
7.9 (1,270)	7.9 (1,270)	7.5 (1,340)	7.6 (1,320)
8.18 (1,270)	8.0 (1,250)	7.6 (1,320)	7.9 (1,270)
8.28 (1,210)	8.18 (1,220)	7.8 (1,290)	8.0 (1,250)
	8.28 (1,210)	7.9 (1,270)	8.18 (1,220)
		8.0 (1,250)	8.28 (1,210)
		8.18 (1,220)	
		8.28 (1,210)	

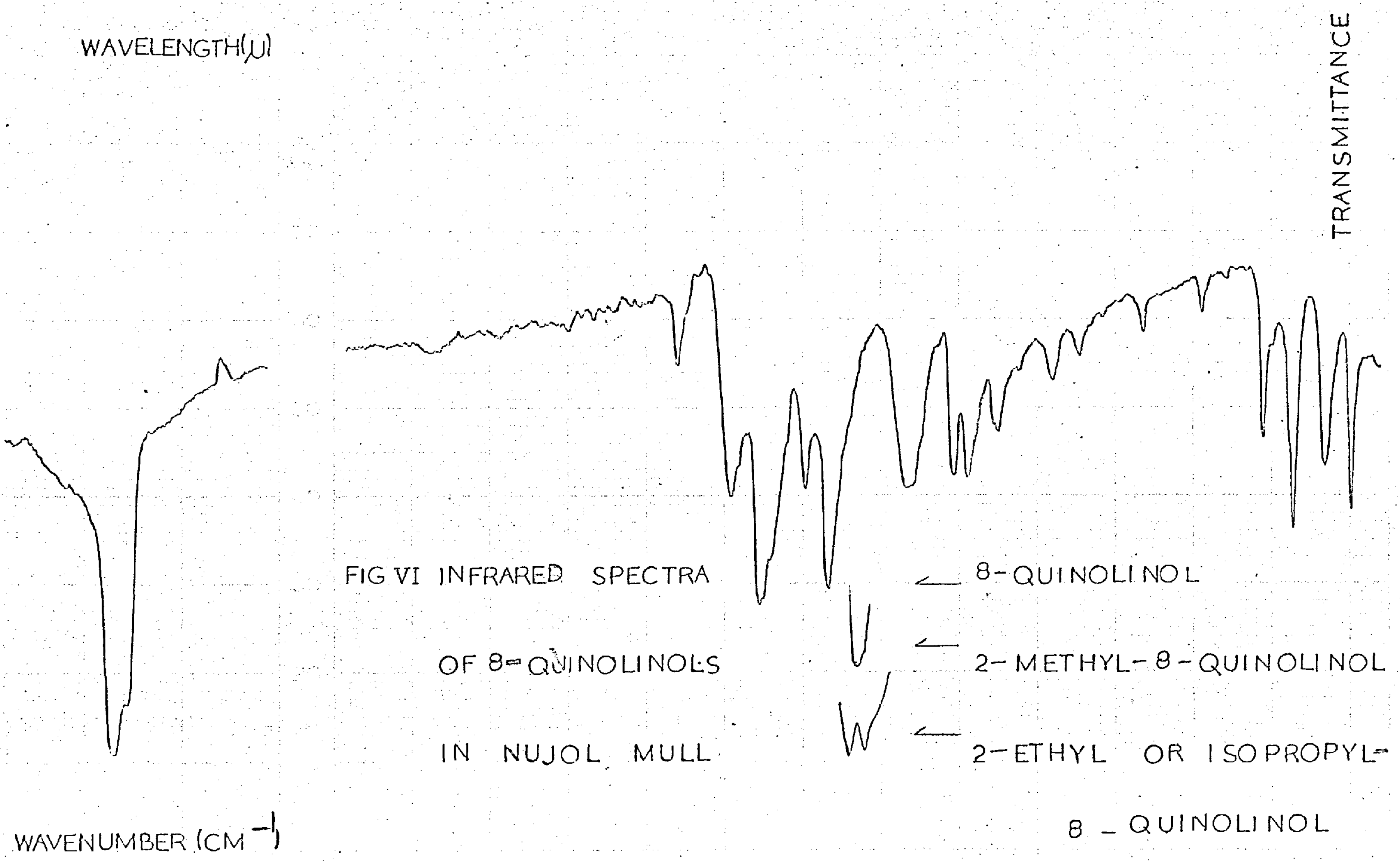


FIG VI INFRARED SPECTRA OF 8-QUINOLINOLS IN NUJOL MULL

Interpretation of the Infrared Absorption Spectra

The absorption band at about 2.93μ (3,495 cm^{-1}) present in these four 8-quinolinols, but absent in the 8-alkoxy compounds, is assigned to the OH stretching frequency observed in all phenols(71, 72).

The strong maxima at about 6.2u(1,603 cm^{-1}), 6.35μ(1,580 cm^{-1}) and 6.65μ (1,520 cm^{-1}) are evidently fundamental frequencies of the aromatic ring(22).

The absorption bands from 7.1-7.6 μ (1,410-1,320 cm^{-1}) are probably due to the aliphatic C-H bending(22).

The band at 7.5 μ (1,340 cm^{-1}) perhaps being caused by the C-H bond in the active alkyl group since it is lacking in 8-quinolinol and 4-methyl 8-quinolinol but apparent in 2-methyl-8-quinolinol(22). An additional band at 7.6 μ (1,320 cm^{-1}) is probably assignable to another C-H linkage in the 2-ethyl- and 2-*iso*propyl substituent, since it is lacking in the 2-methyl.

The maxima from 7.8-8.28μ(1,290-1,210 cm^{-1}) are perhaps associated with C-O and C-N stretching vibrations(22).

Above 8.28 μ (1,210 cm^{-1}) assignment of definite wavelengths to definite structural features is not possible. It is interesting that no C=O band at about 5.8 μ (1,750 cm^{-1}) was observed in any of the compounds, although a keto tautomer of 8-quinolinol has been claimed to constitute about 35% of the total concentration in non-polar solvents(73).

X-Ray Powder Diffraction

The X-ray powder diffraction lines of the 2-ethyl- and the 2-*iso*propyl-8-hydroxyquinoline derivatives were measured and the results were compared with those of 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline and 2,4-dimethyl-8-hydroxyquinoline reported by Merritt et al.(22).

The measurements were made by exposing the finely powdered sample loaded in a 0.3 mm. quartz cappillary to filtered CuK_{α} radiations for five hours, using a Philips X-ray generator at 40 Kv and 20 mA and 1 radian Philips camera for these purposes.

Table X

X-ray powder diffraction lines of 2-alkyl substituted 8-quinolinols.

Compound	'd' values in order of decreasing intensity.				
8-hydroxyquinoline	6.27	3.18	3.82	3.50	
2-methyl-8-hydroxyquinoline	3.92	3.67	3.13	5.45	5.93
	2.07	5.00	7.94		
2,4-dimethyl-8-hydroxyquinoline	7.14	3.55	3.98	4.50	3.24
2-ethyl-8-hydroxyquinoline	7.06	4.90	3.92	3.51	3.22
	6.29	5.24	4.16	4.56	2.91
2-*iso*propyl-8-hydroxyquinoline	7.21	5.02	3.83	4.67	6.42
	3.59	3.52	3.22	3.29	3.52

Literature data on the X-ray diffraction of the 2-substituted 8-quinolinols are very scarce. Though many 2-phenyl and 2-styryl 8-quinolinol derivatives were synthesized, none of them was studied by this technique. The only 'd' values reported, so far, for 2-substituted 8-quinolinols were those of 2-methyl-, 2,4-dimethyl and their halogen substituted derivatives, yet interpretations of these data were not reported. The following, is a brief study made by comparing the 'd' values obtained for the 2-ethyl- and 2-isopropyl-8-quinolinols with those available on the 8-quinolinol, 2-methyl- and 2,4-dimethyl-8-quinolinols. From Table X the following are exhibited:

1. The 1st 'd' value is increasing in the order of the substituent 2-isopropyl- > 2,4-dimethyl- > 2-ethyl- > none. However it is low for the 2-methyl-substituent.
2. The 2nd 'd' value is also increasing in the order of the substituent isopropyl- > ethyl- > dimethyl- > methyl- > none.
3. The 3rd 'd' values are showing no definite trend.
4. The 4th 'd' values for the 8-quinolinol and the 2-ethyl- derivative are comparable, but they are lower than those of the other three 8-quinolinols.
5. The 5th 'd' values of the 2-methyl- and 2-isopropyl derivatives are higher than those of the 2,4-dimethyl and 2-ethyl- derivatives.
6. The 6th 'd' value of the 2-ethyl-8-quinolinol is higher than those of the 8-methyl- and 2-isopropyl-8-quinolinols. The 7th and 8th 'd' values on the other hand are higher for the 2-methyl- and 2-ethyl- than that of the 2-isopropyl-8-quinolinol.

The previous data revealed the fact that the first and second 'd' values increase with increasing size of the 2-substituents. This is attributed to an increase in the dimensions of the unit cell and hence increase in the lattice spacings. However, the first 'd' value reported for the 2-methyl-8-quinolinol, 3.90(22) is considered very low in comparison with that of the 8-quinolinol 6.27, reported by the same authors. Its value should therefore be greater than 6.27 and lower than the corresponding value for the 2-ethyl- derivative 7.06. Such argument was based on a study made on different metals where a similar conclusion could be elucidated. Table XI describes the relationships existing between lattice spacings of different metals and the 'd' values in terms of the strongest lines and relative intensities.

Table XI

X-ray powder diffraction of some metals.

Element	Structure	Spacing Å	Three strongest lines in decreasing intensity order	Relative intensity
Cu	f.c.c.	3.6153	2.09 1.81 1.28	100 46 20
Pd	"	3.8902	2.25 1.95 1.38	100 42 25
Pt	"	3.9237	2.27 1.96 1.18	100 53 33
Al	"	4.049	2.34 2.02 1.22	100 47 24
Au	"	4.078	2.36 2.04 1.23	100 52 36

Note: F.c.c. represents face centered cubic, while the data are those of the A.S.T.M.

TableXI exhibits a disorder in the 3rd 'd' values of the metals, which is in turn parallel to the disorder characteristics of the 3rd 'd' values of the 8-quinolinol homologues studied.

Steric Hindrance, Selectivity and Sensitivity

Selectivity and sensitivity tests were carried out using the method of Lutz(74) used by Irving, Butler and Ring(75) in which the sensitivity of a reagent is recorded in terms of the smallest amount of metal which will give a perceptible precipitate in a fixed volume of a test solution under standard conditions. The buffer solutions designated A, B and C were prepared as follows:

A.	250 ml. 2N acetic acid	
	225 gm. sodium acetate (hydrated)	pH 5.3
	500 ml. of water	
B.	40 ml. 2N ammonium hydroxide	
	320 gm. ammonium acetate	pH 8.35
	30 gm. sodium potassium tartrate	
	850 ml. of water	
C.	500 ml. 2N sodium hydroxide	
	275 sodium potassium tartrate	pH 13.1
	500 ml. of water	

Stock solutions of metals containing 0.01 g.atom/l were prepared from 'spekpure' metals or 'AR' salts. The organic reagent solution was 0.1M in absolute alcohol. The procedure adopted was to take a 0.01M solution of the metal under investigation and 4.0, 0.4, and 0.04 ml. were respectively placed in three test tubes (5 x 5/8 in.) previously boiled in nitric acid and washed repeatedly in distilled water and finally steamed with live steam from boiling redistilled water.

In each tube was placed 2 ml. of buffer A, 0.2 ml. of organic reagent, and sufficient water to bring the total volume to 6.2 ml. A fourth tube containing the buffer solution, reagent solution and water served as a reagent blank and a fifth tube containing 0.4 ml. of the metal solution, 2 ml. of buffer solution A and 3.8 ml. of water served as the metal blank. The latter blank was necessary so that a possible hydroxide precipitation should not be mistaken for complex formation. All tubes were then heated in a water bath at 80° for 15 minutes and examined, hot and after cooling, for precipitation. If results were positive with as little as 0.04 ml. of 0.01 N metal solution, the whole series was repeated with 0.001 N metal solutions and if necessary with 0.0001 N until precipitation did not occur. The limits of sensitivity were then more exactly limited by carrying through a series of tests with 0.4, 0.2, 0.1 and 0.04 ml. of metal solution of the appropriate strength. The sequence of testing was then repeated with buffer solution B and C in turn, and the whole procedure repeated for each reagent and every metal studied. The results obtained under these conditions are given in Table XII. The figures for 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline employed in the comparison are those of Irving, Butler and Ring(75).

Table XII

Records for each combination, the smallest concentration (µg/ml) of metal which gave a precipitate; together with the largest concentration which just failed to do so under the standard conditions of test.

Metal ion used	Al^{+++}			Cr^{+++}			Fe^{+++}		
Buffer	A	B	C	A	B	C	A	B	C
8-hydroxyquinoline	4.4– 1.7	4.4– 1.7	N.p.	8.4– 3.4	16.8– 8.4	N.p.	1.8– 0.9	1.8– 0.9	N.p.
	(yellow)			(yellow-brown)			(greenish-black)		
2-methyl-8-hydroxyquinoline	N.p.	N.p.	N.p.	3.4– 1.7	1.7– 0.8	N.p.	1.8– 0.9	0.9– 0.4	N.p.
	(–)			(yellow-brown)			(greenish-black)		
2-ethyl-8-hydroxyquinoline	N.p.	N.p.	N.p.	1.6– 0.8	3.6– 2.5	N.p.	1.8– 0.9	1.8– 0.9	N.p.
	(–)			(yellow-green)			(greenish-black)		
2-*iso*propyl-8-hydroxyquinoline	N.p.	N.p.	N.p.	0.3– 0.09	0.9– 0.4	N.p.	0.4– 0.09	0.9– 0.4	N.p.
	* (–)			* (yellow-green)			* (greenish-black)		

N.p. signifies that there was no precipitate of complex

*: the reagent was insoluble in the cold buffer, though freely soluble at 80°, whilst the metal complex was sufficiently insoluble for its formation to be detected with certainty when observations were made on the hot solution.

Table XII (cont.)

Metal ion used	Cu++			Zn++			Ga+++		
Buffer	A	B	C	A	B	C	A	B	C
8-hydroxyquinoline	1.0- 0.4	1.0- 0.4	1.0 0.4	1.1- 0.4	1.0- 0.4	10.6- 4.2	2.3- 1.1	2.3- 1.1	N.p.
	(yellow-green)			(yellow)			(yellow)		
2-methyl-8-hydroxyquinoline	1.0- 0.4	1.0- 0.4	20.5- 10.3	21.0- 10.6	1.0- 0.4	2.1- 10.6	22.5- 11.3	2.3 1.1	N.p.
	(salmon)			(yellow)			(yellow)		
2-ethyl-8-hydroxyquinoline	1.8- 0.9	0.9- 0.4	90- 36	N.p.	1.0- 0.4	N.p.	2.3- 1.1	1.1- 0.4	N.p.
	(orange)			(yellow)			(yellow)		
2-_iso_propyl-8-hydroxyquinoline	0.1- 0.04	0.1- 0.04	10.2- 4.0	N.p.	0.4- 0.09	N.p.	0.4- 0.09	1.1- 0.4	N.p.
	(orange)*			(yellow)*			(yellow)*		

N.p. signifies that there was no precipitate of complex.

*: the reagent was insoluble in the cold buffer, though freely soluble at 80°, whilst the metal complex was sufficiently insoluble for its formation to be detected with certainty when observations were made on the hot solution.

Discussion

Complexes of the type $MR_{\frac{m}{n}}$ will not be precipitated until $[M^{m+}]^n \, [R^{n-}]^m$ equals or exceeds the solubility product $S_{MR_{\frac{m}{n}}}$. The observed sensitivity will thus be influenced by the 'visibility' of the precipitate and will depend on the concentration of the reagent, RH_n, the hydrogen ion concentration, pH, and finally on the presence of masking agents such as the tartrate salt.

Reproducibility was judged from the close agreement of duplicates. To avoid a false impression, the sensitivity data are presented in Table XIII in terms of sensitivity exponent pL, and not in the customary manner as µg/ml (where $pL = -\log_{10}$ [limiting concentration in g. equivalent/L]).

In default of comprehensive data relating the percentage of element precipitated to the pH of the solution for each metal and reagent studied, and where the sensitivities in the three test solutions A, B and C were not identical, the values adopted were those from the medium where the greatest sensitivity was shown.

Table XIII

Sensitivity values in terms of sensitivity exponent pL

Metal	8-quinolinol	2-methyl-8-quinolinol	2-ethyl-8-quinolinol	2-*iso*propyl-8-quinolinol
Al^{3+}	3.3	N.p.	N.p.	N.p.
Cr^{3+}	3.3	4.0	4.0	4.8
Fe^{3+}	4.0	4.3	4.0	4.7
Cu^{2+}	4.5	4.5	4.5	5.5
Zn^{2+}	4.5	4.5	4.5	5.5
Ga^{3+}	4.0	4.0	4.3	4.8
Average values excluding those for aluminium				
	4.1	4.3	4.3	5.3

From the results shown in Tables XII and XIII it is apparent that the 2-ethyl- and 2-*iso*propyl-8-quinolinols are selective, in that they do not chelate with aluminium under any conditions. However, the observed selectivity of the two derivatives are comparable with that of 2-methyl-8-quinolinol. The two tables reveal the failure of these two derivatives to enhance selectivity for other tervalent metals besides aluminium. The failure of aluminium to chelate with 2-methyl- oxine has been attributed to steric hindrance. Irving and co-workers(75) have shown stereochemically how heterocyclic ligands could possibly arrange around a tervalent Al^{3+}, Fe^{3+}, Ga^{+3}, In^{+3} in oxine complexes conforming to the general formula MR_m, and why ligands of 2-substituents fail to do so for aluminium. This is summarized as follows: with tervalent elements of co-ordination number six the three heterocyclic ligands form chelate rings in planes mutually at right angles. Figure VII depicts the proposed arrangements for the 2-methyl oxine of a tervalent metal.

In this figure the 2-methyl group of each ligand is directed towards the oxygen or nitrogen of the neighbouring chelate ring at right angles to it. The octahedral covalent atomic radius of Al^{3+} is 1.3A°. Together with conventional atomic radii for the remaining elements (C = .77, O = .74, N = .74) the lengths C_{methyl} - Oxygen and C_{methyl} - Nitrogen are nearly euqal at about 2.7A°, i.e. shorter than the distance of approach accepted for non-bonded atoms. The hydrogen atoms of the methyl group are naturally still

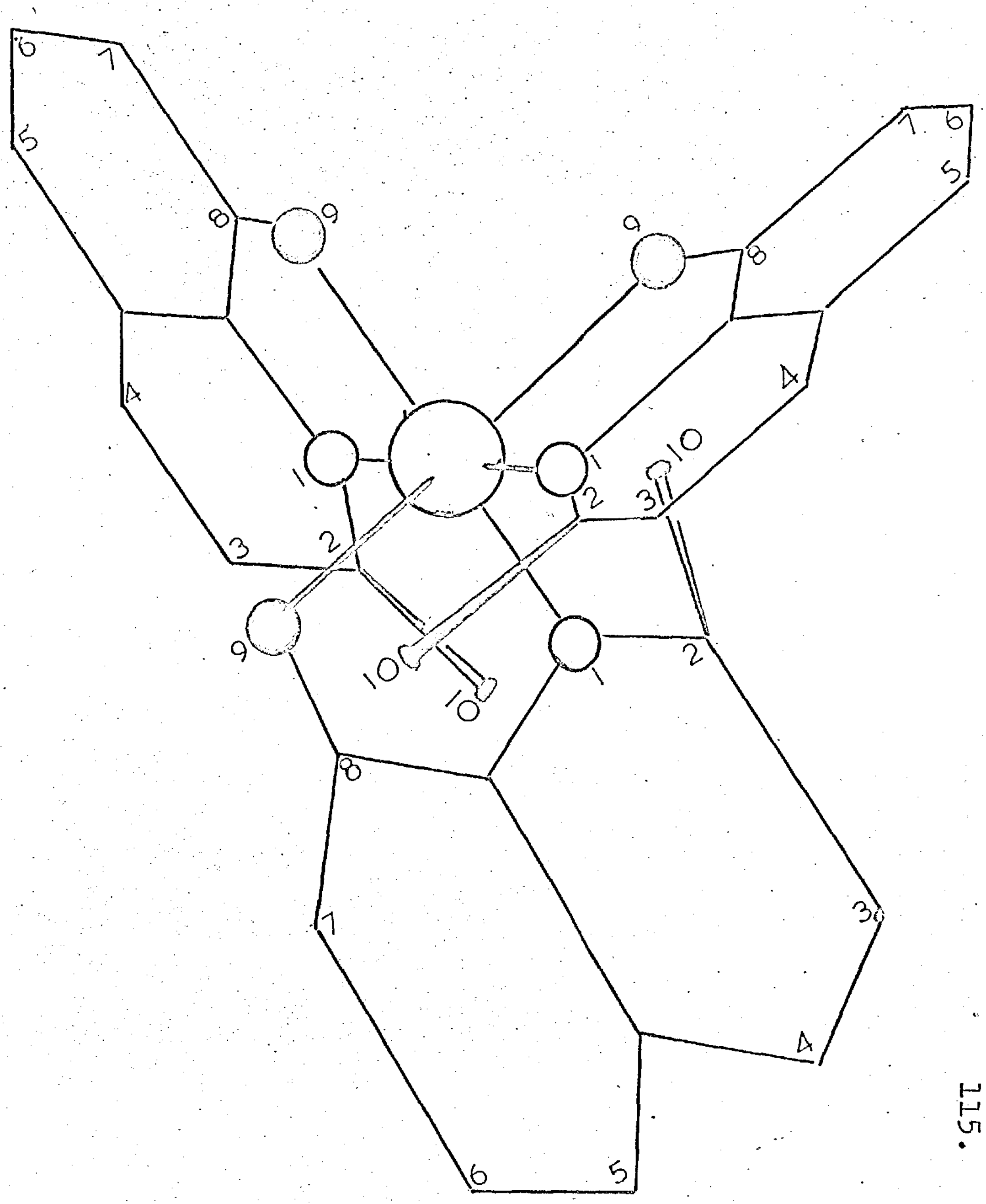
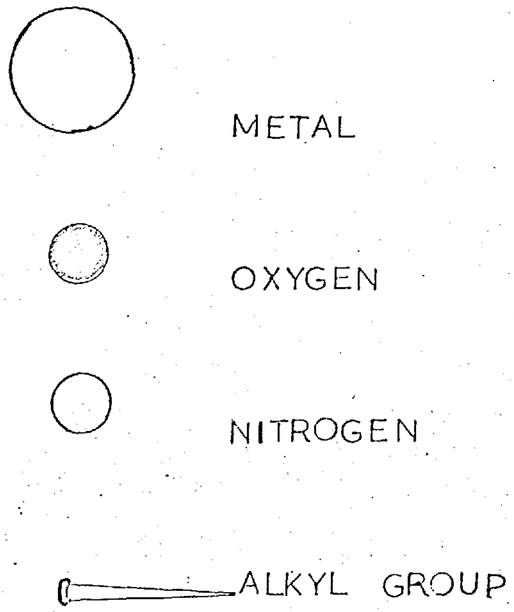


FIG VII 2- ALKYLOXINE COMPLEX OF A TERVALENT METAL



closer, and therefore concluded that purely steric considerations would prohibit the formation of aluminium 2-methyl-8-quinolinate complex.

The arrangements of the 2-ethyl- and 2-*iso*propyl-oxines of a tervalent metal may also be depicted by similar figure. The lengths C_{alkyl}- Oxygen and C_{alkyl} - Nitrogen are equally similar to those of the 2-methyl substituent, but the hydrogen atoms and the side carbon atoms of the alkyl groups are even at shorter distances than the distance of approach for non-bonded atoms, as compared with the 2-methyl- oxine. Therefore greater steric repulsions must have been produced, the order of which is methyl- $<$ ethyl- $<$ *iso*propyl- $<$ t.butyl- and could have been clearly verified with the availability of instability data for the various metal -chelates complexes. It must also be remembered that as the covalent radius of the metal determines the sizes of the groups which could arrange around it, then the steric repulsions will be decreasing with the increase of the covalent octahedral radii of the elements Al $\equiv$ Ga $>$ In $>$ Tl whose covalent radii are 1.3, 1.3, 1.44, 1.48 A°.

In practice, though selectivity of the 2-methyl-8-quinolinol has not been enhanced by substitution in the 2-position with ethyl- and *iso*propyl- groups, and results are therefore disappointing they indicate that 2-t.butyl- derivative if it could have been prepared, may show greater selectivity. Moreover, and in view of these investigations, the distinctive behaviour of aluminium in not forming complexes with 2-methyl, 2-ethyl, 2-isopropyl and with other 2-substituted-8-quinolinols could not be ascribed wholly to its small size. Gallium, which is reported as having equal octahedral covalent radius as that of aluminium (1.3 A°)(75) is anomalous in that it was found reactive with these two new derivatives.

A final conclusion could therefore be drawn which is that the tendency of aluminium towards such complex formation with oxine derivatives substituted adjacent to the nitrogen atom is small and being still further reduced by the additional energy barrier imposed by unfavourable steric factors(75).

The reactivity of gallium and other metal ions of comparable sizes, e.g. Fe^{III}, Cr^{III}, with the 2-substituted 8-quinolinols may therefore be explained in terms of their decreasing electropositivity in comparison with aluminium, hence their bondings to oxygen and nitrogen should be more covalent in character. Other factors such as: the basicity of the reagent; the number and position of the ligands; the electronegativity of the metal; the electronic structure; the orbitals available and the location of these orbitals, etc. may also affect the chelation.

If each of the above factors is to act independent, the result will be as follows:

1. The basicity of the 2-substituted 8-quinolinols is increasing in the order of the 2-substituent $C_4H_9- > C_3H_7- > C_2H_5- > CH_3-$ and therefore more stable metal chelates should be formed with the 2-isopropyl- and 2-t.butyl-8-quinolinols.
2. The number and location of the functional groups in all the chelating anions studied are identical and highly favourable for chelation. The chelate rings produced with these 2-substituted derivatives are all of the most stable five-membered type.
3. The effect of electropositivity of the metals is as explained above.
4. The electronic structure of the metal atoms; the orbitals available and the location of these orbitals have remarkable effect on chelation. The lower the orbitals, the greater the stability of the metal chelates. Accordingly more stable metal chelates are those of the transition elements.

But the outcome is that of all these factors acting collectively. However, for a given metal ion it is that of the inductive and steric effects of the 2-substituents only. Interpretation of the sensitivity results which follow immediately should enlighten the issue further.

Sensitivity

It is obvious from Table XIII that the average sensitivity value for 2-ethyl-8-quinolinol complexes with the metals Al^{3+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+} and Ga^{3+} is comparable with the figure given for 2-methyl-8-quinolinol complexes with the same metal ions(75); average pL = 4.3. However, the average sensitivity value for the 2-*iso*propyl-8-quinolinol chelates with the above metals is much greater; average pL = 5.1. This figure actually is the highest for any known 8-quinolinol- metal chelates. Increased sensitivity is noted especially for the divalent copper and zinc with 2-*iso*propyl-8-quinolinol; average pL for these two metal oxinates 5.5, and may either be ascribed to:

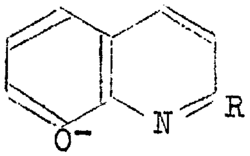
1. The decrease in the metal chelates aqueous solubilities (and increase in organic solvent solubilities) due to the increase of size and molecular weight. Thus the order of aqueous solubility should be that of the 2-substituents $C_3H_7- < C_2H_5- < CH_3-$ and

hence the most aqueous insoluble metal chelates are those produced by the reaction of metals with the 2-isopropyl-8-quinolinol.

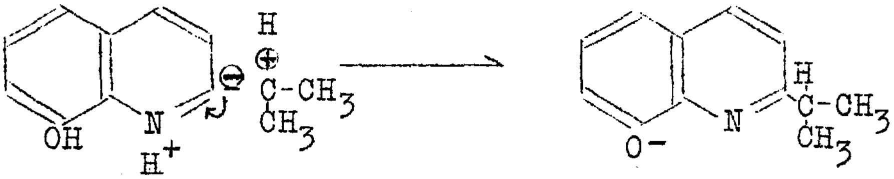
or

2. the powerful inductive effect of the 2-substituent. Here, increased sensitivity mechanism may be described by the following: alkyl groups such as ethyl and isopropyl are electron donating and so will increase electron availability over the nucleus in the order $CH_3 < C_2H_5 < C_3H_7 < C_4H_9$.

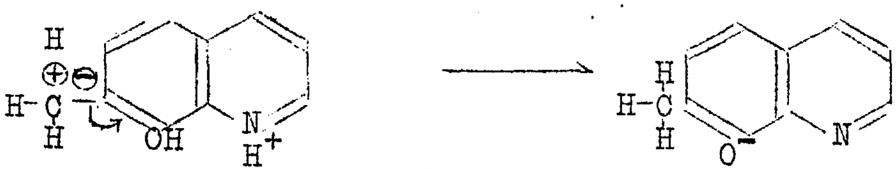
The presence of a powerful inductive group in the 2-position of the 8-quinolinol nucleus may restrict the formation of oxonium ion



and so permit the metal chelate to persist in solutions of greater acidity. Such reactions may be compared with that of 7-methyl-8-quinolinol(75), and can be demonstrated by the following



reaction of the 2-isopropyl-8-quinolinol



reaction of the 7-methyl 8-quinolinol

The compatability of the selectivity and sensitivity results are to be discussed with the aid of the solvent extraction properties data later.

The Solvent Extraction Properties of the 2-Ethyl- and the 2-isopropyl-8-Quinolinols

The solvent extraction properties of the 2-ethyl- and the 2-*iso*propyl-8-quinolinol complexes with some metal ions have been studied. Such properties included wavelengths of absorption maxima, molecular extinction coefficients, and optimum pH ranges for the extraction. The metals selected for these studies were those associated with aluminium in alloys, e.g. Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+}.

Absorption maxima were recorded between 300-700 mµ on an automatic recording Unican spectrophotometer, Sp 800, using a suitable concentration of the metal chelate solution in chloroform, Figs. VIII and IX.
The extractability measurements are similar to those of cupric and ferric oxinates reported earlier in Chapter II of this thesis, i.e. the cation is extracted from aqueous into chloroform phase as either its 2-ethyl- or 2-*iso*propyl-8-quinolinate derivative and at each pH value the optical density (absorption) of the

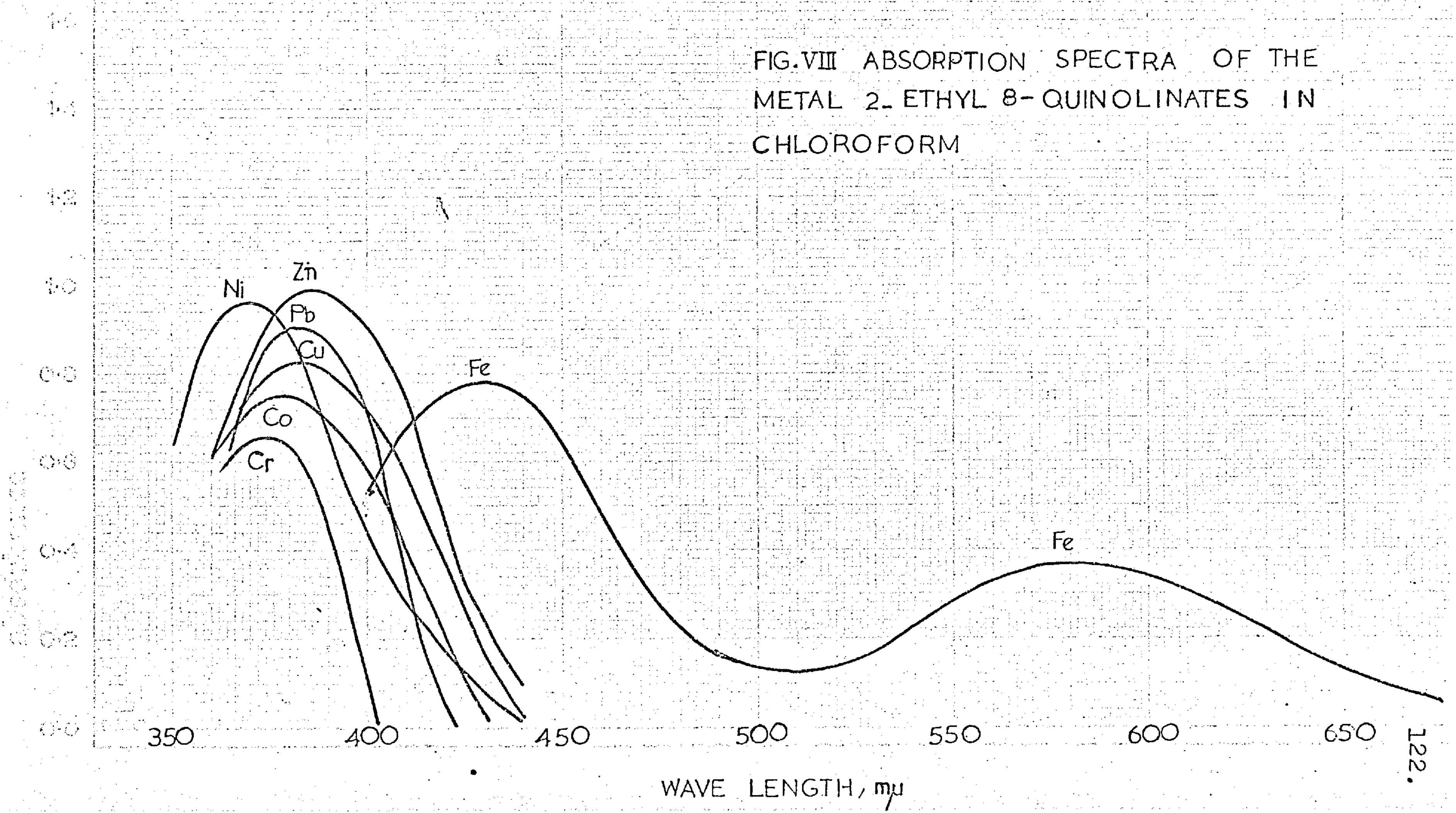
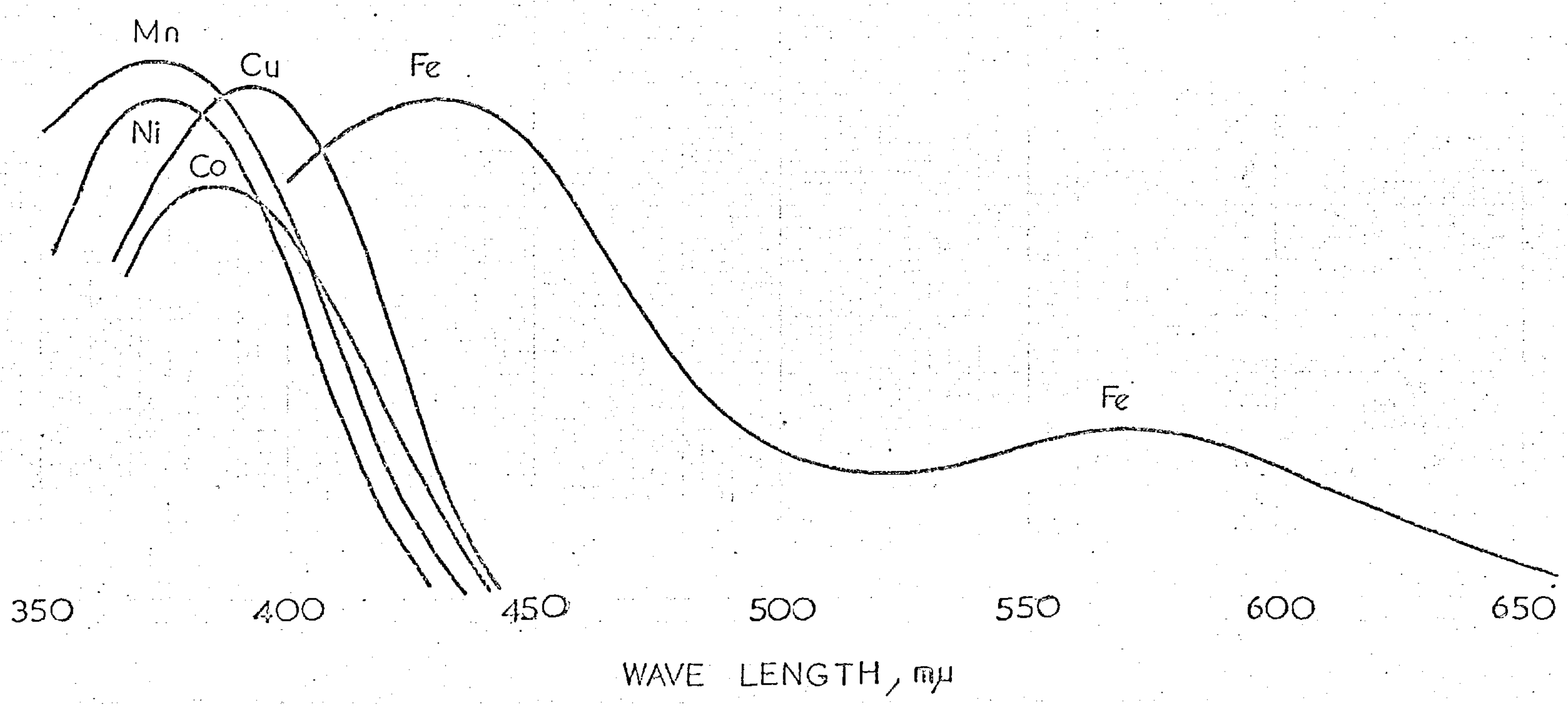


FIG. VIII ABSORPTION SPECTRA OF THE METAL 2-ETHYL 8-QUINOLINATES IN CHLOROFORM

FIG. IX ABSORPTION SPECTRA OF THE METAL 2-ISOPROPYL 8-QUINOLINATES IN CHLOROFORM



organic phase is measured at the respective absorption maximum of the complex. Here, the same apparatus, i.e. Dynacap pH meter and Hilger Uvispek spectrophotometer H 700, were employed for these measurements. In Table XIV the optimum pH's of extraction of the 2-ethyl- and 2-isopropyl-metal-8-quinolinates are presented, while in Table XV the values for absorption maxima of these complexes are given. The figures in paranthesis are the approximate values of the molecular extinction coefficients (data regarding the molecular formulae of the two 2-alkyl-substituted quinolinol metal complexes are not available, so the molecular weights employed in these determinations are therefore estimated from the metal oxinates of similar composition.) The values for 8-quinolinol and 2-methyl-8-quinolinol metal chelates used in the comparative study are those of Motojima et al.(76).

The absorption maxima spectra of the metals - 2-ethyl- or 2-isopropyl-8-quinolinates in chloroform are similar in shape to those of the metals - 8-quinolinates and 2-methyl-8-quinolinates, Figs. VIII and IX. However, they are shifted to lower wavelengths; the shifts amount to ~ 40 mu for λ_{max} of 2-ethyl- and 2-isopropyl-ferric complexes, in comparison with that of the ferric-8-quinolinate, Table XV.

Table XIV

Optimum pH's of extraction of some metals with 8-quinolinol and derivatives

Compound	Reagent concentration (M)	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}	Pb^{2+}
8-quinolinol	0.021	2.4-	2.8-	5.5-8.8	7.3-8.2	9.0-10.5	8.2-11
2-methyl-	0.019	4.5-12.2	4.2-12.5	8.5-10.7	-	-	8.2-11.8
8-quinolinol	0.001	4.5-12.2	4.2-12.5				
2-ethyl-	0.015	4.0-11.5	5.0-	8.5-11.0	8.0-	9.8-	8.0-
8-quinolinol	0.001	4.0-11.5	5.0-				
		(3.05)	(3.75)	(7.20)	(7.00)	(8.3)	(6.65)
2-*iso*propyl	0.001	3.7-	5.3-	8.9-10.5	8.5-	9.8-10.7	-
8-quinolinol		(2.75)	(3.80)	(7.55)	(7.80)	(8.45)	

Note: if not recorded, the second pH values in the above table are those of greater than measurable ($>$ 14).

The figures in paranthesis are those of pH's of $\frac{1}{2}$ extraction (pH$_{\frac{1}{2}}$). pH$_{\frac{1}{2}}$ values for the metal-8-quinolinates and 2-methyl-8-quinolates are not available.

Table XV

Absorption maxima (mμ) and, in paranthesis, molecular extinction coefficients of some metal-oxine and derivatives complexes.

Compound	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	Mn^{2+}
8-quinolinol	470	410	370	420	400	395
	580					
	(5100)	(3100)	(3300)	(-)	(-)	(6500)
2-methyl-	470	395	272	-	384	-
8-quinolinol	580					
	(4300)	(2900)	(3100)	(-)	(1500)	-
2-ethyl-	430	386	370	378	382	382
8-quinolinol	560					
	(4700)	(3700)	(3100)	(-)	(2750)	(4000)
2-_iso_propyl-	430	393	375	385	-	375
8-quinolinol	560					
	(5100)	(3950)	(3100)	(4250)	-	(4000)

Extractability of the metals Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+} with the 2-ethyl- and 2-isopropyl-8-quinolinols were quantitative at their optimum pH values, Figs. X and XI, but generally with a further shift in the extraction curves away from the acid side than those produced with the metal-8-quinolinates and 2-methyl-8-quinolinates and in the order of the substituents $C_3H_7- > C_2H_5 > CH_3 >$ none(23), Table XIV. This indicates that less stable (i.e. more dissociated) metal complexes are formed, due to the increasing steric effect of the 2-alkyl substituents and therefore more alkaline medium is required to promote quantitative extraction. The decrease in the aqueous solubility of these metal chelates in the order of the 2-substituent $C_3H_7 < C_2H_5 < CH_3 <$ none and the respective increase in the organic solvent solubility in the reverse order should result in higher P_c's and P_R's in the order of the 2-substituents $C_3H_7 > C_2H_5 > CH_3 >$ none. Therefore and in reference to the extractability formula shifts in the extraction curves to the acid side should be produced due to the increase in the P_c while the reverse should happen when the P_R increases.

However, such interpretation is not yet conclusive. There are few points which when clarified might affect the outlook of the picture, e.g. the stability constants

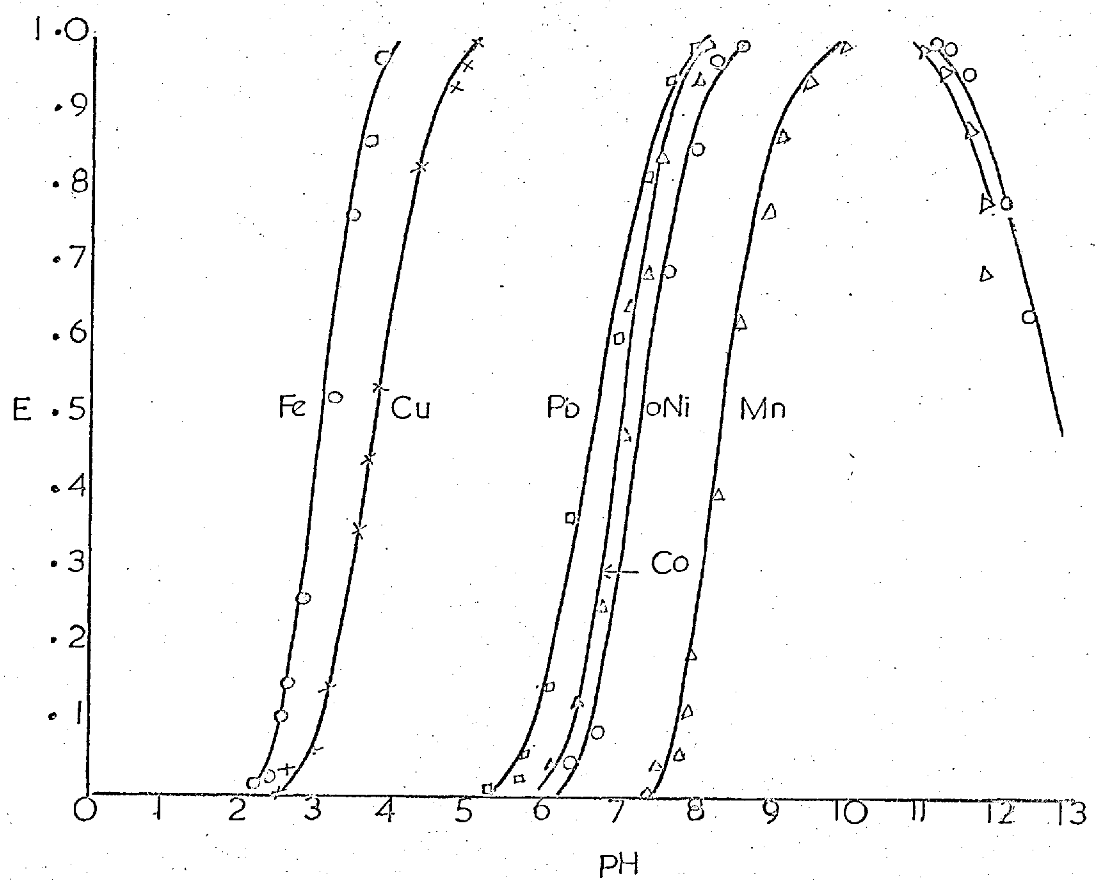


FIG. X EXTRACTION CURVES OF THE METAL – 2 – ETHYL 8 – QUINOLINATES

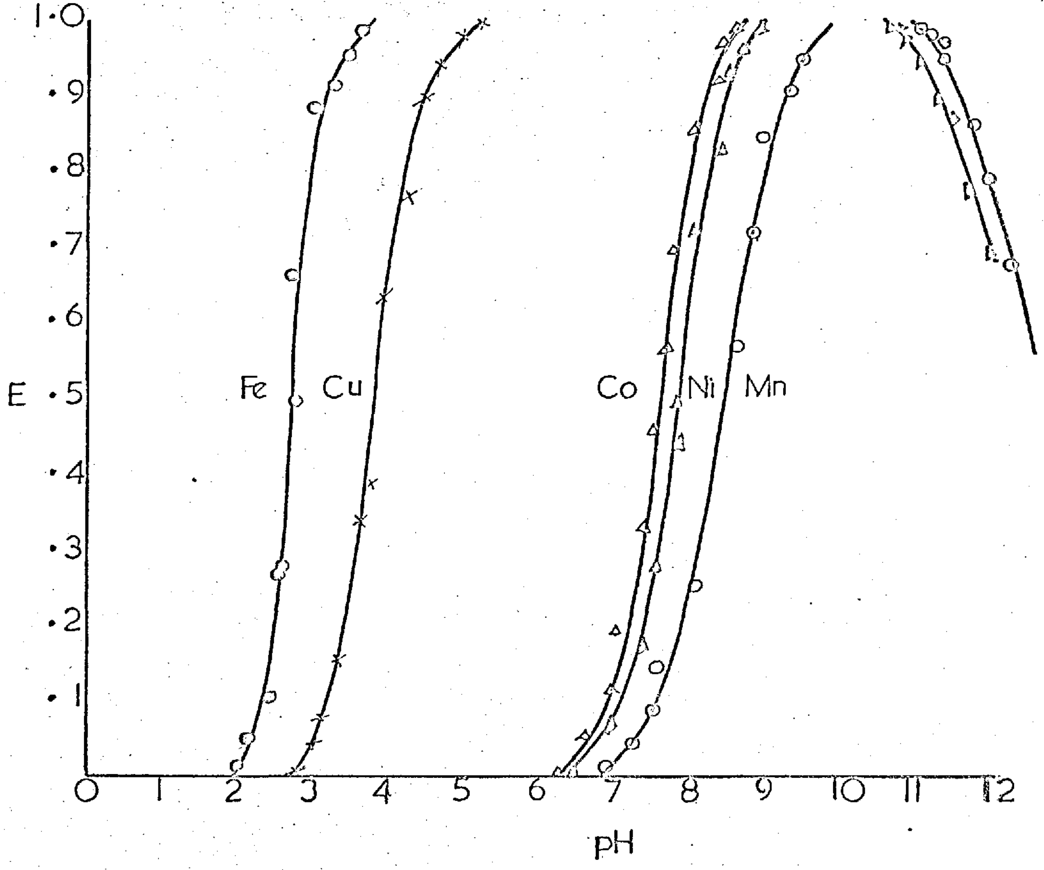


FIG. XI EXTRACTION CURVES OF THE METAL-

2-<u>ISO</u>PROPYL 8-QUINOLINATES

and the composition data regarding the metal 2-alkyl-substituted 8-quinolinates are not available, it is therefore not yet clear whether more stable complexes were produced by the chelation of the metals with such strongly basic or inductive ligands.

Although the extraction measurements were made with organic reagents of variable concentrations, experimentally no shifts in the extraction curves along the pH axis were noted on the application of such low organic reagent concentrations ranging between 0.001-0.021M. This is evident from the extraction measurements of Cu^{2+} and Fe^{3+} 2-methyl- and 2-ethyl- 8-quinolinates with the lower and higher values of reagent concentrations, but in contradiction with the previous extractability formula and with that of Irving et al.(9) $(pH_{\frac{1}{2}})_{1.00} = pH - (\log q)/N + \log [HA]_{org}$ (where $(pH_{\frac{1}{2}})_{1.00}$ = pH at which 50% of the metal is extracted (q = 1) at 1.00 M equilibrium concentration of the organic reagent in the organic phase provided the values of the organic and aqueous phase are equal, q = distribution ratio of the metal between the two immiscible phases, N = the metal ion charge, HA = organic reagent) which expected a decrease of one pH unit in the $(pH_{\frac{1}{2}})_{1.00}$ on an increase of tenfold in the equilibrium reagent.

Ionization Constants of the 2-Alkyl- Substituted 8-Quinolinols

The dissociation constants K_{R1} and K_{R2} of the 2-ethyl- and 2-*iso*propyl-8-quinolinols have not been studied, but from the following data given for the 8-quinolinol(54) and the 2-methyl-8-quinolinol(77)

	pK_{R1}	pK_{R2}
8-quinolinol	9.66	5.00
2-methyl-8-quinolinol	10.15	5.65

it should be possible to predict that the acid dissociation constant, K_{R2}, should decrease in the order of the 2-substituent none $> CH_3- > C_2H_5- > C_3H_7-$. The following ionization data may be assumed for the 2-ethyl- and the 2-*iso*propyl-8-quinolinols by considering similar changes in the values of pK_{R1} and pK_{R2} to those produced on substituting methyl group in the 2-position of the 8-quinolinol

	pK_{R1}	pK_{R2}
2-ethyl-8-quinolinol	10.64	6.30
2-*iso*propyl-8-quinolinol	11.13	6.95

It is interesting that the order of increasing pH at which a given metal ion is extracted by these four reagents is roughly the order of decreasing acidity of the 2-substituted 8-quinolinols.

8-quinolinol — increasing K_{R2} ↑
2-methyl-8-quinolinol
2-ethyl-8-quinolinol
2-*iso*propyl-8-quinolinol — ↓ increasing pH

This is explained by noting that, although the weaker acids should form more stable complexes with metallic ions(23) and the extraction should, therefore, be possible from more acid solutions, it is necessary to use more basic solutions in order to produce comparable amounts of the active chelating ion. The latter effect is apparently the predominant one.

The effects of P_R and P_c are as described under the solvent extraction properties of the 2-ethyl- and the 2-*iso*propyl-8-quinolinols.

Interpretation of Sensitivity and Selectivity in Terms of Inductive and Steric Effects

It was shown from the sensitivity, selectivity and solvent extraction properties of the 2-ethyl- and 2-*iso*propyl-8-quinolinols with various metal ions how steric, inductive and solubility factors affect the results.

The steric factors should be greatly effective in the octahedral chelates of tervalent metal atoms of the type MR_3 which is to be expected from the difficulty arising from fitting large groups around comparatively small ions. However, it should be a minor one for the tetrahedral metal chelates which involve divalent metals of relatively increasing covalent atomic radii and consequently the ligands are not in a crowded position to exercise the steric repulsions.

Steric effects are likely, therefore, to reduce sensitivity on their own but in practice many metals were found reactive and with strong enhancement in the sensitivity values in the order of the 2-substitutents none $< CH_3- < C_2H_5- < C_3H_7-$. The explanation to this may be that in the reaction of these two derivatives with the metal ions under investigation the steric effect was compensated by inductive effect coming from the 2-bulky-alkyl-substituent. Accordingly, more electrons are being pushed into the ring by the 2-substituent which would finally result in lengthening the M-N and M-O bondings by increasing their ionic character and hence reducing the steric effect in allowing larger groups to arrange comfortably around the metal. However, strong enhancement in the sensitivity does not necessarily indicate inductive effects, since the increase expected in the ionic character of the bondings may not be enough to produce stronger chelates. Availability of stability constants data regarding these metal chelates should clarify this issue. The increase in sensitivity may therefore have to be looked at from another aspect: since the sensitivity is measured by the formation of perciptable precipitates in the test solutions it is likely, therefore, that the latter (aqueous insolubility of metal chelate) becomes a determining factor.

The solubility of the metal 2-alkyl-8-quinolinates should decrease according to the increase of the size and molecular weight of the chelating agents in the order $C_3H_7- < C_2H_5- < CH_3-$ and hence more insoluble metal chelates should be produced by the reaction of metals with the 2-isopropyl-8-quinolinol and subsequently higher sensitivity results should thus be produced.

The marked increase in sensitivity with the 2-isopropyl-8-quinolinol, where major steric effects begin to be apparent from 3-dimensional models is therefore expected from the solubility point of view but not from purely steric effects.

The solvent extraction data indicated that less stable metal chelates were produced, due to increasing effects of the 2-alkyl substituents, which required a more alkaline medium to promote quantitative extraction. The greatest shifts, away from the acid side, were noted in the extraction curves of the metal-2-isopropyl-8-

quinolinates. Steric effects may be shown to be predominant, despite the inductive effects, from Figs. XII and XIII plotted from the sensitivity values for a typical tervalent metal, gallium tested with four 8-quinolinols vs. the number of c-atoms in the different 2-substituents.

In conclusion increased pL is attributed to steric rather than to inductive effects. Linear increase in the sensitivity, pL (Fig. XII) as indicated by the dotted line should be ascribed to inductive factors, but since the plot (Fig. XIII) shows breaks at different points the effect is therefore that of steric.

The interpretation is at the present a tentative one because some fundamental data regarding the stability constants, composition, solubility and the minimum and maximum pH ranges of precipitation of the metal chelates under investigations, are still not available.

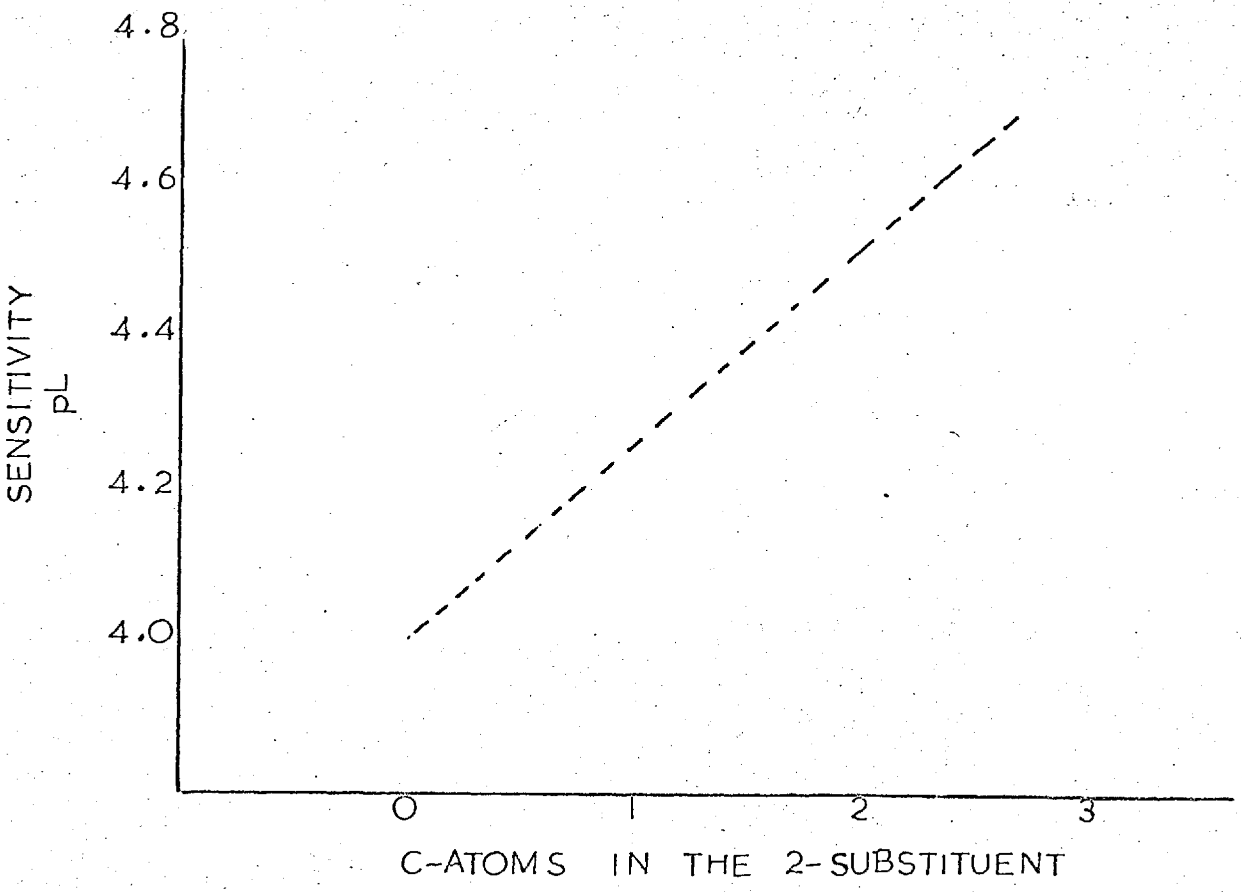


FIG. XII DIAGRAMATIC INDUCTIVE EFFECT ON SENSITIVITY

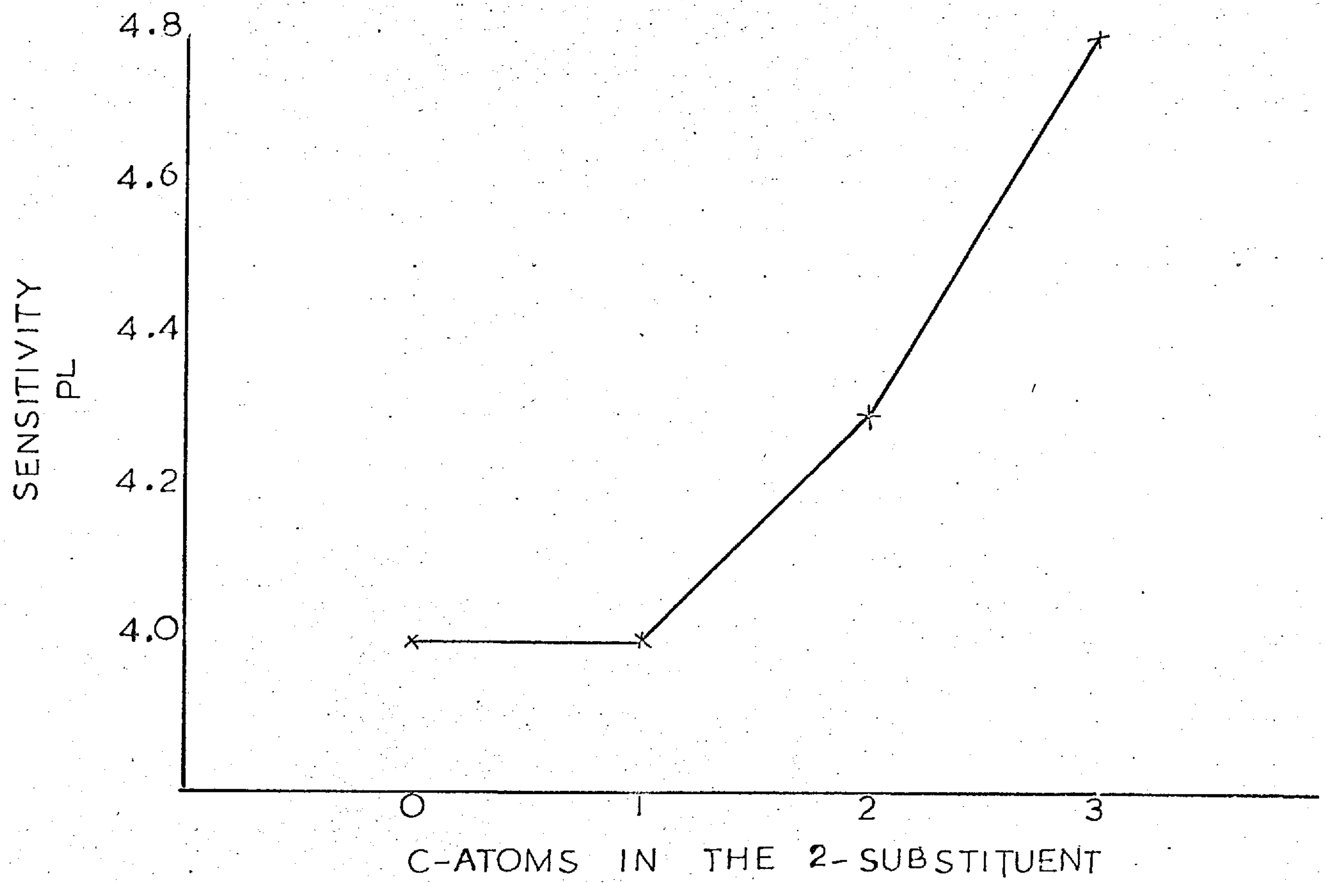


FIG. XIII ANTICIPATED STERIC EFFECT ON SENSITIVITY

Chromium III Extraction with 2-Ethyl-8-Quinolinol

It is well known that the formation of Cr^{III}-8-hydroxyquinolinate complexes is kinetically poor, and even on ageing, the complexes cannot be quantitatively obtained for gravimetry. The effect of ageing with the 2-ethyl-8-quinolinol has been studied for the purposes of solvent extraction: neither precipitation nor extraction of the Cr (III) complex is complete in the cold, but a quantitative extraction became possible after heating the metal-chelate suspension at 60-80°C for 10 minutes. Fig. XIV is plotted from time of ageing in the cold and at 60-80°C vs. the optical density in the organic phase.

Procedure

25 mg. of 2-ethyl-8-quinolinol was dissolved in 4-5 drops of glacial acetic acid by warming on a hot plate. 2 ml. of 0.001M Cr^{3+} solution and 1 ml. of 1% sodium perchlorate were then added. After adjusting the pH to ~ 6, the mixture was heated to 60-80°C for various periods. The Cr (III)-2-ethyl-8-quinolinate thus precipitated was extracted from the aqueous solution with 10 ml. of chloroform and the absorption

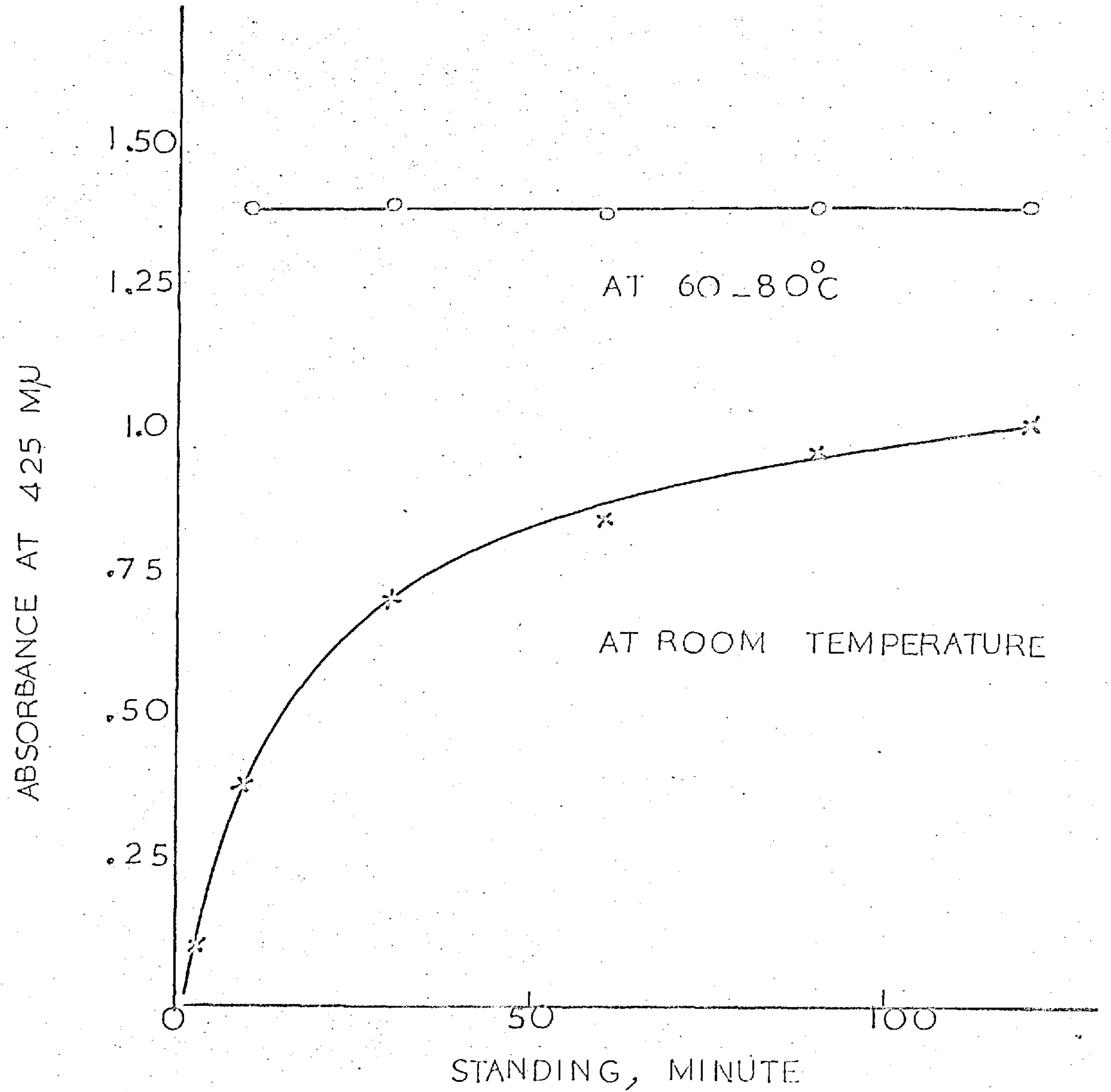


FIG.XIV EFFECT OF AGING ON THE EXTRACTION OF Cr-2-ETHYL 8-QUINOLINATE of the organic phase was measured at the respective absorption maximum of the complex, 425 mu. Similar measurements in the cold were also carried out.

Application of the 2-Alkyl-Substituted 8-Quinolinols to the Analysis of Aluminium Alloys

Utilization of the remarkable property of 2-methyl-8-quinolinol to chelate with very many metals and not to do so with aluminium has already been suggested by Walker and Merritt(18) to eliminate elements that ordinarily interfere in the determination of aluminium. However, the results obtained have not been wholey satisfactory, particularly when the aluminium was a minor constituent. Hynek and Wrangell(48) improved the results by the application of secondary complexing agents in addition to electrolysis with mercury cathode. The method described, however, has no great advantage over existing methods. Earlier Pantony and Selfe have attempted the elimination of interferences in binary alloys by successive extraction with 8-hydroxyquinaldine solution in chloroform. Their investigations showed that, for binary alloys of aluminium with magnesium, nickel, copper and beryllium, accurate analyses for both constituents were obtained by extracting into chloroform the second element with 2-methyl-8-quinolinol and then aluminium with 8-quinolinol and using a spectrophotometric finish. However, in more complex samples, e.g. alnico and an iron ore - the method failed and invariably high results were obtained despite the use of different extraction conditions.

Moreover, the reagents sensitivities, especially of the 2-<u>iso</u>propyl-8-quinolinol are greater when compared with the 2-methyl-8-quinolinol, and therefore successful removal of trace quantities of interferences was expected. A simple method, which is a modification of Riley and William procedure(57), is described. Permanent magnet (BCS No. 233), as a typical alloy was selected for the present brief study. The composition of the alloy is as follows:

Al = 6.98%, Fe = 51.15%, Ni = 11.22%, Co = 23.72%,
Cu = 5.09%, Ti = 0.79%, Mn = 0.235%.

Procedure

Preparation of Sample Solution

20 mg. of the alloy, weighed on a microbalance, were dissolved in 1 ml. perchloric acid, by heating on a hot plate until clear solution was obtained. Heating was

continued until fuming in order to remove excess volatile acid. The solution was then cooled and made up to 100.ml. with distilled water.

25 mg. of the 2-alkyl substituted 8-quinolinol, in a 25 ml. beaker, were dissolved by warming with a few drops of glacial acetic acid, 2 ml. of the alloy solution, accurately measured, and 0.5 ml. of (0.5 M) sodium acetate were then added; followed by 1 ml. of (7% ammonium chloride solution in 3:5 ammonium hydroxide solution) to bring the solution to pH 10.0. The mixture was transferred quantitatively into a 50 ml. separating funnel, using little water and 10 ml. of chloroform, and equilibrated by shaking on a mechanical shaker for 30 minutes. The lower chloroform layer which contained the metal complexes was discarded and the aqueous layer was re-extracted by equilibration for 10 minutes with 5 ml. of 2% reagent in chloroform. This chloroform phase was also rejected. The pH of the aqueous phase was brought to pH 7.0 using 0.4 ml. of glacial acetic acid, and another extraction was carried out by equilibration for 10 minutes with 5 ml. of 2 %. reagent in chloroform. The chloroform phase was rejected. Traces of reagent which were still in the aqueous phase was removed by brief extraction for 30 seconds with 5 ml. of chloroform. The pH of the

aqueous solution was brought down to $\sim$ 4.5 by the addition of 0.2 ml. of glacial acetic acid and the solution equilibrated for 10 minutes with 1% 8-quinolinol in chloroform. The chloroform extract was run through a plug of filter paper (held in the stem of the funnel) into a 25 ml. graduated flask. The aqueous phase was washed with a few mls. of chloroform, by gentle rotation of the separating funnel, and the chloroform wash was run into the flask.

The volume was made up to 25 ml. with chloroform. The optical density of the chloroform extract was measured at 410 mμ on a Hilger Uvispek spectrophotometer, against a compensating cell containing chloroform.

Aluminium content was determined from a graph plotted from aluminium concentrations vs. optical density. Standard aluminium solution was prepared by dissolving 0.0529 g. of "specpure" aluminium in excess of hydrochloric acid and diluted to 1 litre.

Note: The yellow aluminium oxinate extract fades in strong light and the extractions were therefore carried out in artificial light or diffuse daylight.

Table XVI

Determination of aluminium as 8-quinolinate in permanent magnet alloy.

Reagent employed in the removal of interferences	% Aluminium		
	Present	Found	
2-methyl-8-quinolinol	6.98	7.76	
		7.91	
2-ethyl-8-quinolinol	6.98	7.34	7.63
		7.48	7.63
2-*iso*propyl-8-quinolinol	6.98	6.91	
		6.98	

It is obvious from the above Table XVI that aluminium results obtained when applying the two 8-quinolinol derivatives in the aluminium alloy analysis, i.e. by separating the foreign metals from about 200 ug. samples with the 2-alkyl-8-quinolinol and determining aluminium in the aqueous phase with 8-hydroxyquinoline, was slightly high with the 2-ethyl- , but it was quantitative with the 2-*iso*propyl-8-quinolinol.

The analytical improvement over the series methyl < ethyl < *iso*propyl is as anticipated.

It is due to the very limited availability of the reagents that a small number of results are obtained.

CHAPTER VI

CONCLUSION

In the introduction to this thesis it was stated that, although a considerable number of formulae dealing with the solvent extraction equilibria of metal chelates, are available in the literature, only few were of practical importance. The rest are either too complicated or oversimplified. The complicated derivations resulted in hindering the general application of the solvent extraction of metal chelates technique in the inorganic analysis, while the simplified derivations failed to give satisfactory understanding of the functions of all the parameters involved in this system. The stated intention was to investigate the possibility of introducing an extractability equilibria which would employ the fundamental principles of solvent extraction and avoid both the foregoing draw-backs. A considerable success has been achieved in this aim is evident from the extractability equation, presented in Chapter II of this thesis, for the solvent extraction of simple metal chelates. Though verification of the equation has been attempted only with simple metal oxinates system, however, the formula may be of practical application in other systems also. The extention of the formula to systems in which hydrolysis of the metal takes place or involve other competing ligands (masking agents), has shown with no doubts the extent to which the characteristics of the formula can be taken. This may encourage more work to be carried out to extend the formula to mixed complexes of the type $MR_m(RH_n)_\gamma$, $MR_m(OH)_p$, $MR_m(RH_n)_\gamma.(OH)_p$ and $MR_m(RH_n)_\gamma.(OH)_p.(H_2O)_t.(\text{organic solvent})_1$. The original aim of this work was also to investigate and resolve the elements which interfere in the reaction of aluminium with the 2-methyl-, the 2-phenyl- and the 2-styryl-8-quinolinols, and to increase the selectivity and sensitivity of the 2-methyl- derivative, so that wider application could be made out of it. Such requirements demanded the synthesis of three 2-alkyl-8-quinolinol homologues characterised with both powerful steric and inductive 2-substituents. These were 2-ethyl-, 2-isopropyl- and 2-t.butyl-8-quinolinols. The attempted synthesis met with partial success. Two derivatives out of the three were produced after a very lengthy and rigorous investigation for a suitable method of synthesis. These are 2-ethyl- and 2-isopropyl-8-quinolinols. The third derivative, 2-t.butyl-8-quinolinol could not be made under the conditions of the Doebner von Miller reaction applied in the synthesis of the previous two derivatives. It is noteworthy to point out here that the possibility of producing this reagent is not completely out of the question especially after having succeeded in preparing the necessary α:β-unsaturated aldehyde by the unsymmetrical aldol condensation.

An assessment was made in the beginning that more sensitive and selective reagents should be produced on substituting bulkyl alkyl groups, of both powerful inductive and steric effects, in the 2-position of the 8-quinolinol nucleus.

In the course of investigation the selectivity and sensitivity of the synthesized 2-ethyl- and 2-isopropyl-8-quinolinols, it was realised that no obvious gain, as regarding selectivity, has been achieved in terms of indirect tests.

The 2-ethyl- and 2-isopropyl-8-quinolinols are still only selective for aluminium. In chelation the greatest steric hindrance was that exerted by the 2-isopropyl substituent, yet insufficient to isolate other metals besides aluminium. Though results are disappointing, they indicate that 2-t.butyl-8-quinolinol if it could have been produced, may show greater selectivity.

The main objectives have, however, been fully materialised for sensitivity. Sensitivity results, as shown earlier, have been enhanced especially with the 2-isopropyl-8-quinolinol. The enhancement was very great in comparison with the 2-methyl- derivative and was ascribed to the effect of the 2-substituent. A satisfactory though tentative interpretation to the enhancement of the sensitivity with the 2-isopropyl-8-quinolinol has been given. The increase in the size of the 2-substituent though tending to produce less stable metal chelates, however, also causes decrease of the aqueous solubility of these chelates in the order of increase of the size and molecular weight of these products. The sensitivity which is determined by the aqueous insolubility was therefore the highest for the metal-2-isopropyl-8-quinolinates. The inductive effects of the 2-alkyl groups may compensate the barrier imposed by steric factors but the compensation is so small that stable complexes are not to be expected as evident from the sensitivity and solvent extraction data. It is expected that an even greater sensitivity increase should result with 2-t.butyl-8-quinolinol.

Failure of aluminium to react with the 2-ethyl- and the 2-isopropyl- derivatives has been partially clarified. Failure of reaction cannot be ascribed substantially to steric factors alone. The reaction between these two reagents and the metal ions under investigation has been shown to be affected by steric factors. Extractability measurements have given the evidence for this. They indicated that dissociation of the metal 2-alkyl-8-quinolinates increases in the order of the 2-alkyl substituents. This was predicted from the shifts of the extraction curves away from the acid side in the same order.

Also evident from Table XVII that the quantity q which contains some thermodynamic quantities [determined from the experimental extractability values according to the formula $E = \frac{1}{1 + q[H^+]^m}$ and which is equivalent to

$$\frac{K_c Vaq}{P_c Vorg} \left(\frac{Vorg\ P_R}{K_R\ T_R}\right)^{\frac{m}{n}} \quad]$$ was increasing in the increasing order of the 2-substituents. This indicates that themore ionized or dissociated metal chelates were those produced with the highly substituted 8-quinolinol (the 2-*iso*propyl-8-quinolinol), provided the dissociation constants of the reagents decrease in the reverse order of the increase in the 2-substituents, and the increase in $P_R^{\frac{m}{n}}$ and P_c is not substantial.

Table XVII

q values for metal oxinates and derivatives.

Metal	Oxine	2-methyl	2-ethyl	2-*iso*propyl
Al^{3+}	2.51×10^{11}	-	-	-
Fe^{3+}	1.00×10^{6}	2.00×10^{12}	1.41×10^{9}	1.25×10^{8}
Cu^{2+}	1.58×10^{4}	3.98×10^{6}	3.16×10^{7}	3.16×10^{7}
Ni^{2+}	5.00×10^{5}	6.31×10^{12}	2.16×10^{14}	3.98×10^{15}
Co^{2+}	2.51×10^{5}	not available	2.51×10^{13}	1.25×10^{15}
Mn^{2+}	3.98×10^{13}	not available	2.98×10^{16}	6.31×10^{16}

The differences between the q values of metal chelates could also be employed in the separation of various metals. A difference of 10^6 in q values of metals bearing similar charges is considered adequate to achieve separation.

A measurable success has also been achieved on application of the two derivatives in the metal analysis. A brief application of the two derivatives in the analysis of aluminium alloy has proved the superiority of especially the 2-*iso*propyl derivative over the 2-methyl-8-quinolinol in obtaining a quantitative result for aluminium. The procedure followed is simple, direct and avoids the complication of incorporation of other techniques (e.g. mercury cathode electrolysis) or masking agents (cyanide, hydrogen peroxide, etc.) in the removal of the interfering metal ions. Other applications of the two 8-quinolinols in quantitative extraction and determination of various metal ions were shown to be possible. The 2-ethyl- derivative has been employed successfully in the determination of chromium (III) which is known to be characterised with kinetically poor oxinate complexes. This behaviour should precipitate in an extensive use of the reagents under conditions where other reagents are less effective.

In conclusion the main objectives of this work, set forth in the introduction, has been materialised to some extent, although some side problems arose throughout needed to be sought with extensive investigation.

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