PHASE EQUILIBRIUM STUDIES OF ORGANOMETALLIC CHELATES FOR ANALYTICAL APPLICATION

BY

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Abstract

The synthesis of 2 - ethyl -, 2 - isopropyl - and 2 - tert - butyl - 8 - quinolinols has been successfully accomplished with reasonable yields. Physicochemical methods, such as, ultraviolet, infrared and mass spectroscopy, proton magnetic resonance, x-ray powder diffraction, electron spectroscopy for chemical analysis, "ESCA", and cyclic voltammetry have been employed to investigate various properties of the reagents.

o - Dichlorobenzene, a non-volatile and highly water-immiscible solvent has been used in the phase equilibrium work. The extractability and the solubility ratio of the reagents and corresponding metal chelates have been evaluated using the equilibria relationships derived in this work. Detailed and comparative data obtained experimentally were further analyzed statistically. The best results so obtained were used to evaluate the stability constants of some metal chelates. Simple aqueous and water-dioxan media have been employed to determine the protonation and dissociation constants of the reagents.

The method of continuous variations has been employed to solve the problem of predominant species of the metal chelates extracted into the organic phase. Statistical treatment showed that stoichiometric relationship was established between the metal ion and the ligand molecules.

2 - Tert - butyl - 8 - quinolinol which has been synthesised for the first time did not form insoluble metal chelates with the trivalent metal ions but allowed their normal solvent extraction. It also reacted with few divalent metal ions to give insoluble metal chelates in quantitative yield.

In general, a gradation in most of the properties of these reagents was observed. Also an alternating mode of some physical properties such as melting points and solubility ratio was noted. The detailed and comparative physicochemical data have been used to interpret the steric and inductive effects operating in the 2 - alkyl homologues.

These potentially useful 2 - alkyl - 8 - quinolinols could be valuable addition to those already employed in chelate and analytical chemistry.

To my Mother

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1.1 Introduction

Solvent extraction (liquid-liquid extraction) offers simplicity, convenience and scope as a technique in separation of macro and microquantities of ion mixtures. The required results are obtained by varying properties of the system such as pH, concentration of the reagents and ratio of volumes. The method is based on the distribution of a solute between two essentially immiscible solvents, one of which is usually an aqueous solution and the other an organic liquid.

The solvent extraction data of 8-quinolinol and 2-methyl-8-quinolinol chelates of wide selection of metals has already been reported.[1,2] The introduction of the methyl group on the 2-position of 8-quinolinol prohibits its reaction with aluminium ions. This has been considered largely due to a stereochemical effect. In view of the above fact the work was started in these laboratories[3] in 1963 with an object in mind of synthesising higher alkyl homologues of 8-quinolinol such as, 2-ethyl-, 2-*iso*propyl-, and 2-*tert*-butyl-8-quinolinol and studying the effect of such compounds in the metal extraction equilibria. The early work consisted essentially in preparing 2-ethyl-, and 2-*iso*propyl-8-quinolinols by unequivocal syntheses. The procedures were successful but the yields were low. Obviously, more economical methods of synthesis, other than the classical ring closure, were needed. In the second phase of the work, described in this thesis, the condensation of 8-quinolinol with ethyl-, *iso*propyl-, and *tert*-butyl lithium reagents in ethereal solutions proved highly successful. The corresponding 2-alkyl-

8-quinolinols have been obtained in satisfactory yield. The identity of the 2-ethyl-, and 2-isopropyl- homologues was established by comparison of properties with that produced by the unequivocal method of synthesis used by Haba.[3] Also the trend in properties recorded for 2-alkyl-homologues of 8-quinolinol helped to establish the experimental conditions for the successful synthesis and identification of 2-tert-butyl-8-quinolinol.

Some of the physicochemical work carried out has been compared with that of Haba, the only reference work available for these compounds. It has also been extended further to calculate additional physicochemical constants; the more detailed and comparative results obtained for 8-quinolinol and 2-alkyl homologues and the corresponding metal chelate systems are given in this thesis.

1.2 Abbreviations and symbols.

M^{m+} = Metal ion.

n = Coordination number.

m = Oxidation state.

RH = Neutral molecule of chelating agent.

RH_2^+ = Protonated form of the chelating agent.

R^- = Dissociated form of the chelating agent.

K_{R_1} = Dissociation constant of the reagent RH.

K_{R_2} = Dissociation constant of the reagent RH_2^+
or
protonation constant of the reagent RH.

K_{C_1} = Dissociation constant of the monoligand chelate $MR^{(m-1)+}$

K_{C_i} = Dissociation constant of the chelate containing i ligands "$MR_i^{(m-i)+}$".

K_C = Dissociation constant of the fully chelated species "MR_m".

P_C = $\{MR_m\}_O / \{MR_m\}_A$

P_R = $\{RH\}_o / \{RH\}_A$

S_o = Molar solubility in *o*-dichlorobenzene.

S_A = Molar solubility in water.

S_C = S_o / S_A for metal chelate "MR_m".

S_R = S_o / S_A for reagent "RH".

T_M = Total number of moles of the metal in the whole two-phase system.

T_R = Total number of moles of the reagent in the whole two-phase system.

V_o = Volume of the organic phase in litres.

V_A = Volume of the aqueous phase in litres.

ϕ = Chemical potential of a solute.

a = Activity of a solute.

C^* = Molal concentration of a solute.

γ^* = Molal activity coefficient of a solute.

D = Distribution ratio or extraction coefficient.

E = Extractability.

Z = Number of metal atoms in a molecule of hydrolysis product.

f^* = Complex activity coefficient.

YH_n = Secondary complexing agent.

C_Y = Total concentration of the reagent YH_n.

Θ = $C_Y/f^*\{Y^{n-}\}$.

$K_{Y_1}, K_{Y_2} \ldots K_{Y_n}$ = Stepwise dissociation constant of YH_n.

ε = Molar extinction coefficient.

1.3 General concepts and definitions of the parameters.

The definitions of most of the terms used in this thesis are those described earlier[3] except that some of them have been considered in a more generalized way such as the following.

1.3.1 Metal ions: Metal ions in aqueous solutions in absence of other complexing ions are in solvated form and are bound to water molecules to form weak complexes of the type $[M(OH_2)_n]^{m+}$.

The geometrical disposition of the water molecules around the metal ion will depend upon the electronic configuration of the metal ion in such complexes e.g. octahedral (Sp^3d^2), tetrahedral (Sp^3) or planar (dsp^2) and so on. The number of water molecules removed from the aqueometal system during the complex formation will depend upon the properties of the donor Lewis base and its replacable hydrogen atoms e.g.

$$\begin{tikzcd}
{[M(OH_2)_n]^{m+} + R^-} \arrow[r, shift left, "K_{C_1}"] & \{MR(OH_2)_{(n-1)}^{(m-1)+}\} \arrow[l, shift left] \arrow[d, shift left, "K_{C_2}"] \\
& \{MR_2(OH_2)_{(n-2)}^{(m-2)+}\} \arrow[u, shift left] \arrow[d, shift left, "K_{C_m}"] \\
& \{MR_m\} \arrow[u, shift left]
\end{tikzcd}$$

The value of m and n normally varies between zero and six and stepwise equilibrium is given by

$$K_{C_1} = f_1 f_m \{M^{m+}\} \{R^-\} \Big/ f_{(m-1)} \{MR^{(m-1)+}\} \qquad (1)$$

$$K_{C_2} = f_1 f_{(m-1)} \{MR^{(m-1)+}\} \{R^-\} \Big/ f_{(m-2)} \{MR_2^{(m-2)+}\}$$

$$\vdots \qquad \qquad \vdots$$

$$K_{C_{(m-1)}} = f_2 \{MR^{2+}_{(m-2)}\} \{R^-\} \Big/ \{MR^{+}_{(m-1)}\}$$

$$K_C = \frac{f_m f_1^m \{M^{m+}\} \{R^-\}^m}{\{MR_m\}}$$

1.3.2 Hydrolysis of the metal ions.

Due to the electropositive character of the metal ions the oxygen atoms in the water molecules surrounding them occupy a greater share of the electron pair from one of their two covalent bonds with hydrogen atoms. This shift in electron balance allows the water molecules to dissociate leaving behind hydroxyl groups to associate more firmly with the metal ions, or, in other words, metal ions of more electropositive nature react vigorously with water. The hydroxo forms of the metal ions may be considered as simple type of complexes e.g.

$$M^{m+} + OH^- \underset{}{\overset{S_1}{\rightleftharpoons}} \{M(OH)^{(m-1)+}\}$$

$$\vdots \qquad \vdots \qquad \qquad \vdots$$

$$\{M(OH)_{(n-1)}^{(m-n+1)+}\} + OH^- \overset{S_n}{\rightleftharpoons} \{M(OH)_n^{(m-n)+}\}$$

where $S_1 = f_1 f_m \{M^{m+}\} \{OH^-\} \Big/ f_{(m-1)} \{M(OH)^{(m-1)+}\}$ (2)

$$S_n = f_{(m-n+1)} f_1 \{M(OH)_{(n-1)}^{(m-n+1)+}\} \{OH^-\} \Big/ f_{(m-n)} \{M(OH)_n^{(m-n)+}\}$$

For a polynuclear hydrolysis product, the reaction can be written as follows:

$$M^{m+} + 2(m-1 + 1/Z)\ OH^{-} \underset{}{\overset{S^{*}}{\rightleftharpoons}} MO_{1-1/Z}\ O_{(m-2+2/Z)}^{(m-2+2/Z)-} + (m-1+1/Z)\ H_2O$$

where

$$S^{*} = \frac{f_m f_1^{2(m-1+1/Z)} \{M^{m+}\}\ \{OH^{2(m-1+1/Z)}\}}{f_{(m-2+2/Z)} \{MO_{1-1/Z} O_{(m-2+2/Z)}^{(m-2+2/Z)-}\}} \qquad (3)$$

1.3.3 Distribution Law.

The phase equilibrium is governed by Gibb's equation[4] i.e.

$$P + F = C + 2 \qquad (4)$$

In solvent extraction work one solute is distributed between two immiscible solvents, hence $P = 2$ and $C = 1$, therefore, at constant temperature and pressure $F = 1$. According to Nernst, at equilibrium the chemical potentials of the solute in each phase are equal i.e. $\phi_1 = \phi_2$

$$\therefore\ \phi_1^{o} + RT\ln C_1^{*} + RT\ln\gamma_1^{*} = \phi_2^{o} + RT\ln C_2^{*} + RT\ln\gamma_2^{*}$$

Therefore the distribution coefficient "K_D" of the metal and in turn of the chelate is given by

$$K_D = \frac{C_2^{*}\gamma_2^{*}}{C_1^{*}\gamma_1^{*}} = \frac{a_2}{a_1} = e^{-(\phi_2^{o}-\phi_1^{o})/RT} \qquad (5)$$

1.3.4 Competing ionic chelate formation.

The equilibrium between a metal ion and reagent YH_n is written as:

$$M^{m+} + Y^{n-} \overset{K_{MY}}{\rightleftharpoons} MY^{(m-n)+}$$

$$\text{where } K_{MY} = \frac{f_m f_n \{M^{m+}\}\{Y^{n-}\}}{f_{(m-n)}\{MY^{(m-n)+}\}} \qquad (6)$$

and the quantity θ is given by

$$\frac{C_Y}{\{Y^{n-}\}} = f^{*}\theta = \frac{\{H^+\}^n + K_{Y_1}\{H^+\}^{(n-1)} + K_{Y_2}\{H^+\}^{(n-2)} + \,.....}{K_{Y_1}\,K_{Y_2}\,........\,K_{Y_n}} \qquad (7)$$

CHAPTER TWO

2. Quantitative relationships in the phase equilibrium studies of 8-quinolinols and their metal chelates.

2.1 Discussion.

The basic principles of phase equilibrium relationships are simple. However, most of their theoretical treatments[5-9] have rarely been used to correlate the experimental data and predict or evaluate additional constants. Most of the results presented in this thesis have been based on the extraction equilibria described by Haba[3]. This was necessary in absence of any experimental data such as protonation, dissociation or stability constants and solubility ratio of these new reagents and their metal chelates. The treatment given by Haba was unique but was capable of extension. The preliminary work done by Haba was not sufficient to check fully the validity of his derived relationships. Therefore, more comprehensive experimental work was carried out and equilibrium equations employed to evaluate more physicochemical constants separately for 8-quinolinol, 2-alkyl-8-quinolinols and corresponding metal chelate systems and to confirm Haba's first findings.

Although the final form of equations used in such evaluations was similar to that given by Haba, the activity coefficients and the activities of the species involved in the system have been taken into consideration and other refinements have been made. The improved forms of equations should be of great advantage in their possible extension to the present and other systems. The validity of approximations as applied in evaluation of final results is discussed under subheading in this chapter.

2.2 Mathematical approach to phase equilibrium studies.

In the equilibrium between organic and aqueous phases the total quantity, T_R, of reagent will be given by[5]

$$T_R = m\{MR_m\}_o V_o + m\{MR_m\}_A V_A + (m-1)\{MR_{(m-1)}^{+}\}_A V_A \cdots$$

$$+ 2\{MR_2^{(m-2)+}\}_A V_A + \{MR^{(m-1)+}\}_A V_A$$

$$+ \{RH\}_o V_o + \{RH\}_A V_A + \{R^-\}_A V_A$$

$$+ \{RH_2^+\}_A V_A \qquad (8)$$

and according to equilibrium equations as described by Haba[3] this is simplified to

$$T_R = \{MR_m\}_A \left[mV_o P_C + V_A \left(m + \Sigma(m-x) \frac{xK_C}{K_{C_1} K_{C_2} \ldots K_{C_{(m-x)}} R^{-\,x} f_{(m-x)} f_1^x} \right) \right]$$

$$+ f_1^{\,2}\{R^-\} \left[V_A + \frac{(V_A + V_o P_R)\{H^+\}}{K_{R_1}} + \frac{V_A\{H^+\}^2}{K_{R_1} K_{R_2}} \right] \qquad (9)$$

$$\text{or} \quad T_R = \{MR_m\}_A\, \alpha + \{R^-\}_A \beta \qquad (10)$$

Similarly, the total gram molecules of the metal, T_M, is

$$T_M = \{MR_m\}_o V_o + \{MR_m\}_A V_A + \{MR_{(m-1)}^{+}\}_A V_A + \cdots\cdots + \{MR^{(m-1)+}\}_A V_A$$

$$+ \{M^{m+}\}_A V_A + \{MY^{(m-n)+}\}_A V_A + \cdots\cdots\cdots\cdots$$

$$+\{M(OH)^{(m-1)+}\}_A V_A + \ldots + \{M(OH)_n^{(m-n)+}\}_A V_A +$$

$$\{MO_{(1-1/Z)}\ O^{(m-2+2/Z)-}_{(m-2+2/Z)}\}_A V_A \qquad (11)$$

using the equilibrium equations[3], this becomes

$$T_M = \{MR_m\}_A \Bigg[V_o P_C + V_A + \Sigma \frac{V_A K_C}{K_{C_1} K_{C_2} \ldots K_{C_{(m-x)}} \{R^-\}^x f_1^x\ f_{(m-x)}} + \frac{V_A K_C}{\{R^-\}^m f_1^m f_m} + \frac{V_A K_C}{\Theta K_{MY} \{R^-\}^m f_1^m f^*}$$

$$+ \Sigma \frac{V_A K_C K_W^Y}{\{H^+\}^Y S_Y \{R^-\}^m f_1^{Y+m}}$$

$$+ \frac{V_A K_C K_W^{2(m-1)+2/Z}}{\{H^+\}^{2(m-1)+2/Z} S^* f_1^{3m-2+2/Z} \{R^-\}^m} \Bigg] \qquad (12)$$

$$\text{Say } T_M = \{MR_m\}_A \gamma \qquad (13)$$

combining equations (10) and (13) gives

$$\{MR_m\}_A = \frac{T_M}{\gamma} = \frac{T_R - \beta\{R^-\}}{\alpha} \qquad (14)$$

$$\text{and } \{R^-\} = \frac{T_R - \frac{\alpha}{\gamma} T_M}{\beta} \qquad (15)$$

considering $\alpha/\gamma \ngtr m$ and since experimentally $T_R >> T_M$,

$$\{R^-\} = \frac{T_R}{\beta} \qquad (16)$$

$$\text{or, at its minimum, } = \frac{(T_R - mT_M)}{\beta} \qquad (17)$$

If hydrolysis, competing complexes and intermediate chelated species are ignored the former becomes an exact solution. Since extractability, E, is defined as

$$E = \frac{\text{Total quantity of metal in the organic phase}}{\text{Total quantity of metal in both phases}} \qquad (18)$$

$$\text{i.e. } E = \frac{\{MR_m\}_o \; V_o}{T_M} = \frac{\{MR_m\}_A \, P_C \, V_o}{\{MR_m\}_A \, \gamma} = \frac{P_C \, V_o}{\gamma} .$$

This is expanded using equation (12) and (8) considering $P_C V_o >> V_A$ so that, E, becomes

$$E = 1 \Big/ 1 + \frac{V_A K_C}{P_C V_o} \left[\Sigma \frac{\beta^x}{K_{C_1} K_{C_2} \cdots K_{C_{(m-x)}} T_R^x \, f_{(m-x)} f_1^x} + \frac{\beta^m}{T_R^m \, f_1^m f_m} + \frac{\beta^m C_Y}{\Theta K_{MY} T_R^m \, f_1^m \, f^*} + \Sigma \frac{\beta^m \; K_W^Y}{\{H^+\}^Y S_Y T_R^m \, f_1^{Y+m}} + \frac{\beta^m \, K_W^{2(m-1 + 1/Z)}}{\{H^+\}^{2(m-1 + 1/Z)} \, S^* \, T_R^m \, f_1^{3m-2+2/Z}} \right] \qquad (19)$$

From practical point of view a quantity Q given by equation $Q = \beta/V_A$ is used

$$\text{where } Q = 1 + \frac{\left(1 + \frac{P_R V_o}{V_A}\right) \; \{H^+\}}{K_{R_1}} + \frac{\{H^+\}^2}{K_{R_1} K_{R_2}} \qquad (20)$$

The parameters such as partition coefficient and dissociation constants of the reagents, the hydrogen ion concentration and ratio of volumes of two phases can be evaluated by separate experiments as done in this thesis. Therefore Q, is of general nature containing a ratio of volumes and actual volumes of the immiscible phases are not needed. Accordingly the parameter, β, on replacement with the term Q, involves the ratio T_R^i / V_A^i. Hence the total (original) concentration of reagent, C_R, in the aqueous phase can be used instead of total quantity of the reagent Therefore the equation for, E, will be

$$E = 1 \Big/ 1 + \frac{V_A K_C}{P_C V_o} \left[\Sigma \frac{Q^x}{K_{C_1} K_{C_2} \cdots K_{C_{(m-x)}} C_R^x f_{(m-x)} f_1^{\,x}} + \frac{Q^m}{C_R^m f_1^m f_m} + \frac{Q^m C_Y}{\theta K_{MY} C_R^m f_1^m f^*} + \Sigma \frac{Q^m \cdot K_W^Y}{\{H^+\}^Y S_Y C_R^m f_1^{\,Y+m}} + \frac{Q^m K_W^{\,2(m-1+1/Z)}}{\{H^+\}^{2(m-1+1/Z)} S^* C_R^m f_1^{\,3m-2+2/Z}} \right] \qquad (21)$$

2.3 Influence of pH on extractability and evaluation of Q values.

The Q values change as the pH changes: in the pH range 0 → 1.5, $Q \alpha \{H^+\}^2$, and 4 → 10, $Q \alpha \{H^+\}$. In the experimentally important ranges 1.5 → 4 and above 10 there is a gradual change of power dependence. Therefore the resulting extractability versus pH curves are not expected to be symmetrical. Hence plots of E versus log Q are more useful. Since allowance for the change of power dependence can be anticipated. If the extraction occurs in the pH ranges of 1 → 2.5 in the absence of masking agents, involving no hydrolysis, the equation (21) may be simplified to

$$E = 1 \Big/ 1 + \frac{V_A K_C}{P_C V_o}\left[\frac{Q^m}{C_R^m f_1^m f_m} + \frac{Q^{(m-1)}}{C_R^{(m-1)} f_1^{(m-1)} K_{C_1}} \right.$$

$$\left. \frac{Q^{(m-2)}}{f_1^{(m-2)} C_R^{(m-2)} K_{C_1} K_{C_2}} + \frac{Q}{C_R f_1 f_{(m-1)} K_{C_1} K_{C_2} \dots K_{C_{(m-1)}}}\right] \qquad (22)$$

In case of predominance of one species of chelate, the equivalent distribution or extraction ratio, D, is equivalent to E/1-E and given by:

$$\log D = \log \frac{P_C V_o C_R^x f_1^x f_{(m-x)} K_{C_1} K_{C_2} \cdot\cdot K_{C_{(m-x)}}}{V_A K_C} - x \log Q \qquad (23)$$

Similarly in the significant extraction region of pH, viz 3 → 8, in the absence of masking agents:

$$E = 1 \Big/ 1 + \frac{V_A K_C}{V_o P_C} \left[\Sigma \frac{Q^x}{C_R^x f_1^x K_{C_1} K_{C_2} \cdots K_{C_{(m-x)}}} + \Sigma \frac{Q^m}{S_Y f_1^{(Y+m)} \{H^+\} C_R^m} \right]$$

Finally, the extractability reaches unity over the pH range 8-12 in absence of masking agents but hydrolysis becomes of paramount importance. Hence, E, is given by the equation

$$E = 1 \Big/ 1 + \frac{Q^m V_A K_C}{C_R^m \; P_C \; V_o f_1^m} \left[\frac{K_W^Y}{S_x f_1^Y \{H^+\}^Y} \right] \qquad (25)$$

and if one species predominates the equivalent distribution, D, is described by:

$$\log D = \log \frac{C_R^m \; P_C V_o f_1^{(m+Y)} \; S_Y}{K_W^Y \; V_A K_C} - \log \frac{Q^m}{\{H^+\}^Y} \qquad (26)$$

The relationships described above illustrate that the graphs of log D versus log Q or log $Q^m/\{H^+\}^Y$ will be straight lines if one species of chelate predominate. However, this will be true only if ionic strength is kept constant for all experiments. The value of slope will allow the value of x to be evaluated and from the intercepts (at $pH_{E=0.5}$ or log $Q_{E=0.5}$ etc.) or directly from the values of E, certain dissociation constants can be calculated and the values can be compared with those obtained in independant experimentation; using techniques other than solvent extraction.

2.4. The validity of neglecting the activity coefficients in the formulae.

In phase equilibruim studies the partition of neutral metal chelates between an aqueous and organic phase fulfils the requirements of a thermodynamically ideal system. It does not involve transfer of charged species from one phase into another. Therefore, the electrolytes used to maintain ionic strength constant do not pass into organic phase and the ratio of ionic strength of two phases is constant. According to the extractability formula[3];

$$E = \frac{1}{1 + \frac{K_C V_A}{P_C V_o}\left[\frac{P_R V_o}{T_R K_{R_1}} + \frac{\{H^+\}V_A}{K_{R_1} K_{R_2} T_R}\right]^m \quad \{H^+\}^m}$$

value of "E" is dependent on values of K_C, P_C, P_R, K_{R_1} and K_{R_2}.

Under the experimental conditions used in this work, the concentration may replace activity values in parameters such as P_R and P_C. For example, in the measurement of P_C, the solute is a neutral chelate. Therefore in aqueous phase γ_1 = constant. The organic phase contains less than 0.1 mole fraction of the solute, therefore, γ_2 = constant and relationship $\gamma_2 = \gamma_1$ is valid and the values of P_C or P_R will not be affected by small changes in ionic strength or concentration. However, the values of K_{R_1}, K_{R_2} and K_C are subject to change with change of charge and therefore, of ionic strength.

In the case of dilute solutions, as employed in phase equilibrium work, these values follow the Debye-Huckel equation[71], viz

$$\log K = \log K^{o} - \frac{A\ \Delta Z^{2}\mu^{1/2}}{1 + a^{o}\ B\mu^{1/2}}$$

where A is a constant dependent on the dielectric properties of the medium.

B is an empirical constant $\approx 3.3\times10^{7}$

$\Delta Z^{2} = Z^{2}(\text{products}) - Z^{2}\ (\text{reactants})$

μ = ionic strength.

K = is the dissociation constant of the extractable species or the reagent.

K^{o} is the value of this constant at zero ionic strength.

A = 0.509 for water at 25°C.

a^{o} = ion size parameter. hen $\mu = 0.1$, $1 + a^{o}B\mu^{1/2} \simeq 1.4$

$$\therefore \log K = \log K^{o} - \frac{A\Delta Z^{2}\mu^{1/2}}{1.4} = \log K^{o} + 0.34$$

The above relationship has been used to calculate the error in the stability constants and the following results are obtained for copper-chelates.

Chelating agent	K (o.1M ionic strength)	K^{o} (Zero ionic strength)
8-quinolinol	3.98×10^{-24}	1.8×10^{-24}
2-methyl- 8-quinolinol	7.94×10^{-22}	3.6×10^{-22}
2-ethyl 8-quinolinol	1.12×10^{-23}	5.1×10^{-24}
2-isopropyl- 8-quinolinol	5.01×10^{-21}	2.3×10^{-21}
2-tert-butyl- 8-quinolinol	1.25×10^{-23}	8.8×10^{-24}

The effect, however, is arithmetically small and is probably within limits of experimental error. Therefore, activities have been replaced by concentrations and activity coefficients omitted, and considered as unity or approaching unity at constant ionic strength of 0.1M used in this work.

In practice ideal solutions or solutions of zero ionic strength are never encountered in analytical systems. It is rational, therefore, to use conditional dissociation constants pertaining to systems of reasonable ionic strengths. In most of this work 0.1M or 1M inert salts such as sodium perchlorate were introduced to maintain such a concentration constantly throughout a series of experiments. In this way salt effects were reproducible and, as shown above, small and the complexing effects were minimised.

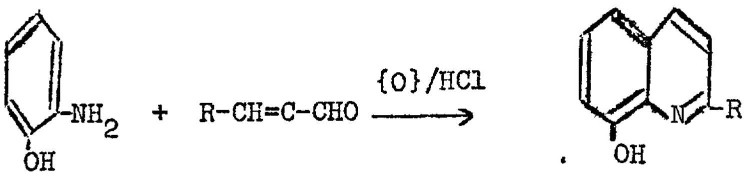
CHAPTER THREE

3. Discussion of the methods of synthesis of 2-alkyl-substituted 8-quinolinols.

3.1 General.

A comprehensive literature survey of the possible methods of synthesis of quinoline compounds was carried out. The noteworthy reactions which may be used with slight variations to obtain 8-quinolinol and 2-alkyl - homologues are syntheses due to;
V. Neimentowski,[10] Combes,[11] Bayer,[12] Conrad - Limpach,[13] Knorr,[14] Friedlander,[15] Pftizinger,[16] Kulisch,[17] Skraup,[18] Doebner-Von Miller[19] and replacement of α-hydrogen of 2-alkyl-quinolines using potassium amide,[20-23] halogens in presence of glacial acetic acid, sulphuric acid,[25,26] and alkali fusion.[27]

Perhaps the most versatile method is the Skraup, or its modification, the Doebner Von-Miller condensation reaction between an aromatic amine and an α:β-unsaturated carbonyl compound. It has been successfully applied[3] in the preparation of 2-ethyl- and 2-*isopropyl* - 8-quinolinols but not the 2-*tert*-butyl-homologue:



(where R = ethyl, *iso*propyl, or in principle, *tert*-butyl group).

The complete synthesis, including the preparation of the unsaturated aldehydes is extremely lengthy and the cumulative yields after several steps may be as low as 1%. The fact that condensation proved partially successful to produce the ethyl and isopropyl derivatives, although in poor yield, indicated that the approach in principle was correct but not practicable. Especially when it was a total failure in producing the tert-butyl derivative. It will be fair to comment that this scheme proved unsuccessful in case of the tert-butyl homologue because of unfavourable conditions, viz temperature of the reaction and susceptibility of the side chain in the pyridine ring of the quinoline nucleus towards elimination. The rearrangement, bulkiness and steric arrangement of the tert-butyl group may be considered to have enhanced it. Polymerization and copolymerization of α:β-unsaturated carbonyl compounds with o-aminophenol also limits the efficiency of the condensation. Finally doubted purity of the reported intermediate[3] and competitive decomposition reactions involved in purification may have been the main inhibiting factors in synthesising the product. The small quantities of the synthesised ethyl and isopropyl derivatives obtained by Haba were of great value in identification of the products obtained later. However, his tedious synthetic route made the use of these reagents impracticable from an analytical point of view, and more direct and efficient methods of synthesis were investigated as follows:

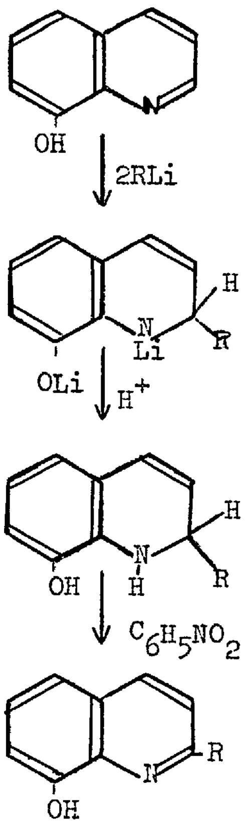
3.1.1 Direct alkylation of 8-methoxy-or 8-hydroxy-quinoline by alkyllithiums.

The reaction may be accomplished by the method[27-30] described by Sorm and Sicher.[31] However, a considerably modified scheme (ii) proved highly successful. The reaction is as follows:

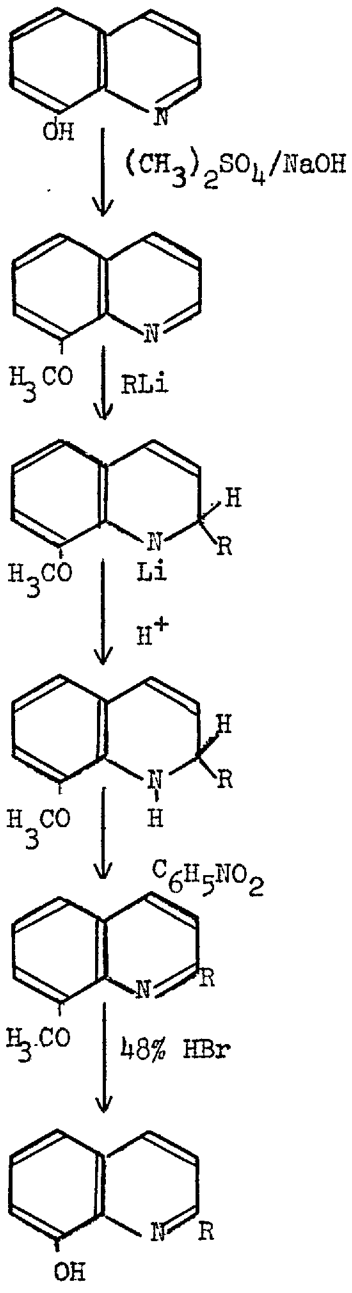
(i) $RX + 2\,Li \xrightarrow[-LiX]{} RLi$

(where R = ethyl, isopropyl, or tert-butyl group and X = chloride, bromide, or iodide).

Scheme (ii)



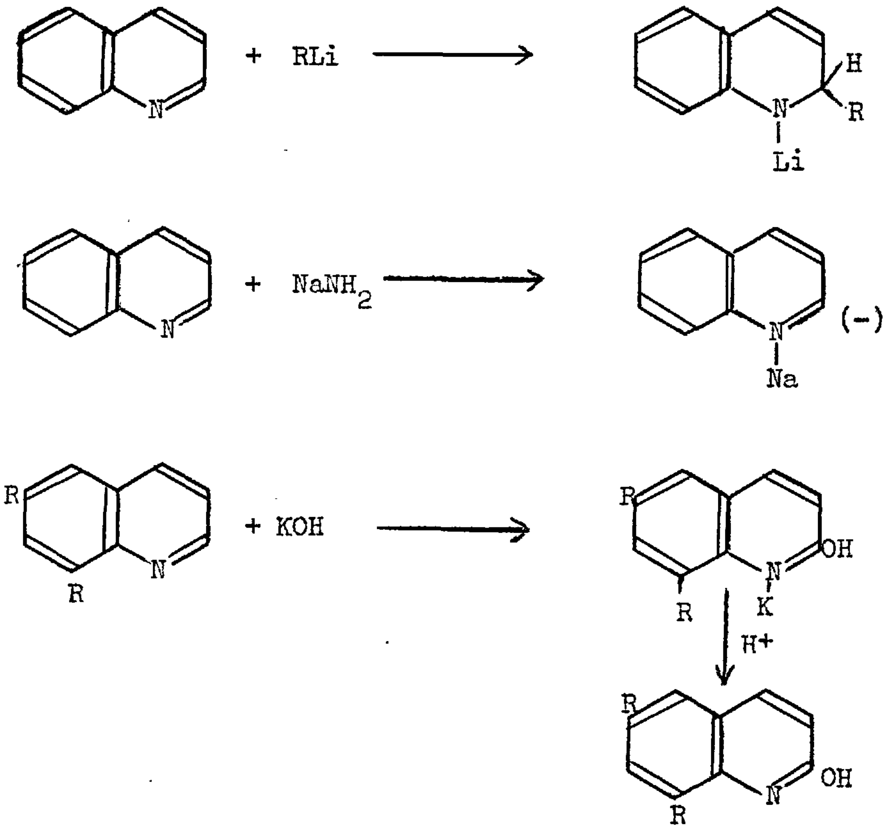
Scheme (iii)



The experimental evidence substantiated a hypothesis that the treatment with nitrobenzene[32,33] could be omitted taking into account the elimination of lithium hydride during the condensation. Also, the use of 8-quinolinol as starting material was preferred on account of the fact that demethoxylation of the product obtained from the condensation of 8-methoxyquinoline was sluggish and involved competitive decompositions in getting a pure product. Thus the whole scheme was reduced to two steps only i.e.

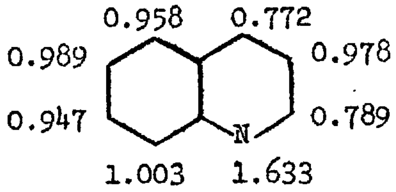
(i) Preparation of alkyllithium.
(ii) Condensation of alkyllithium with 8-quinolinol.

The condensation has been mainly based on the reactions involving the azomethine group in the quinoline nucleus; due to this the carbon atom in the 2-position undergoes a variety of addition reactions, e.g.

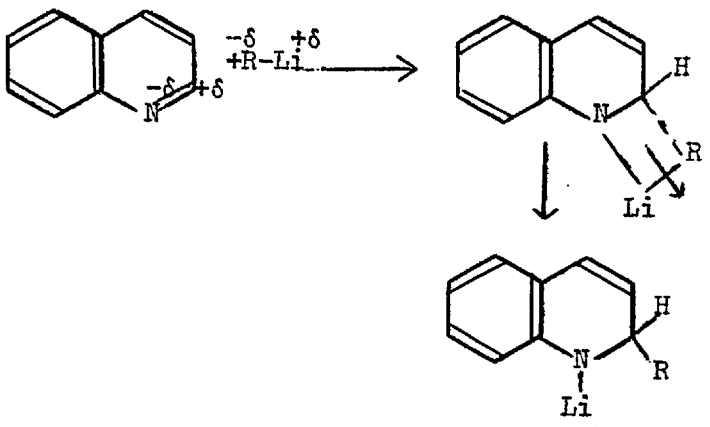


The fact that >C = N- group is related to ammonia as -CHO is related to water[21], it follows that the heterocyclic nitrogen compounds such as pyridine and quinoline are aldehydeacetals of an ammonia system, but the aldehydic properties of these compounds are not pronounced because of the stability of the six membered ring in which they are contained. Nevertheless the quinolines react with Grignard reagents in ether and it is also known that lithium alkyls and aryls add to the >C=N- group in ethereal solution at ordinary temperature. Therefore in the quinoline nucleus the azomethine position is likely to undergo substitution with the alkyl group when alkyllithium is used as a reagent.

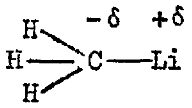
According to Longuet-Higgins[34] the presence of a hetero atom should activate other positions towards nucleophilic substitution. For example, the replacement of 2- or 4- carbon atoms in naphthalene by nitrogen results in activation of 1-position strongly towards nucleophilic substitution and deactivates towards electrophilic substitution. This is found true in case of compounds like 4-chloroquinoline and 1-chloroisoquinoline. They undergo nucleophilic replacement of chlorine much more readily than does α-chloranaphtalene. In presence of a heteroatom the inductive effect plays an important role to orientate an incoming group. For example, the electron densities in quinoline at various positions as referred to uniform distribution in benzene as 1 are as follows:

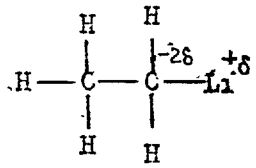


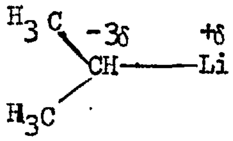
Therefore, a nucleophile should attack 4- and 2- positions in order of preference. 1- and 8- positions should be attacked by an electrophile respectively. However, according to Branch and Calvin[35] the inductive effect at the 2-position due to adjacent nitrogen atom is nearly thirty three times greater compared with the 4-position. This reverses the order of nucleophilic substitution at the 4-position in favour of the 2-position. The 2-alkylation of 8-quinolinol is also favoured when alkyl lithium reagents are used while metallation will dominate in the case of alkyl potassium or sodium reagents. This is based on the fact that lithium is an electron deficient atom and therefore the alkyl lithium reagents are less ionic in character as compared to highly ionic alkyl potassium or sodium reagents. Therefore, the polarization and ultimate break of lithium atom bound to an alkyl group depends on the availability of an electrophilic position for lithium stronger than the alkyl group. Correspondingly the alkyl group set free will attack a nucleophilic position. The reaction may be illustrated as follows:

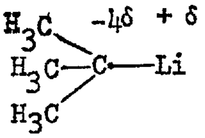


This hypothesis also excludes the possibility of a free radical mechanism, in which case the possibility of 4-alkylation is enhanced. Therefore, in principle the greater the residual negative charge present on an alkyl group, the more effective will be the substitution at the 2-position. In the case of branched alkyl chains the α-carbon atom bound to lithium should be more negative than in straight chains, viz,









Therefore the tert-butyl group should attack the 2-position of 8-quinolinol easily as compared with other alkyl groups. However, the steric requirements necessitated the dispersion of charge over the molecule which results in less electron density on the tertiary carbon. Therefore in the whole series secondary carbon has the maximum negative charge. This increases the anionic behaviour of isopropyllithium. In practice it has been found true since the yield of 2-isopropyl -8-quinolinol obtained was the best of the series of synthesis.

However, in presence of excess of organolithuim reagent as used in this work, the possibility of 4-alkylated or 2:4 dialkylated 8-quinolinol cannot be excluded even if of low probability. Even if a mixture of such products was produced, the contamination by the 4-alkylated product was automatically eliminated in a purification procedure designed to remove compounds which do not contain 2-alkyl substitution; the procedure involved addition of aluminium ions during purification tages. Aluminium does not form complexes with

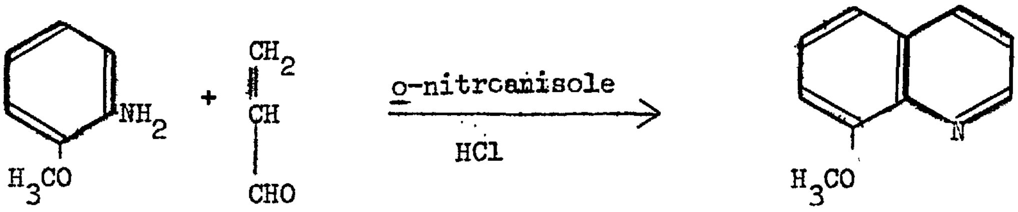
2-alkyl-8-quinolinol. Reliance of the foregoing theory and purification procedure was justified when it was found that, the physical methods of identification applied in this work excluded the presence of 4-alkyl and 2:4 - dialkyl substituted products.

The remaining methods of syntheses were not extensively investigated. A preliminary investigation of reaction of 2-quinolyl anion[24,26] and its possible 2-alkylation by generation of tertiary carbonium ion in presence of sulphuric, formic, or phosphoric acid proved unsuccessful. It was not considered worthwhile continuing this investigation further, since the desired products were obtained by easily accessible route described above and in satisfactory yield.

3.2 Preparation of 8-methoxyquinoline.

3.2.1 Skraup Condensation.

The synthesis of 8-methoxyquinoline was attempted according to skraup[18] condensation as follows.

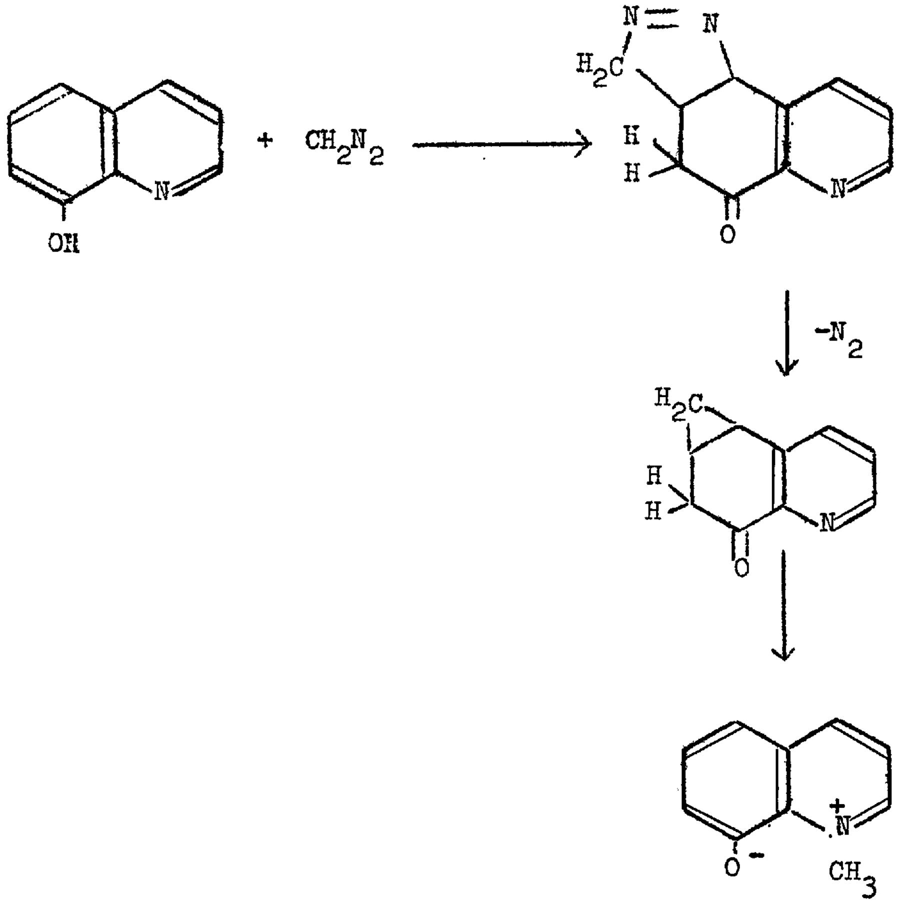


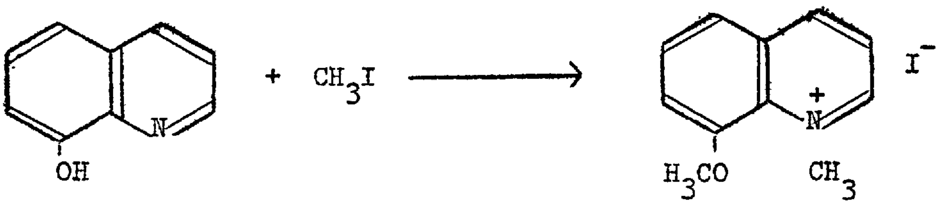
o-ansidine Acrolien 8-methoxyquinoline.

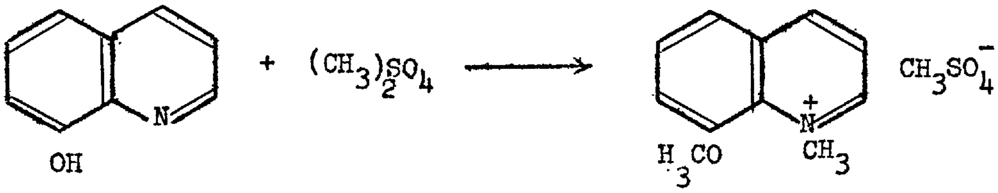
The yield of 8 methoxyquinoline obtained after lengthy and tedious synthesis and rigorous purification steps was very poor i.e. ~ five percent and of no advantage over the earlier methods used. The experimental conditions such as temperature, catalyst, medium, ratio of reactants, and length of the reaction were also varied but the yield could not be improved. The experimental observations indicated that due to exothermic nature of the reaction and tendancy of lower aldehydes towards polymerization under such streneous conditions, the condensation remained ineffective. This necessitated search for an alternative method such as follows.

3.2.2 Direct alkylation of 8-quinolinol.

A large variety of alkylating agents such as diazomethane[36-38], methyliodide[39-42], or dimethyl sulphate[41,43] are mentioned in the literature for this purpose but great contrasts in the yield and nature of the products obtained have been reported. Examples of possible reactions are:





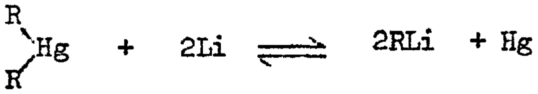


It may be owing to the spatial relationship of the nitrogen atom with the hydroxyl group that different alkylating agents react with 8-quinolinol to give anomalous products. However, it was decided to use aqueous alkaline dimethyl sulphate[43] for o-methylation and a yield ~ 70% of 8-methoxyquionoline was obtained by the method, slightly modified as described in "Experimental".

3.3. Preparation of Organolithium Compounds

3.3.1 Methods of preparation.

The discovery of zinc alkyls[44], mercury alkyls[45], Grignard reagents[46] and lithium derivatives[47] are the four notable chronological developments in the field of organometallic chemistry. The lithium derivatives are preferred as synthetic intermediates for the simplicity with which they can be prepared[48-49] and used in subsequent reactions. The organolithium derivatives may be prepared by direct, indirect, exchange or addition reactions as described below.

i) 

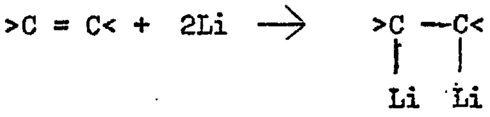
$R_2Hg + 2Li \rightleftharpoons 2RLi + Hg$

ii) $RX + 2Li \rightarrow RLi + LiX$

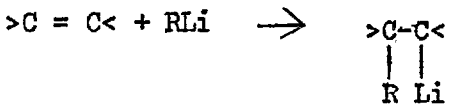
iii) $RX + R'Li \rightarrow RLi + R'X$

iv) $RH + R'Li \rightarrow RLi + R'H$

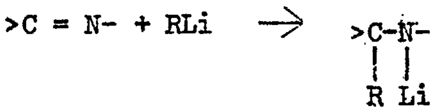
v) $RM + R'Li \rightarrow RLi + R'M$

vi) 

$>C=C< + 2Li \rightarrow \underset{Li}{>C}-\underset{Li}{C<}$

vii) 

$>C=C< + RLi \rightarrow \underset{R}{>C}-\underset{Li}{C<}$

viii) 

$>C=N- + RLi \rightarrow \underset{R}{>C}-\underset{Li}{N}-$

(where R = alkyl, alkenyl, alkynyl, aryl or heteryl group.

R' = n - butyl or phenyl group,

X = chloride, bromide or iodide).

The preparation of ethyl-, isopropyl-, and tert-butyl lithium reagents in the present work was based on the reaction (ii), i.e. direct reaction between an alkyl halide and lithium metal. This reaction provides an important and fairly general route to organometallic compounds. The nature of metal, halogen atom, the branching of alkyl group, solvent and temperature are important factors to be considered in getting satisfactory yields of these intermediates. For example, the reaction between a metal atom and an organic halogen compound is mainly influenced by their thermochemistry. The heats of reaction rather than free energies of reaction have to be taken into account since published data on the standard entropies of organometallic compounds are negligible. For example the reaction between a metal and methylchloride to produce methyl-metal and chloride is exothermic and therefore might be expected to provide an important synthetic route.
The mechanism of reactions and conditions under which they occur, however, vary greatly with different metals. Therefore kinetic as well as thermodynamic factors are important in controlling the reactions. E.g, the carbon-halogen bond energies decrease from C-F (439), C-Cl (330), C-Br (276) 2C-I(238 K Joule/mole) in methyl compounds.
Whereas the relative reactivities (rates of reaction) of organic halides towards metals usually rise:
$RF << RCl < RBr < RI$.

Therefore, the efficiency of reaction of lithium with an alkyl group depends on the best selection of an alkyl halide. For example, ethyl lithium was prepared using ethyl bromide. The condensation required high temperature (55°C), inert solvent such as benzene, and slow addition of very dilute solution of ethyl bromide to the reaction mixture. This was necessary to increase the ion-forming tendancy of ethyl bromide, to retard the hydrogen abstraction, to resist olifine elimination (Wurtz reaction), and to prevent metal-halogen exchange and lithium alkyl-lithium halide complex formation reactions. iso-Propyl lithium was prepared at room temperature and in presence of 1 + 1 ether + benzene mixture.

The synthesis of tert-butyl lithium was carried out at temperatures as low as -55°C in ether using the corresponding chloride. These conditions were chosen because of the high volatility of tert-butyl chloride, the ease of elimination reactions of other halides and the increased carbanion character of tert-butyl group.
Theoretically, chlorides are preferred to bromides and iodides. Since the ionic fluorine associated with lithium is able to undergo further exchange reactions with at least the α-hydrogen atom of the lithium alkyl, fluorides are not used.

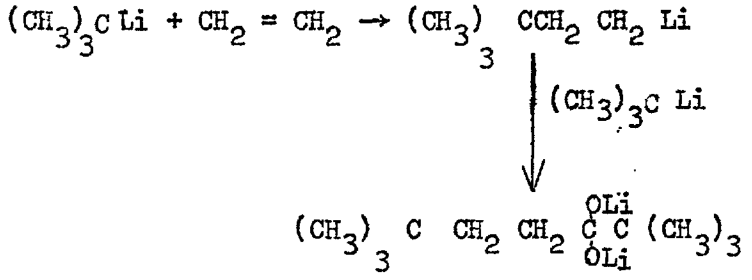
The choice of an alkyl halide also depends on the nature of alkyl group involved which will determine the polarization of halide ion. For example methyl lithium is best prepared using corresponding iodide. It seems fair to comment at this stage that some of the literature reporting yields as high as 70% in preparations of alkyl lithium reagents in hydrocarbon media and at temperatures from 0° to 55°C are quite misleading and inaccurate. Many painstaking attempts to reproduce some of this work resulted in continued and almost total failure. Yields never exceeded 15% and these observations are not surprising in view of the foregoing discussion. Perhaps some of the literature claims may be described as ambitious, or some essential feature had been omitted in the experimental descriptions. As a consequence methods were evolved, as described in the "Experimental" section, based on the use of ether solutions with the preparation and synthetic reactions moderated by addition of benzene and by extending the working temperature range to -55° .

3.3.2 Choice of conditions for the reaction between Lithium alkyls and 8-quinolinol.

Most of the potassium and sodium alkyls are regarded as salts and cannot be used for 2-alkylation of 8-quinolinol. The small size (ionic radius 0.6^{o}A) and high polarizing power (0.08 in arbitrary units F = 1.00) of the lithium ion results in lithium alkyls' having characteristics of covalent compounds and it seems unreasonable to associate them with a simple salt-like constitution. This argument is further substantiated by the electron deficient structure[50] and polymeric state of various alkyl lithium derivatives, e.g. ethyl lithium is either a tetramer or hexamer and tert-butyl lithium a tetramer in hydrocarbon solutions. This may be considered in the light of dimeric, tetrameric and hexameric aggregates held together by electron deficient bonds. The actual degree of association depends on the alkyl group involved and the solvent or solvents used. e.g. in ether medium the order of increasing stability[51] of the lithium alkyls is tert-butyl < sec-butyl ≈ isopropyl ≈ cyclohexyl <isobutyl < n-propyl < methyl. Use of the ether lowers the dissociation energy of the polymeric species and speeds up the exchange process shown below. The reaction consists mainly of nucleophilic attack on the α-carbon atom followed by olefine elimination e.g.

$$\begin{tikzcd}
\underline{n}\text{-BuLi} + CH_3\,CH_2O\,C_2H_5 \arrow[r] & CH_3\,CHLiOC_2H_5 + C_4H_{10} \arrow[d] \\
 & C_2H_4 + C_2H_5OLi
\end{tikzcd}$$

Similarly $(CH_3)_3CLi + C_2H_5OC_2H_5 \rightarrow (CH_3)_3CH + C_2H_5OLi$
$+CH_2 = CH_2$



$$\begin{tikzcd}(CH_3)_3CLi + CH_2 = CH_2 \arrow[r] & (CH_3)_3CCH_2CH_2Li \arrow[d, "(CH_3)_3CLi"] \\ & (CH_3)_3C\,CH_2CH_2\overset{OLi}{\underset{OLi}{C}}C(CH_3)_3\end{tikzcd}$$

This exchange process[52,54] between alkyl lithium and lithium halide (by product) in condensation of lithium with an alkyl halide is also rapid at room temperature but it is stopped at low temperature with the formation of alkyl lithium lithium halide molecular complexes. This interaction of alkyl lithium, ether (a Lewis base) and lithium halide at low temperature has been successfully used in promoting α-alkylation of 8-quinolinol to obtain 2-tert-butyl-8-quinolinol.

Thus each 2-alkyl substituted 8-quinolinol required its own exact conditions for optimum yield, as could be predicted from the theory outlined above.

CHAPTER FOUR

4.1. Preparation of 8-methoxyquinoline:

Apparatus: A one litre three necked reaction flask fitted with stirrer, condenser and a dropping funnel was used for all experimental variations as shown in Fig. 1, (page 39).

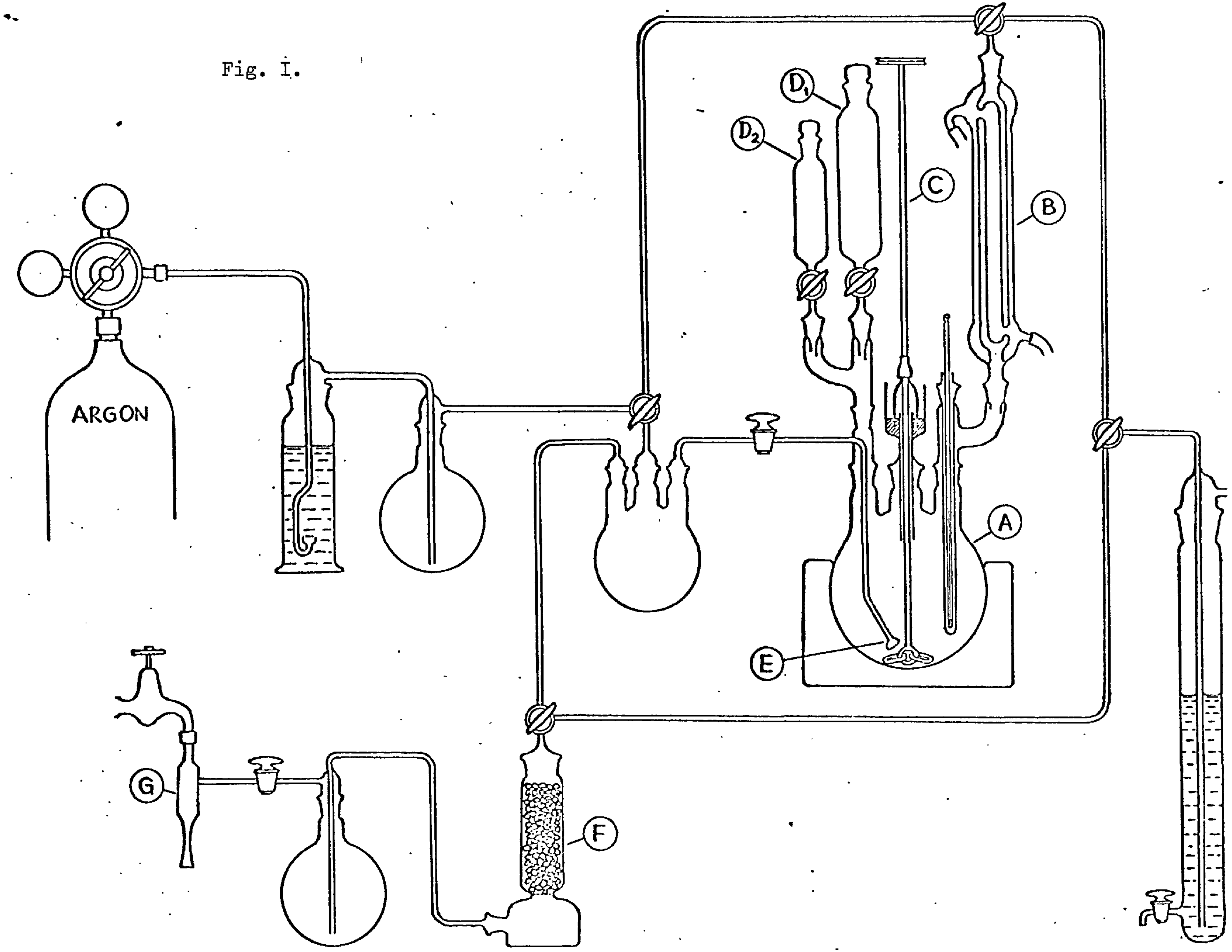
4.1.1 Skraup condensation.[18,55]

The condensation of o-ansidine with acrolien in presence of o-anisole was found unsatisfactory. The experimental conditions were varied as described by Haba[3]. Acrolien was double distilled to avoid polymerized material. The temperature was varied from 60° to 140°C. Acrolien was also replaced by glycerol and o-anisole by arsenic oxide to establish milder conditions for condensation. Sulphuric acid was used in place of hydrochloric acid to minimize dilution effect. The condensation time was varied from few minutes (after addition of aldehyde) to 48 hours. However, in most cases the resulting products were either resinous matter or the unreacted materials. The yield of the desired product did not exceed 5%. Therefore the method was abandoned.

4.1.2 Direct methylation of 8-quinolinol.

The method described by Vargolici and Rothlin[43] was successfully used to get the desired product. The methylation of aqueous alkaline 8-quinolinol using dimethyl sulphate is highly exothermic. Therefore the temperature was controlled at 60-70°C while dimethyl sulphate was being added. After the addition was complete, the reaction mixture required 8-10 hours additional stirring at 70°C for completion of the reaction. The separation of the product could not be affected by steam distillation as it was expected, and found, to be non-volatile. The product vacuum distilled at ~ 1mm

Fig. I.



and 100°C, was identified as 8-methoxyquinoline m.p. 45°c. The yield calculated on the basis of 8-quinolinol used was ~70%.

4.2 Condensation of lithium alkyls with 8-quinolinol

Apparatus: The assembly of apparatus used in the preparation of lithium sand and subsequent condensations with alkyl halide and 8-quinolinol was similar to that used by Perrine,[56] slightly modified for experimental requirements of this work as shown in Fig. I.

4.2.1 Preparation of lithium sand.

The lithium sand[56] or ribbon[57] suspended in the appropriate solvent under a stream of dry argon has been used successfully for the preparation of lithium alkyls. The presence of any metal oxide or traces of moisture decreased the efficiency of condensation drastically. However, the sodium content of the commercial lithium used (maximum limit 2%) was found advantageous in initiating the reaction between lithium and alkyl halides, especially at low temperature. If sodium content of lithium was increased by deliberate addition during the sand or ribbon making process so that the total sodium content was above 2%, then the titration results indicated a poor yield of lithium alkyl. At the same time the insoluble residue normally found at the end of preparations was considerably increased in bulk and consisted mainly of lithium halide. Higher proportions of sodium were therefore disadvantageous and the fortuitous 2% content of the commercial lithium appeared to be a suitable compromise for optimum yield.

4.2.2 Preparation of 2-ethyl- 8- quinolinol.

Scheme (ii):- 1.5 mole of lithium sand was suspended in 200 ml of dry benzene under a stream of dry argon. 0.2 mole of 8-quinolinol dissolved in 200 ml of ether and 0.5 mole of ethyl bromide diluted to 200 ml with benzene were added alternatively to the lithium with vigorous stirring in 5 ml increments. The temperature of the flask was maintained at 55-60°C. The addition of reactants was completed in 3 hr. The reaction mixture was left stirring overnight (12 hr).

The reddish-brown solution was filtered through a plug of glasswool and extracted into warm aqueous acidic phase. After neutralization with sodium carbonate, it was re-extracted in 500 ml ether and dried over anhydrous sodium sulphate. The product was concentrated by distilling off the ether and was then subjected to steam distillation[3]. The distillate was cooled in an ice box for 12 hours and the solidified product was filtered and collected. After several recrystallizations coupled with activated charcoal treatment and n-pentane, pure product was obtained; melted at 50-1°c and was identified by mixed melting point identity with that produced by Haba[3]. A 30% yield was obtained, calculated on the basis of 8-quinolinol used.

Scheme (iii). The experimental details were similar to those described for scheme (ii), except that, 8-methoxyquinoline was used in place of 8-quinolinol. The crude product after removal of ether obtained was refluxed with 48% hydrobromic acid for 48 hours. After neutralization, repeated steam distillations and then rigorous recrystallizations and charcoal treatment in n-pentane, a very small amount of the desired product was obtained.

4.2.3 Preparation of 2-isopropyl-8-quinolinol.

The procedure followed was essentially similar to that used for preparation of 2-ethyl homologue. But the addition of the reagents was carried out at room temperature and the reaction mixture was left stirring for ~ 15 hours. After neutralization of the aqueous acidic extract, the solid product was obtained. Therefore, the final ether extraction was omitted. The purified product melted at 90-1°C and was identical with that reported by Haba[3]. A yield of 50% was obtained calculated on the basis of 8-quinolinol used.

4.2.4 Preparation of 2-tert-butyl-8-quinolinol.

The condensation was carried out in two stages. First tert-butyllithium was prepared as described by Bartlett and Lefferts[58]. However, the experimental details were chosen as described here i.e. 2. mole of lithium sand suspended in 200 ml ether were cooled to -35 to -40°C. 1.0 Mole of tert-butyl chloride diluted with an equal volume of ether was added dropwise with vigorous stirring over a period of three hours followed by 100 ml of solvent. The stirring was continued for an additional two hours. A 5 ml aliquot of the reaction mixture was pipetted out in duplicate and titrated.[57,59] The titration was repeated thrice at 30 minutes intervals. The consistancy in titration for a period of 2 hours indicated little change in concentration of tert-butyl lithium formed which amounted to ~ 50% yield.

Second 0.25 mole of 8-quinolinol in 200 ml of ether was added to this analysed solution drop by drop and the temperature maintained at -35°C. After the addition of 8-quinolinol the temperature was allowed to rise to room temperature while stirring was continued (~ 12 hr). The rest of the procedure was identical to that applied for purification of 2-ethyl homologue. The product obtained melted at 70-1°C (mixed with 8-quinolinol, m.p 55°C). A yield of 20% was obtained calculated on the basis of 8-quinolinol used.

4.3 Materials used.

All the chemicals were A.R. grade supplied by B.D.H, Griffin and George, Hopkin and Williams, and Koch-light laboratories. They were further purified by recrystallization and double distillation etc. as necessary immediately before use. Tert-butyl chloride was prepared[60] freshly. Solvents such as ether, benzene and n-pentane were dried over sodium wire.

CHAPTER FIVE

5 Physical properties of 8-quinolinol and 2-alkyl homologues.

The physical properties, related to structure, identification and analytical tests of 8-quinolinol and 2-alkyl homologues have been studied extensively. A remarkable feature of alternation of some properties such as melting point and solubility along the series was noted. This has been employed to predict physicochemical parameters such as K_C/P_C ratio and stability constants of metal chelates in solvent extraction work. Emphasis has also been placed on comparison of the properties of 2-alkyl-8-quinolinols between themselves and with 8-quinolinol.

5.1 Melting points and microanalyses.

The melting points and elemental analysis recorded table (I) identified presence of new products, which were substantiated by other methods of identification.

Table I

Compound	Empirical formula	Molecular weight	M.p °C	Analyses					
				C		H		N	
				%found	%calculated	%found	%calculated	%found	%calculated
8-quinolinol	C_9H_7ON	145	75	—	74.5	—	4.9	—	9.6
2-methyl-8-quinolinol	$C_{10}H_9ON$	159	74	—	75.5	—	5.7	—	8.8
2-ethyl-8-quinolinol	$C_{11}H_{11}ON$	173	50-1	76.1	76.3	6.3	6.4	8.2	8.1
2-<u>isopropyl</u>-8-quinolinol	$C_{12}H_{13}ON$	187	90-1	76.8	77.0	6.9	7.0	7.0	7.5
2-<u>tert</u>-butyl-8-quinolinol	$C_{13}H_{15}ON$	201	70-1	77.5	77.6	7.5	7.5	7.0	7.0

5.2 Determination of U.V. absorption maxima.

The ultra violet absorption spectra of 8-quinolinols and metal chelates were recorded in the range of 220-500 nm using Hilger Uvispeck model 402 spectrophotometer, for aqueous and o-dichlorobenzene solutions. The results were reproducible to ± 1 nm. The molar absorptivities of 8-quinolinols in water at 240-260 nm were of the order of 15,000-70,000 - remarkably high figures approaching the "theoretical maxima"[64]. Therefore reasonable absorbances were obtained even on 10^{-4} - 10^{-6} M aqueous solutions. The overall pattern of the spectra was similar to that reported by Haba[3]. However, the use of o-dichlorobenzene in place of cyclohexane has shifted the absorption maxima by 10 nm in either direction. The λ_{max} and molar absorptivity values of 8-quinolinols and metal chelates are summarized in table II and III

where HR = Neutral species of the 8-quinolinol at pH≈7.

H_2^+R = Protonated form of the reagent at pH<2

R^- = Dissociated form of the reagent at pH>13

Table II

U.V. absorption maxima of 8-quinolinols(molar absorptivities in parentheses)

Compound	Absorption maxima in *o*-dichlorobenzene (nm)	Absorption maxima in aqueous solution						
		pH ≈ 7 "HR"		pH<2 "H_2R^+"			pH>13 "R^-"	
		I	II	I	II	III	I	II
8-quinolinol	297 (4100)	260 —	306 (2600)	260 —	361 (1350)	317 (1300)	260 —	334 (2050)
2-methyl-8-quinolinol	298 (4500)	—	—	—	—	—	—	—
2-ethyl-8-quinolinol	316 (1900)	254 (1900)	321 (1800)	255 (42000)	321 (1600)	310 (1400)	256 (36000)	336 (1700)
2-*isopropyl*-8-quinolinol	298 (4100)	241 (38000)	–	253 (62400)	320 (4400)	-	254 (50000)	330 (6000)
2-*tert*-butyl-8-quinolinol	318 (1900)	256 (44000)	321 (6000)	256 (69000)	321 (5700)	-	255 (67200)	334 (11400)

Table III

U.V. absorption maxima of metal- 8-quinolinol chelates in *o*-dichlorobenzene (Molar absorptivities in parentheses)

Chelating agent	Cu^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Ga^{3+}	In^{3+}	Fe^{3+}
8-quinolinol	402 (4600)	394 (5000)	392 (1900)	385 (5200)	400 (8000)	400 (8200)	472 (8000)
2-methyl-8-quinolinol	402 (4500)	387 (5900)	390 —	378 (4500)	400 (3900)	402 (7500)	460 —
2-ethyl-8-quinolinol	400 (3900)	392 (4200)	392 (2400)	390 (3050)	—	—	406 (6000)
2-*iso*propyl-8-quinolinol	402 (4300)	394 (4600)	392 (2500)	375 (4500)	400 (9300)	400 (12,000)	406 (5300)
2-*tert*-butyl-8-quinolinol	402 (10,000)	—	—	395 (3500)	400 (6900)	(9600)	471 —

5.3 Infrared spectroscopic interpretation.

Solutions of 8-quinolinol and its 2-alkyl homologues in carbon tetrachloride or carbon disulphide were examined at concentrations of 10 mg/ml in 0.5 mm potassium bromide cells on a Perkin Elmer model 621 instrument. The 8-quinolinol and 2-alkyl homologues have no significant absorption at the regions where total absorption of carbontetrachloride (820-725 cm^{-1}) and carbon disulphide (2,220-2,120 cm^{-1}), (1,630-1,420 cm^{-1}) occurs.

The few characteristic Peaks are assigned as follows:

(i) At 3,400 ± 10 cm^{-1} a strong absorption band is obtained in all spectra which is probably due to the O-H bond stretching. It is found absent in the 8-methoxyquinoline.

(ii) At 3050 ± 10 cm^{-1} the band observed in 8-quinolinol is probably due to C-H stretching. In the 2-methyl homologue an additional band at 2920 cm^{-1} is observed but in 2-ethyl, 2-isopropyl and 2-tert-butyl homologues three more bands at 2,970, 2,930 and 2870 ± 10 cm^{-1} are probably due to replacement of H-atoms of the 2-methyl group with alkyl groups increasing the intensity of bands due to C-H stretching.

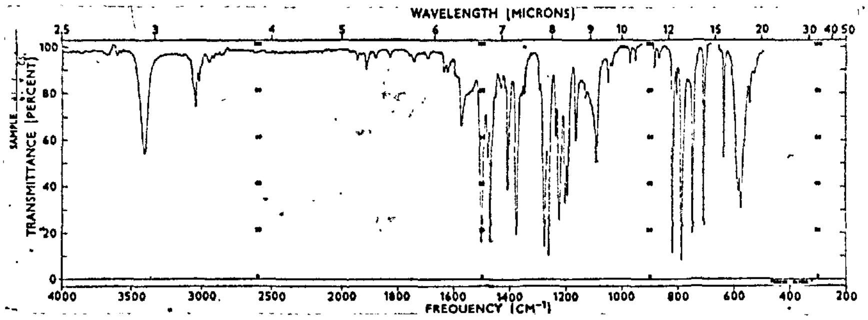
(iii) At 1600-1570 ± 10 cm^{-1} the bands observed in all 8-quinolinols are probably due to $C{=\!=}C$ vibrations mixed with C = O stretching frequency.

(iv) The deformation and broadening of the bands in the region 1470-1300 ± 10 cm^{-1} of the spectra may probably be assigned to the stretching vibrations of the substituent alkyl groups at the 2-position of 8-quinolinol.

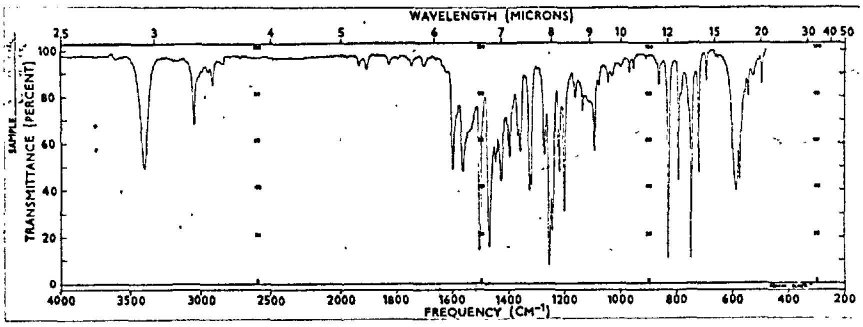
(v) The identical bands observed in the region 1300-650 cm^{-1} of the spectra of 8-quinolinol and its 2-alkyl homologues may probably be due to hetrocyclic ring system and overtones.

It appears from the development of the spectra along the series $-H \rightarrow -CH_3 \rightarrow -C_2H_5 \rightarrow -C_3H_7 \rightarrow -C_4H_9$ that the bands in the 2900-3100 cms^{-1} and 1400-1600 cm^{-1} regions are most useful for characterization purposes. Other features remain remarkably constant throughout the series. The spectra are given on page 53.

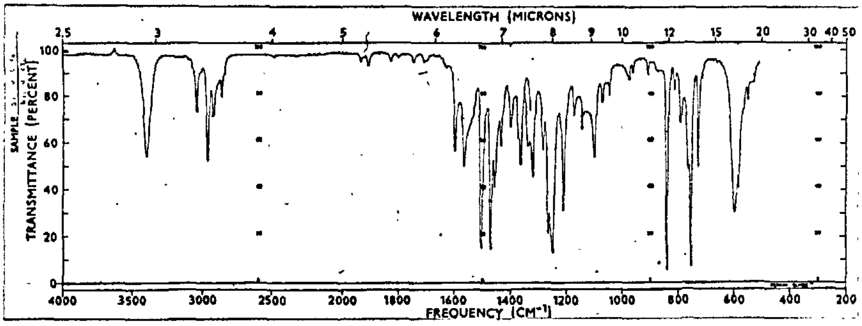
2-substituent



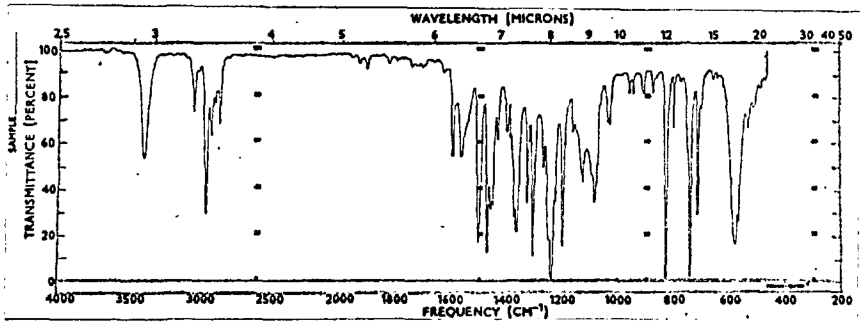
-H

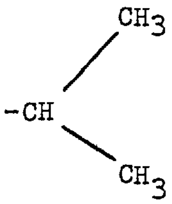


$-CH_3$

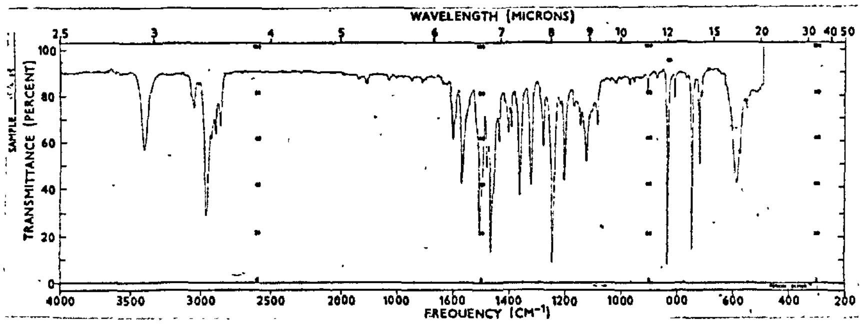


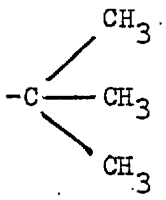
$-C_2H_5$





$-CH(CH_3)_2$





$-C(CH_3)_3$

Infra red spectra of 8-quinolinols.

5.4 Interpretation of mass spectra.

The mass spectra of 8-quinolinols were recorded on AEI - MS12 doublefocussing spectrometer. The compounds show considerable stability as the parent molecule "p" continues to be present in abundance. The possible fragmentation is considered to have produced ions of mass numbers (p+1), (p-1), (p-15), (p-27), (p-29), (p-43) and (p-57) as stable ions. The numbers subtracted from "p" in these brackets correspond to mass numbers of H-, $-CH_3$, HCN, $-CH_2-CH_2-$, $-CH(CH_3)_2$ and $C(CH_3)_3-$ respectively. Some lines observed in spectra have also been considered to have emerged from the (p+1) ion. For example (p-27) may be written as (p + H - 28). Similar argument may be extended for (p-56) and (p-58) ions.

The values are also recorded for the small mass numbers considered to have been ejected from the parent molecule during fragmentation. They are not in accordance with the corresponding residual large fragments. This is quite possible since these ions rearrange during the process and give rise to numerous metastable transitions. In case of 2-methyl homologue the low abundance of "p" may be attributed to different setting of instrument. In general, mass spectra are in accordance with the pattern of fragmentation observed for quinoline compounds and verify the individual structural features of each homologue. The results are presented in table IV.

Table IV

Relative abundance of selected ions in the spectra of 8-quinolinols

Compound	Molecular weight	Mass number.														
		P	P+1	P-1	P-15	P-27	P-28	P-29	P-43	P-56	P-57	P-58	128	129	27	28
8-quinolinol	145	100	16	16	-	96	24	-	-	50	4	4	8	8	4	4
2-methyl-8-quinolinol	159	4	36	4	-	100	56	-	-	28	20	-	-	-	40	20
2-ethyl-8-quinolinol	173	100	24	96	12	4	-	96	4	96	99	99	40	8	52	40
2-*iso*propyl-8-quinolinol	187	100	12	52	99	36	-	-	20	8	4	-	8	4	16	8
2-*tert*-butyl-8-quinolinol	201	80	12	40	100	8	56	4	4	32	8	4	8	8	8	4

5.5 Interpretation of proton magnetic resonance spectra.

Proton magnetic resonance spectra of 8-quinolinol and 2-alkyl homologues were taken on a Varian HA - 100 instrument. The positions of the proton resonance were measured relative to single line due to resonance position of the twelve equivalent protons of tetramethylsilane "TMS" by arbitrarily assigning $\nu_{TMS} = 0$. The chemical shifts "τ" of the protons were calculated according to the relation;

$$\tau = 10 - \delta \text{ (ppm)}$$

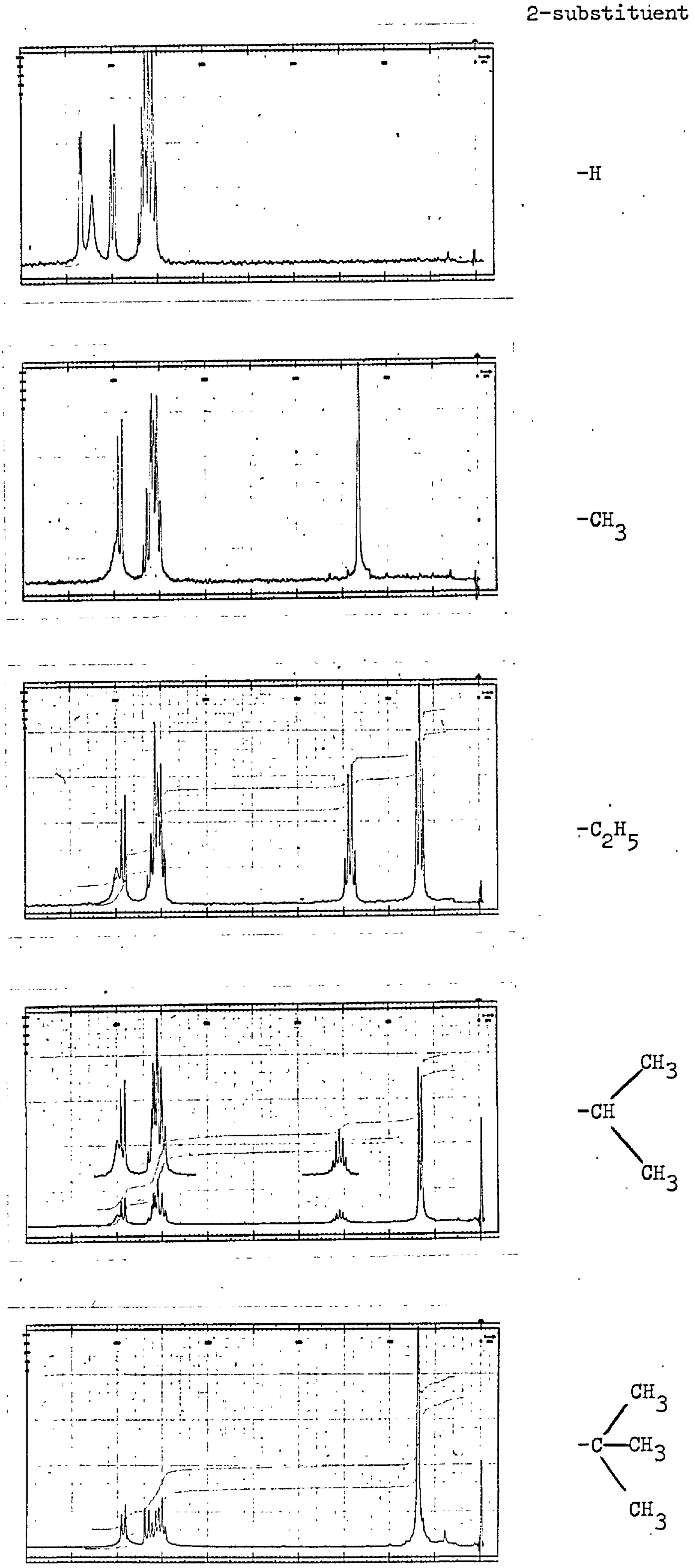
where $\delta = \nu_S - \nu_{TMS}/100$

The chemical shifts are completely in keeping with the change of proton environment along the series, and with the substitution in the 2-position in all cases; the areas under the various regions of the spectra are also in correct ratio with the number of protons in the corresponding various chemical environments. Results are summarized in table V

Table V

N.M.R. Spectra assignment.

Compound	"τ" values	Multiplicity of the peak.	Assignment					
			Phenolic protons	Hetrocyclic ring protons	Aliphatic side chain protons			
					methyl $-CH_3$	methylene $-CH_2-$	methine $>CH-$	tertiary butyl C-
8-quinolinol	2.02	doublet	✓					
	2.92	complex superimposed		✓				
2-methyl-8-quinolinol	2.12	doublet	✓					
	2.82	complex		✓				
	7.38	singlet			✓			
2-ethyl-8-quinolinol	2.15	doublet	✓					
	2.88	complex		✓				
	7.12	quadraplet				✓		
	8.68	triplet			✓			
2-*isopropyl*-8-quinolinol	2.14	doublet	✓					
	2.88	complex		✓				
	6.90	heptet					✓	
	8.64	doublet			✓			
2-*tert*-butyl-8-quinolinol	2.14	doublet	✓					
	2.86	complex		✓				
	8.64	singlet						✓



P.M.R. Spectra of 8-quinolinols.

5.6 X-ray powder diffraction

The x-ray powder diffraction studies were made on 8-quinolinol, 2-alkyl homologues and corresponding chromium chelates using a Phillips PW 1310 diffractometer. The "d" values were calculated according to Bragg equation

$$n\lambda = 2\ d\ \sin\ \theta$$

The data obtained were not enough to draw definite conclusions. However, the d-values reported by Merrit[65], Haba[3], ASTM were compared with those obtained in present work. Minor differences in the numerical values recorded by each worker may be attributed to experimental conditions used. In the present work, no definite trends are observed in the intensity order of the d-space calculations as attempted by previous workers.[65,3] But the comparison of "d" values of 8-quinolinols among themselves and with corresponding chromium chelates indicated that it may be possible to identify components of a mixture, e.g. a mixture of 8-quinolinol + 2-alkyl homologue or 8-quinolinol + chromium- 8-quinolinol chelate. This is possible because the equivalent d-values of metal chelates are higher than for 8-quinolinol. This indicates that chelation results in formation of new unit cells quite different from those present in free reagents. Also, the comparison of first eight "d" values for chelates of 2-ethyl- and 2-isopropyl - 8- quinolinols indicated that electron density for M-O and M-N bonds in case of 2-ethyl - 8-quinolinol may be lower than in 2-isopropyl homologue. This could be explained by arguing that

M-O and M-N bonds are lengthened in case of chelation of 2-isopropyl homologue to accommodate the influence of steric effect of branched isopropyl group. However, the increased electron density of such bonds may be attributed to operation of the inductive effect due to the shift of lone pair of electrons on nitrogen in coordination process. This explanation may also be extended to chromium chelates of highly branched tert-butyl homologue. In such case it may be predicted that the steric effect will increase the bond length. More useful conclusions can be drawn from the present work only if indexing and space group determinations were possible. Indexing powder patterns is simple only for cubic space groups. In this series of compounds or chelates, a single crystal work is necessary for space group determinations and establishing of a unit cell and crystal structures.

Table VI

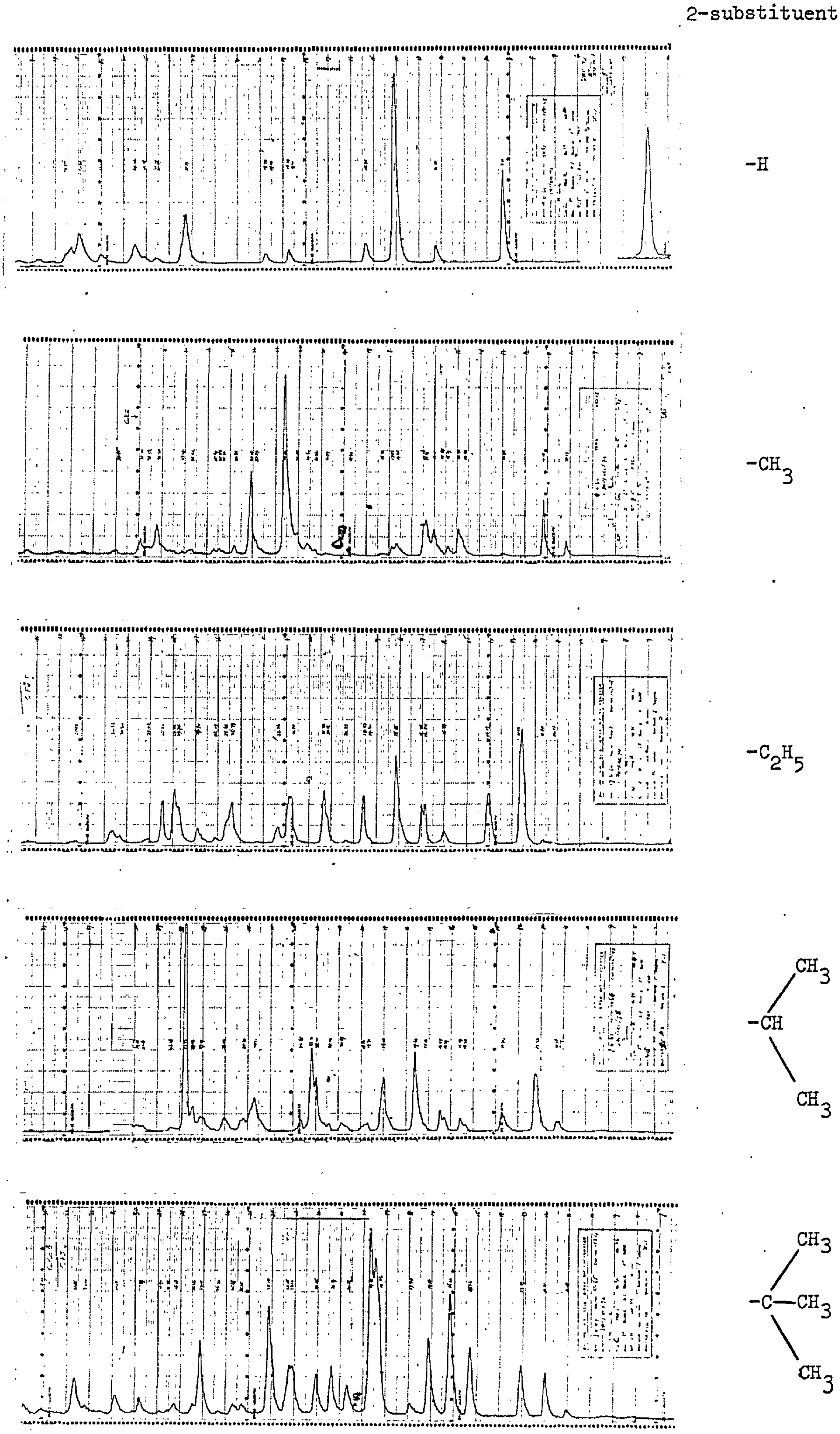
X-ray powder diffraction lines of 8-quinolinol and 2-alkyl homologues.

Compound	'd' values in order of decreasing intensity															
8-quinolinol	6.28	9.49	3.82	3.19	7.23	5.78	3.49	4.73	3.15	4.50	3.30	2.37	3.62	3.55	3.13	2.88
2-methyl-8-quinolinol	3.93	3.69	7.91	5.42	3.16	5.93	5.53	4.03	8.70	3.09	5.98	5.02	4.11	5.76	4.96	3.73
2-ethyl-8-quinolinol	7.03	4.89	4.17	3.19	6.30	4.53	3.89	3.51	3.14	5.26	5.22	3.81	5.54	3.31	2.92	2.41
2-*isopropyl* 8-quinolinol	3.21	4.00	5.03	7.24	4.67	4.04	3.60	5.38	3.25	6.46	5.69	5.44	3.42	3.29	3.92	3.53
2-*tert*-butyl 8-quinolinol	4.51	4.56	5.47	3.69	5.17	3.28	5.78	6.76	4.15	7.37	4.03	2.74	3.84	3.82	4.29	2.93

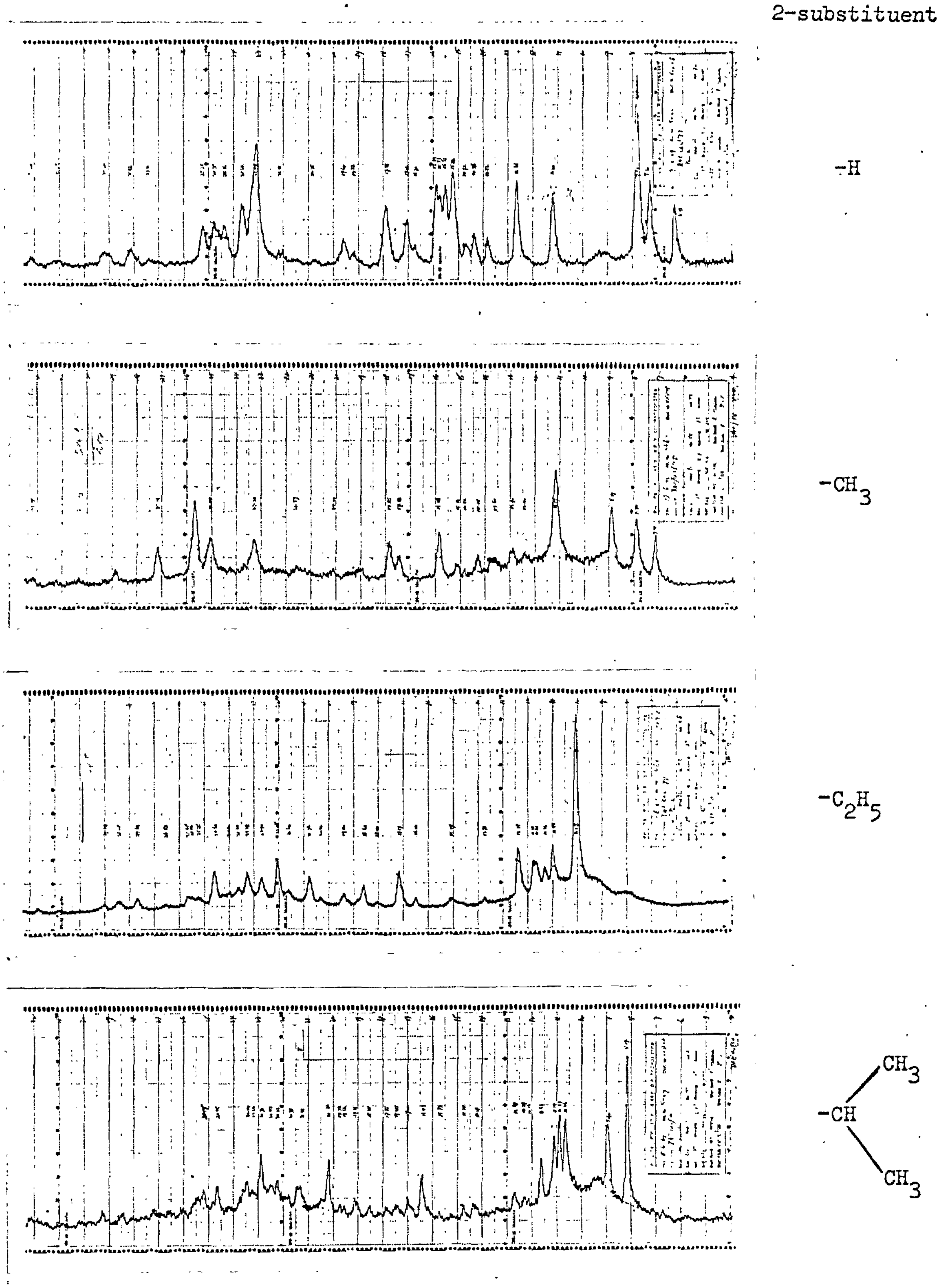
Table VII

X-ray powder diffraction lines of chromium chelates.

Chelating agent	"d" values in order of decreasing intensity.														
8-quinolinol	11.29	3.85	5.82	12.11	7.00	5.71	5.58	7.90	13.96	4.96	3.76	5.21	3.60	3.65	5.63
2-methyl-8-quinolinol	7.92	9.95	11.19	3.47	5.59	12.38	4.97	3.28	3.82	3.51	5.09	6.86	6.20	5.87	3.09
2-ethyl-8-quinolinol	8.78	7.15	8.06	5.16	4.03	3.62	4.27	4.77	3.82	7.52	3.92	7.58	7.82	4.57	5.37
2-isopropyl 8-quinolinol	10.82	8.12	8.30	9 89	7.97	4.39	7.61	5.39	3.88	3.79	3.61	4.15	3.53	5.21	6.99



X-ray powder diffraction spectra of 8-quinolinols



X-ray powder diffraction spectra of chromium-8-quinolinol chelates.

5.7 Determination of solubility ratio.

Saturated aqueous and o-dichlorobenzene solutions of the reagents or metal chelates were obtained by shaking excess of the solid with water and o-dichlorobenzene separately in a thermostat at 25 ± 0.1°C, using an atmosphere of pure nitrogen and then filtering. The aqueous solutions were back-extracted in small known volumes of o-dichlorobenzene and the o-dichlorobenzene solutions were appropriately diluted. Absorbance of the filtrate was measured at the λ_{max} of the respective compound in a high precision spectrophotometer (Hilger Uvispec H 700). The solubility ratio "S_R" or "S_C" was calculated according to relation.

$$\text{Solubility ratio} = \frac{\text{Molar solubility in o-dichlorobenzene}}{\text{Molar solubility in water}}$$

This solubility ratio has been taken to be the same as the partition coefficient, as similarity has been established with P_R values calculated from extractability formula[3]

$$E = \frac{1}{1 + \frac{V_A}{P_R V_O}\left(1 + \frac{K_{R_1}}{\{H^+\}} + \frac{\{H^+\}}{K_{R_2}}\right)}$$

using experimental values of E, H^+, K_{R_1}, K_{R_2}, V_A and V_O.

The experimental values of "S_R" or "S_C" are also in close agreement with previous work[3]. It is also interesting to note that a plot of log P_R versus number of methyl groups substituted in 2-position of

8-quinolinol gives a good linear relationship for the reagents. Similar relationship could not be found for "S_C" for copper chelates due to alternation of results. The alternation of "S_C" values may be attributed to "K_C", K_{R_1}, and K_{R_2} values. In absence of experimental "S_C" value for copper-2-tert-butyl - 8-quinolinol chelate, it was predicted and then used in subsequent calculations for evaluation of stability constants. The results obtained were found to be in close agreement with stability constants of other copper chelates. This confirmed the validity of experimental approach in evaluating "S_R" and "S_C" values.

Table VIII

Solubility ratio data. (Figures in parentheses indicate P_R values calculated from extractability formula[3])

Compound	Solubility ratio of the reagents "S_R"	Solubility ratio of copper chelates "S_C"
8-quinolinol	3.6×10^2 (2.5×10^2)	1.5×10^2
2-ethyl- 8-quinolinol	1.2×10^3 (9.5×10^2)	1.0×10^4
2-ethyl- 8-quinolinol	4.4×10^3 (4.0×10^3)	4.7×10^3
2-isopropyl- 8-quinolinol	1.5×10^4 (4.1×10^3)	1.1×10^5
2-tert-butyl 8-quinolinol	7.1×10^4 (6.9×10^4)	(7.9×10^4)*

*Predicted value.

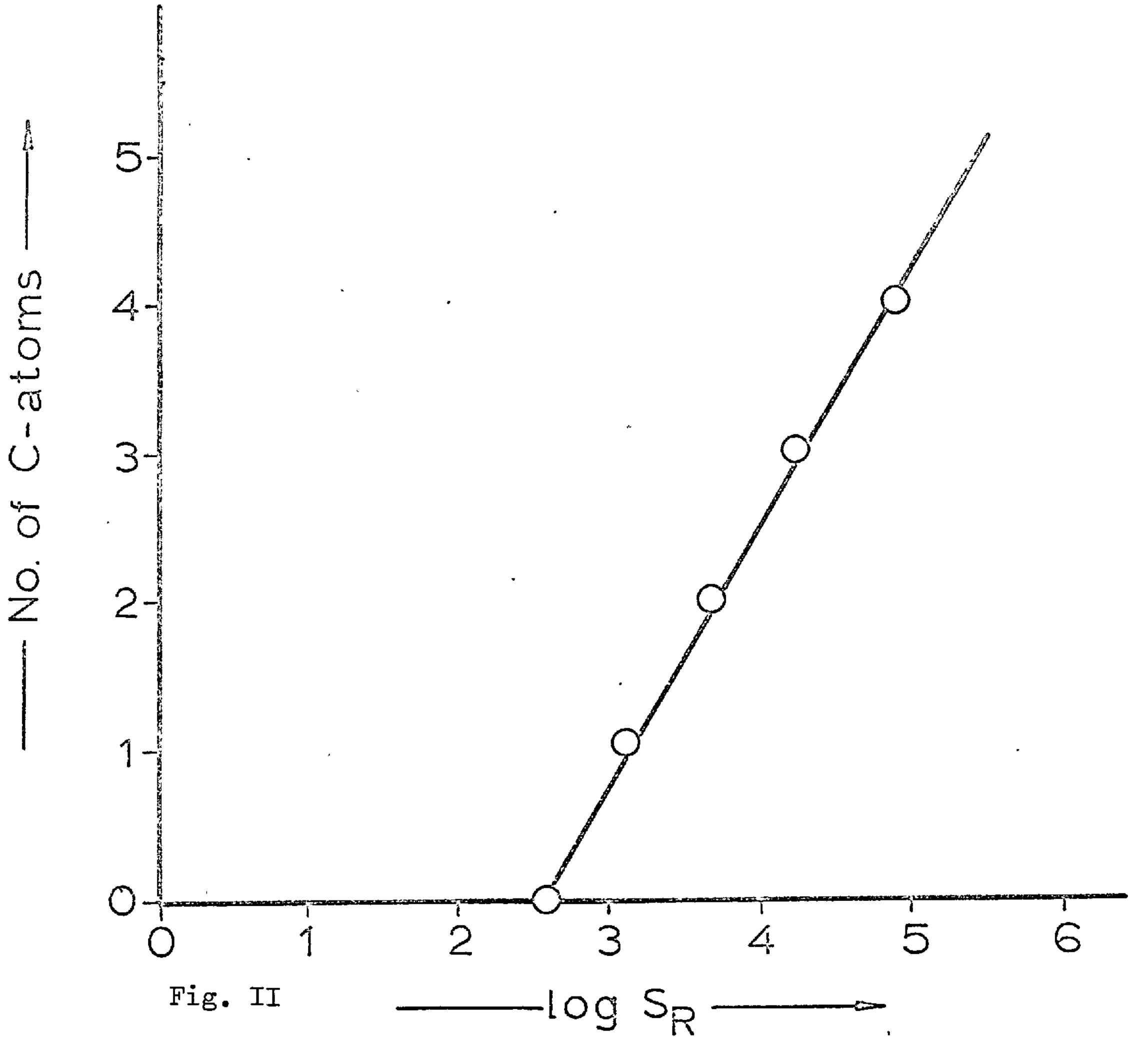


Fig. II

CHAPTER SIX

6.1 Chelation properties of the reagents.

Attempts have been made to prepare chelates of a wide selection of metals with 8-quinolinol and 2-alkyl homologues. 10.0 ml of 0.1M solutions of the metal ion were diluted to 50 ml with water, 10 ml of 2N acetic acid and a slight excess of tartaric acid were added, followed by 10-15% excess of the reagent in either dilute acetic acid or methanol. Precipitation was affected at ~60°C by careful addition of 1 + 1 aqueous ammonia solution until the precipitation appeared to be complete, and the suspension was digested on the steambath for 20-30 minutes. Where precipitation was obviously inefficient or even absent, tartaric acid was omitted and the solution was basified cautiously with dilute sodium hydroxide solution. The pH was measured with the narrow range pH papers with an accuracy of ± 0.3 units. In general, yields decreased with increasing size of alkyl group and, in the case of the 2-tert-butyl-8-quinolinol, were clearly affected by ionic radius of the cation. At the same time, the pH required for initiating precipitation, and for making it reasonably effective, increased along the series

$$-H \longrightarrow -CH_3 \longrightarrow -C_2H_5 \longrightarrow -CH(CH_3)_2 \longrightarrow -C(CH_3)_3.$$

For the isopropyl and tert-butyl homologues, extensive digestion times and use of aqueous methanol as solvent were often found necessary for even partial recovery of the chelates. This indicated that the higher homologues were unsuitable for gravimetry of most metals.

Table IX

Results of precipitation of metal-8-quinolinol chelates. (Figures in parentheses indicate pH range used for effective precipitation).

Metal ion	Ionic radii			2-substituent →		
		-H	$-CH_3$	$-C_2H_5$	$-CH(CH_3)_2$	$-C(CH_3)_3$
Al^{3+}	0.50	++ (3.0→5.5)	-	-	-	-
Ga^{3+}	0.62	++ (3.0→5.5)	++ (5.5→8.0)	++ (5.5→8.0)	++ (5.5→8.0)	- -
Co^{3+}	0.63	++ (4.0→5.5)	+ (4.0→5.5)	+ (4.5→6.0)	+ (5.5→10.5)	- -
Fe^{3+}	0.64	++ (4.3→5.0)	++ (3.0→5.5)	+ (3.0→5.5)	+ (4.5→7.0)	-
Cr^{3+}	0.69	++ (4.5→8.0)	++ (4.5→8.0)	+ (4.5→8.5)	+ (5.5 → 10.0)	-
In^{3+}	0.81	++ (2.5→4.5)	++ (5.5→8.5)	+ (5.5→9.0)	+ (5.5 → 9.0)	-
Tl^{3+}	0.95	++ (4.0→8.0)	++ (4.0→8.0)	+ (4.0→8.0)	+ (5.0 → 8.0)	⊕ (5.0→8.0)
Cu^{2+}	0.60	++ (3.5→5.5)	++ (3.5→5.3)	+ (4.0→7.0)	+ (4.5 → 7.0)	⊕ (5.5→10.0)
Mg^{2+}	0.65	++ (5.5→8.5)	++ (5.5→8.0)	+ (5.5→8.0)	+ (5.5 → 8.5)	⊕ (5.5→11.0)
Ni^{2+}	0.72	++ (4.5→9.0)	++ (5.5→10.0)	+ (5.5→10.0)	+ (5.5 → 10.0)	⊕ (5.5→10.0)
Zn^{2+}	0.74	++ (3.5→5.5)	++ (4.5→5.5)	+ (5.0→6.5)	+ (5.5→10.0)	+ (8.5→12.0)
Mn^{2+}	0.80	++ (4.0→5.5)	++ (5.0→7.0)	+ (5.5→8.0)	+ (5.5→9.0)	⊕ (5.5→10.5)
Hg^{2+}	1.10	⊕ (3.0→7.0)				
Pb^{2+}	1.20	++ (3.5→8.0)	++ (3.5→8.0)	+ (3.5→9.0)	+ (5.5→10.0)	+ (5.0→12.0)

Key: ++ quantitative or almost quantitative precipitation.

\+ >50% precipitation

⊕ incomplete (≪ 50%) or product of doubtful composition.

\- does not react.

6.2 Dissociation and protonation constants.

The dissociation and protonation constants of 8-quinolinol and 2-alkyl homologues were determined spectrophotometrically at constant ionic strength of 0.1M in sodium perchlorate. Absorbances were measured at preselected wavelengths, as a function of pH. The dissociation and protonation constants were calculated according to relation.

$$\mathrm{pH} = \mathrm{p}K + \log \frac{\{\text{dissociated form} = R^-\}}{\{\text{undissociated form} = HR\}}$$

when:

A_{min} = minimum absorbance by the reagent at one extreme value of pH = $\varepsilon_{HR}bc$

A_{max} = maximum absorbance by the reagent at opposite extreme values of pH = $\varepsilon_R\ bc$

and A_i = absorbance by the reagent at any pH

then $A_i = \varepsilon_{HR}\ b\{HR\} + \varepsilon_R\ b\ \{R^-\}$

$$\therefore \quad \frac{\{R^-\}}{\{HR\}} = \frac{(A_i - A_{min})}{(A_{max} - A_i)}$$

and $\mathrm{pH} = \mathrm{p}K + \log \dfrac{(A_i - A_{min})}{(A_{max} - A_i)}$

This expression has been applied in the excellently linear plots of pH vs log $\dfrac{(A_i - A_{min})}{(A_{max} - A_i)}$.

Some of the results were determined for solvents of dioxan-water mixtures, since it was originally intended to use such media for the relatively insoluble higher 2-alkyl homologues and then obtain pK values in water by extrapolation to zero dioxon content.

This method appeared to be satisfactory, but unnecessary, as reasonable absorbances were obtained at very low concentrations of the reagents in aqueous solutions, especially while operating at the little used 240-260 nm range of absorption maxima. The results are summarized in table X and XI.

Table X

Protonation and dissociation constants of 8-quinolinol and 2-alkyl homologues (literature values in parentheses).

Reagent	Wavelength used (nm)	pK_{R_1}	pK_{R_2}
8-quinolinol[61,62]	306	9.18±0.02 (9.81)	4.74±0.06 (4.91)
2-methyl-8-quinolinol[63]	-	(10.31)	(5.54)
2-ethyl-8-quinolinol	254	9.97 ± 0.16	5.38± 0.05
2-*isopropyl*-8-quinolinol	241	9.20 ± 0.06	5.12 ± 0.03
2-*tert*-butyl-8-quinolinol	256	10.05 ± 0.07	4.72 ± 0.04

Table XI

Protonation and dissociation constants of 8-quinolinol in Dioxan - water solution (wavelength used = 306 nm)

% Dioxan (v/v)	pK_{R_1}	pK_{R_2}
5	9.12 ± .01	4.72 ± .01
10	9.24 ± .01	4.69 ± .02
15	9.79 ± .03	4.56 ± .01
20	9.98 ± .03	4.21 ± .07
25	10.07 ± .02	4.31 ± .04
0% intercept	8.85 ± 0.14	4.89 ± 0.12

6.3 Electron Spectroscopy for chemical analysis "ESCA".

This new technique was pioneered by K. Siegbahn et-al.[72] The main purpose of the work described here was to study the chemical environments of various atoms present in free reagents and corresponding metal chelates, for example, calculate electronegativity of nitrogen in these compounds or the part played by inductive effect due to 2-substitution of 8-quinolinol with different alkyl groups. The technique is based on the fact that the wave function of the outer electrons (valence electrons) of different atoms overlap each other when they are combined. This overlapping involves a displacement and redistribution of electric charge over the atoms in combined state. The redistribution affects the core electrons (inner electrons such as " 1S " electrons). The effect is of the same order of magnitude as energy of a chemical bond i.e. ≈ 418.6 Kjoule/mole or 4ev.
In fact, the core electrons of different atoms are not involved in direct interaction when atoms form a molecule and should not be mistaken to have taken part in bond formation or any other phenomenon as outer electrons do. However, a high precision spectrometer such as the "ES 100" is quite useful to monitor the different energy states of core electrons.

The difference of energy between standard and combined states is taken as a measure of binding energy of an atom, also termed as chemical shift.
This chemical shift is based on the following relationships.

$$\Delta E = q_A K_{AC} + \sum_{B \neq A} q_B / R_{AB}$$

where K_{AC} = Average interaction between core electron and valence electron on an atom A.

q_A = Charge difference on that atom between the molecule and the reference system (provided the two centre electron interaction is assumed as between two point charges = $1/R_{AB}$

∴ it may be rewritten as

$$\Delta E_A = kq_A + V + l$$

where k and l may be determined by least square fit to experimental data.

$$V = \sum_{B \neq A} qB/R_{AB}$$

= interatomic effective potential i.e. molecular potential

or $\Delta E_A = k\ q_A$.

Experimentally following simplified relationship was used

$$E_S = \frac{E_o - E_b}{n}$$

where E_S = energy at which the line occurs.

E_o = energy of X-ray source

E_b = binding energy of element under investigation.

n = instrumental factor

= 15.

This gives a direct measure of absolute charge on an atom in its various states of combination and can easily be correlated with different properties of an element, such as electronegativity, and partial ionic character.

Although, correlation between measured chemical shifts and the above mentioned parameters have been established for a number of gaseous and solid diatomic and polyatomic molecules[73], lack of sufficient experimental data and limitations imposed by the use of prototype ES 100 do not permit the author to interpret the exploratory findings (table XII) of the "ESCA" work carried out on 8-quinolinol and metal complexes on quantitative basis. Therefore the results given for this work have been interpreted qualitatively with caution as under.

The chemical shifts indicated more electronegative character for carbon atom; less for nitrogen, oxygen and magnesium atoms as compared with their reference state.

The observation is in line with the theoretical predictions that 2-alkyl substituted-8-quinolinols will form less stable complexes with metal ions due to steric hindrance exerted by an alkyl group in 2-position and operation of an inductive effect. The steric effect will be pronounced in case of more branched alkyl groups such as <u>iso</u>propyl or <u>tert</u>-butyl which in turn increased M—O and M—N bond length to allow disposition of reagent molecules octahedrally around a trivalent metal ion in chelate formation.

Acknowledgement. The author thanks the management and staff of the consultant laboratories of GEC-AEI (Electronics) Ltd. Manchester, for their cooperation to use prototype electrospec ES 100 and MS 12 spectrometers.

Table XII

Electron Spectroscopy for Chemical Analysis data.

No.	Compound used	Elements							
		Carbon		Oxygen		Nitrogen		Magnesium	
		A	B	A	B	A	B	A	B
1	Apizon grease*	80-3.8ev	2.3ev	-	-	-	-	-	-
2	Magnesium oxide*	-	-	-	-			78.6-7.0ev	3.3ev
3	Paraformaldelyde*	-	-	63.4-4.8ev	2.7ev	-	-	-	-
4	Silicon nitride*	-	-	-	-	72.5-5.8ev	2.6ev	-	-
5	Magnesium-8-quinolinol	80-3.6ev	2.9ev	63.5-2.5ev	2.6ev	72.5-5.5ev	2.2ev	78.7-4.7ev	3.1ev
6	Magnesium-2-*isopropyl*-8-quinolinol	80-4.9ev	3.0ev	63.5-3.7ev	2.7ev	no signal	-	78.7-6.0ev	3.3ev
7	1+1 mixture of No. 5 and 6 complexes	80-4.1ev	3.1ev	63.5-2.9ev	2.6ev	no signal	-	78.7-5.7ev	3.0ev

Key :*=Reference compounds used for corresponding element.

A = peak height

B = peak half width

6.4 Cyclic voltammetry of 8-quinolinol and 2-alkyl homologues

The cyclic voltammetric investigations of the reagents were attempted with and without the presence of aluminium in DMF solution, using the hanging mercury drop electrode.

The drawn out form of the cyclic voltammogram in all cases indicated an irreversible reduction of the reagents, possibly the formation of 1:2:3:4 tetrahydro-8-quinolinols. However, according to stock[66], the electron capture followed by abstraction of a proton from the solvent and dimerization of the free radical, instead of further reduction may be assumed to have prevented the full development of the drawn out wave. The voltammograms obtained for 8-quinolinol and 2-alkyl homologues in presence of aluminium (111) showed that the potentials of reduction of aluminium (11.) and the reagents can be measured except for 2-<u>tert</u>-butyl 8-quinolinol. However, in case of 2-<u>tert</u>-butyl-8-quinolinol + aluminium the overlapping of the potentials of reduction may be used advantageously as reported by Galova[67]. Therefore, it may be concluded that, these reagents, especially, 2-<u>tert</u>-butyl-8-quinolinol can be applied successfully in the study of metals in exceptionally small quantities by cyclic voltammetry. The peak maxima values have been summarised in table XIII.

Table XIII

Cyclic voltammetric results. (Figures for reagent + aluminium (III) are given in parentheses).

Reagent	Peak maxima (volts)		
	Reagent		Aluminium
	I	II	III
8-quinolinol	-2.0 (-2.08)	-2.62 (-2.70)	(-2.30)
2-methyl- 8-quinolinol	-2.06 (-2.14)	-2.63 (-2.72)	(-2.30)
2-ethyl- 8-quinolinol	-2.05 (-2.12)	-2.70 (-2.72)	(-2.28)
2-*isopropyl*- 8-quinolinol	-2.09 (-2.11)*	-2.75 (-2.75)	(-2.25)*
2-*tert*-butyl- 8-quinolinol	-2.04 (-2.17)*	-2.81 (-2.79)	(-2.27)*

*Peaks overlapping.

6.5 Method of Continuous variations.

To establish the exact composition and nature of the extractable chelate species taken into o-dichlorobenzene and which absorb in the wavelength region used for experimental purposes, the method of continuous variations was used. The solutions of cupric and ferric chelates of 8-quinolinol and 2-alkyl homologues were studied. The results (table XIV) indicated that mixed chelates of the type $MRClO_4$, $MR_2\ ClO_4$ and $MR(Cl\ O_4)_2$ etc. were not extracted into the organic phase. However, it was found in case of 2-tert-butyl-8-quinolinol chelate that the maximum absorbance occurred at a composition which did not conform to the expected stoichiometric composition of the chelate. The number of molecules of the reagent associated with an atom of metal were in the ratio of approximately 9:1. Such a remarkably high ratio may be considered due to loose association of the excess reagent with the stoichiometric chelate to give extractable species of the type $MR_m\ XHR$. Due to this physical interference of the reagent with the complex of the proper composition (MR_m), the actual maximum corresponding to MR_m could not be located and a steadily increasing absorbance was noted even for $C_M/C_M + C_Z$ values lower than 0.33. If secondary complexing agents such as Na_2. E.D.T.A. were used and pH raised to 12, the excess of the reagent remained dissociated (R^-) and was not extracted with metal chelate MR_m. This was confirmed by the shift of the maximum at C_M/C_M+C_Z values from 0.1 to ~ 0.3 i.e. the number of reagent molecules associated with an atom of metal obeyed the stoichiometric relationship.

However, the possibility of formation of mixed chelates cannot be excluded completely. The maximum absorption corresponding to the reagent:metal mole ratio of 2:1 or 3:1 could also be extended to cover extraction of mixed chelates of the type $MRClO_4XHR$. Therefore in principle the existence of such extractable species is possible. However, under experimental conditions used in this work i.e. extended time given for extraction and equilibriation, excess reagent, working at λ_{max} approximately optimum pH values of extraction of the respective copper or iron - 8 - quinolinol and 2-alkyl homologue chelates it can be assumed that ClO_4^- is displaced by R^- to give neutral chelate species MR_m or MR_mXHR. The reaction may be written as follows.

$$MR\ ClO_4\ XHR \quad + \quad HR \longrightarrow MR_2XHR \quad + \quad HClO_4$$

This could not be confirmed in absence of dissociation data of complexes such as $\left[CuR^+\right]\ ClO_4^-$ and $\left[FeR^{2+}\right]\left(ClO_4\right)_2$ However, the log k values of 3.50 and 17.94 reported in literature [68,69] for $\left[Cu(bipy)_2\ ClO_4^+\right]$ and $\left[Cu(bipy)_2^{2+}\right]$ respectively indicated that chelate species of the type $MRClO_4$ could not be extracted into organic phase in presence of excess reagent as stable neutral chelates. In presence of excess reagent the effect may be compared with that described by Stary[70] and Morgerum[74] i.e. competitive displacement of one ligand by another from a molecule of achelate as follows:

$$MR_2 \quad + \quad R' \longrightarrow MRR' \xrightarrow{\quad R' \quad} MR'_2$$

or

$$M(ClO_4)_2 \quad + \quad \left[R^-\right] \longrightarrow MRClO_4 \xrightarrow{\quad \left[R^-\right] \quad} MR_2$$

The absence of mixed chelates as mentioned above was substantiated further by comparison of UV absorption spectra of solution obtained by dissolving solid chelate in o-dichlorobenzene with that obtained by extraction of metal chelate in o-dichlorobenzene from aqueous solutions of metal ion and organic ligand. Similarity of extrinisic properties of two solutions such as molar exttinction coefficient "ε" and λ_{max} values indicated presence of only one type of chelate species MR_m. Therefore, it may be concluded that the observed low values of $C_M/(C_M + C_Z)$ for copper - 2 - tert- butyl - 8 - quinolinol chelate could only be due to MR_mXHR species and no mixed chelates of the type $MRClO_4$ were formed and extracted in o-dichlorobenzene.

Table XIV

Continuous variations results.

Reagent	Metal ions	pH	Maximum absorbance at C_M/C_M+C_Z	Approximate metal to ligand ratio	Additional remarks
8-quinolinol	Copper	3.0	0.33	1:2	
8-quinolinol	Iron	2.0	0.28	1:3	
2-isopropyl-8-quinolinol	Copper	3.5	0.32	1:2	
2-tert-butyl 8-quinolinol	Copper	3.5	0.10	1:9	
2-tert-butyl 8-quinolinol	Copper	5.6	0.25→0.10	~1:7	Ill defined maximum
2-tert-butyl-8-quinolinol	Copper	10.0	0.28	1:3	
2-tert-butyl-8-quinolinol.	Copper	12.0	0.30	1:2	Na_2E.D.T.A is used as secondary complexing agent.

6.6 Solvent extraction

Most of the physicochemical parameters used in this work were evaluated by separate and independent experiments. The important observation was the alternation of the some physical and chemical properties of 8-quinolinol, 2-alkyl homologues and metal chelates such as, m.p., solubility ratio, protonation and dissociation constants.

Therefore, the results of solvent extraction work for one or two members of the series could not be generalized for whole series as attempted by Haba[3]. For example, using the extractability equation, he calculated the pK_{R_1} and pK_{R_2} values of the higher 2-alkyl homologues. However, the values obtained in this work from direct experiments were quite different as exemplified below.

Reagent	pK_{R_1}	pK_{R_2}
2-ethyl-8-quinolinol	10.64* 9.97±0.16	6.30* 5.38±0.05
2-<u>iso</u>propyl-8-quinolinol	11.13* 9.20±0.06	6.95* 5.12±0.03

* Habas thesis[3].

Obviously, this was contrary to theoretical assumptions used by Haba[3] to correlate various solvent extraction properties. Also, in turn, the physicochemical data obtained for 8-quinolinol and 2-alkyl homologues affected the corresponding metal chelate equilibria results.

This necessitated evaluation of most of the parameters by independent experimentation. The comprehensive data obtained in this way was used in subsequent calculations. Therefore, some of the extrapolated or predicted values used in this work for 2-tert-butyl-8-quinolinol or corresponding metal chelates may be considered reasonable and valid in absence of independently evaluated parameters due to experimental limitations. For example, the copper-2-tert-butyl-8-quinolinol could not be obtained as insoluble compound by gravimetric method of precipitation. This prevented independent evaluation of "S_C" value of the chelate and in turn of "K_C".

6.6.1 Effect of T_R on pH.

6.8×10^{-4} and 3.4×10^{-3}M solutions of the reagent were used, for extraction of copper chelates under identical experimental conditions. $pH_{E=0.5}$ values decreased by 0.2 units in the latter case. This was in line with the argument[3] that the higher the total reagent, T_R, higher the yield of chelating anion and higher the extractability.

Therefore, more H^+ ions would be present in solution and pH would decrease according to reaction:

$$M^{2+} + 2HR \rightarrow MR_2 + 2H^+$$

6.6.2 Interpretation of the slope value.

The slope of the plot of log extraction ratio versus log Q has been considered to denote the degree of dissociation of the fully chelated metal chelates in aqueous phase. For example, a value of unity showed that $MR^+_{(m-1)}$ species were predominant in aqueous phase, according to dissociation reaction:

$$MR_m \xrightarrow{K_{C_m}} MR^+_{(m-1)} + R^-.$$

$$\text{eg} \quad MR_3 \xrightarrow{K_{C_3}} MR_2^+ + R^-$$

$$\text{or} \quad MR_2 \xrightarrow{K_{C_2}} MR^+ + R^-$$

In the case of the trivalent metal ion if the predominant species in aqueous phase are considered to be MR^{2+}, the value of slope obtained would be equal to two. The significance of the value of the slope has been shown by the following relationships which are an extension of the extraction equilibria relationships derived by Haba[3].

Considering the dissociation of MR_3 as under:

$$MR_3 \xrightarrow{K_{C_3}} MR_2^+ + R^-$$

the total reagent, T_R, is given by

$$T_R = 3\{MR_3\}_o V_o + 2\{MR_2^+\}_A V_A + \{RH\}_o V_o + \{RH\}_A V_A + \{RH_2^+\}_A V_A + \{R^-\}_A V_A$$

substituting values of different species as described in chapter II we get,

$$T_R = 3\{MR_3\}_A V_o P_C + \frac{2 K_{C_3} \{MR_3\}_A V_A}{\{R^-\}} + \{R^-\}\beta$$

$$= \{MR_3\}_A \left[3V_o P_C + \frac{2 K_{C_3} V_A}{\{R^-\}} \right] + \{R^-\}\beta$$

$$= \{MR_3\}_A \alpha + \{R^-\}\beta$$

$$\therefore \{MR_3\}_A = \frac{T_R - \{R^-\}\beta}{\alpha} \qquad \text{(i)}$$

Similarly,

$$T_M = \{MR_3\}_o V_o + \{MR_2^+\}_A V_A$$

$$= \{MR_3\}_A V_o P + \frac{\{MR_3\}_A V_A K_{C_3}}{\{R^-\}}$$

$$= \{MR_3\}_A \left[V_o P_C + \frac{V_A K_{C_3}}{\{R^-\}} \right]$$

$$= \{MR_3\}_A \gamma$$

$$\therefore \{MR_3\}_A = \frac{T_M}{\gamma} \qquad \text{(ii)}$$

equating (i) and (ii) we get,

$$\frac{T_M}{\gamma} = \frac{T_R - \{R^-\}\beta}{\alpha}$$

$$\text{or } \{R^-\} = \frac{T_R - \frac{\alpha}{\gamma} T_M}{\beta}$$

$$\because \quad T_R >> T_M$$

$$\{R^-\} = \frac{T_R}{\beta} \qquad \text{(iii)}$$

$$\text{Now } E = \frac{\{MR_3\}_o V_o}{\{MR_3\}_o V_o + \{MR_2^+\}_A V_A}$$

$$= \frac{\{MR_3\}_o V_o}{\{MR_3\}_o V_o + \frac{K_{C_3}\{MR_3\}_A V_A}{\{R^-\}}}$$

substituting value of $\{R^-\}$ from (iii), we get

$$E = \frac{V_o P_C T_R}{V_o P_C T_R + V_A K_{C_3} \beta}$$

$$\therefore \frac{E}{1-E} = D = \frac{V_o P_C T_R}{V_A K_{C_3} \beta}$$

substituting $\beta = Q V_A$ and $T_R = C_R V_A$

$$D = \frac{V_o P_C C_R}{K_{C_3} Q V_A}$$

$$\text{or } \log D = \log \frac{V_o P_C C_R}{V_A K_{C_3}} - \log Q$$

$$\text{but } K_{C_3} = \frac{K_C}{K_{C_1} K_{C_2}}$$

$$\therefore \log D = \log \frac{V_o P_C C_R K_{C_1} K_{C_2}}{V_A K_C} - \log Q$$

Arranging in the form Y = mX + C, a plot of log D versus log Q gives a slope of unity. This signifies the degree of dissociation of the chelate in aqueous phase.

Similarly, a general form of equation is derived as follows:

$$\log D = \log \frac{P_C\, V_o C_R^x\, K_{C_1}\, K_{C_2} \cdots K_{C(m-x)}}{V_A K_C} - x \log Q$$

where x = degree of dissociation of the fully chelated species MR_m in aqueous phase.

Thus, for a monoligand species of the trivalent ion "MR^{2+}" the equation takes the form of

$$\log D = \log \frac{P_C\, V_o\, C_R^2\, K_{C_1}}{V_A K_C} - 2 \log Q$$

and for a monoligand species of the divalent ion "MR^{+}" it simplifies to

$$\log D = \log \frac{P_C V_o C_R K_{C_1}}{V_A K_C} - \log Q.$$

Table XV

Slopes and intercepts with errors of linear graphs of log extraction ratio versus pH or log Q for 8-quinolinol and 2-alkyl homologues.

Reagent	Intercept		Slope		$\overline{\mathrm{pH}}_{E=0.5}$	$\overline{\log Q}_{E=0.5}$
	vs pH	vs log Q	vs pH	vs log Q		
8-quinolinol	-2.42±0.14	6.39±0.04	0.89±0.05	-0.70±0.05	2.71±0.06	9.10±0.10
2-methyl-8-quinolinol	-2.31±0.11	5.44±0.53	0.80±0.04	-0.51±0.05	2.92±0.05	10.70±0.15
2-ethyl-8-quinolinol	-2.06±0.13	10.14±0.04	0.93±0.05	-0.90±0.04	2.21±0.06	11.25±0.05
2-*isopropyl*-8-quinolinol	-1.25±0.09	7.10±0.03	0.69±0.03	-0.62±0.03	1.83±0.05	11.41±0.06
2-*tert*-butyl-8-quinolinol	-0.40±0.07	7.10±0.37	0.51±0.03	-0.48±0.03	0.13±0.13	14.72±0.18

Table XVI (Contd)

Slopes and intercepts, with errors of linear graphs of log extraction ratio versus pH or log β for metal chelates of 8-quinolinol and 2-alkyl homologues.

Metal ion: Copper (11)	Intercept		Slope			
Chelating agent.	vs pH	vs log β	vs pH	vs log β	$\overline{pH}_{E = 0.5}$	$\overline{\log \beta}_{E = 0.5}$
8-quinolinol	-4.03±0.74	15.67± 1.95	2.16±0.36	-1.70±0.22	1.92±0.04	9.20±0.05
2-methyl-8-quinolinol	-4.46±0.62	8.97±1.56	1.37±0.17	-1.00±0.18	3.28±0.07	8.94±0.08
2-ethyl-8-quinolinol	-3.33±0.23	9.41±0.57	1.17±0.08	-0.98±0.06	2.83±0.06	9.62±0.07
2-*iso*propyl-8-quinolinol	-3.64±0.21	10.13±0.59	1.11±0.06	-1.13±0.07	3.27±0.05	8.95±0.05
2-*tert*-butyl-8-quinolinol	-2.74±0.16	8.33±0.83	0.76±0.05	-0.83±0.08	3.55±0.08	10.15±0.11

Table XVII (Contd)

Slopes and intercepts, with errors of linear graphs of log extraction ratio versus pH or log β for metal chelates of 8-quinolinol and 2-alkyl homologues.

<u>Metal ion: Nickel (11)</u>

Chelating agent	Intercept		Slope		-	-
	vs pH	vs log β	vs pH	vs log β	$pH_{E=0.5}$	$\log \beta_{E=0.5}$
8-quinolinol	-3.41±0.55	6.79±0.94	1.11±0.17	-0.90±0.12	3.07±0.11	7.52±0.12
2-methyl-8-quinolinol	-2.83±0.65	5.64±1.17	0.78±0.19	-0.65±0.13	3.52±0.18	8.69±0.20
2-ethyl-8-quinolinol	-	-	-	-	-	-
2-isopropyl-8-quinolinol	-1.47± 0.12	2.64±0.20	0.33±0.03	-0.34±0.02	4.26±0.18	7.81±0.14
2-*tert*-butyl-8-quinolinol	-3.2±0.50	7.84±1.42	0.81±0.15	-0.81±0.14	3.91±0.20	9.68±0.16

Table XVIII (Contd)

Slopes and intercepts with errors of linear graphs of log extraction ratio versus pH or log β for metal chelates of 8-quinolinol and 2-alkyl homologues.

Metal ion: Iron (111)

Chelating agent	Intercept		Slope			
	vs pH	vs log β	vs pH	vs log β	$\overline{pH}_{E=0.5}$	$\overline{\log\beta}_{E=0.5}$
8-quinolinol	-2.90±0.80	11.09±1.72	1.83±0.36	-1.14±0.20	1.73±0.11	9.51±0.18
2-methyl-8-quinolinol	-6.87±0.95	15.66±2.62	2.38±0.33	-1.65±0.28	2.89±0.05	9.47±0.09
2-ethyl-8-quinolinol	-2.84±0.24	7.61±0.99	1.06±0.10	-0.78±0.10	2.66±0.05	9.83±0.08
2-*isopropyl*-8-quinolinol	-2.74±0.37	10.78±1.31	1.18±0.15	-1.10±0.13	2.36±0.09	9.85±0.06
2-*tert*-butyl-8-quinolinol	-5.44±0.52	18.80±1.92	1.79±0.18	-1.78±0.18	3.04±0.04	10.57±0.04

(Contd)

Table XIX

Slopes and intercepts, with errors of linear graphs of log extraction ratio versus pH or log β for metal chelates of 8-quinolinol and 2-alkyl homologues.

Metal ion: Gallium (111)	Intercept		Slope		–	–
Chelating agent	vs pH	vs log β	vs pH	vs log β	$pH_{E=0.5}$	log $\beta_{E=0.5}$
8-quinolinol	-5.54±0.86	16.29±2.14	2.88±0.43	-1.77±0.24	1.93±0.05	9.19±0.08
2-methyl-8-quinolinol	-4.21±0.70	9.96±0.42	1.40±0.22	-1.07±0.05	3.03±0.11	9.29±0.05
2-ethyl-8-quinolinol	–	–	–	–	–	–
2-*isopropyl*-8-quinolinol	-4.06±0.48	14.11±2.24	1.67±0.22	-1.45±0.22	2.41±0.08	9.79±0.09
2-*tert*-butyl-8-quinolinol	-4.12±0.99	11.47±3.61	1.41±0.30	-1.08±0.35	2.96±0.18	10.49±0.29

Table XX (Contd)

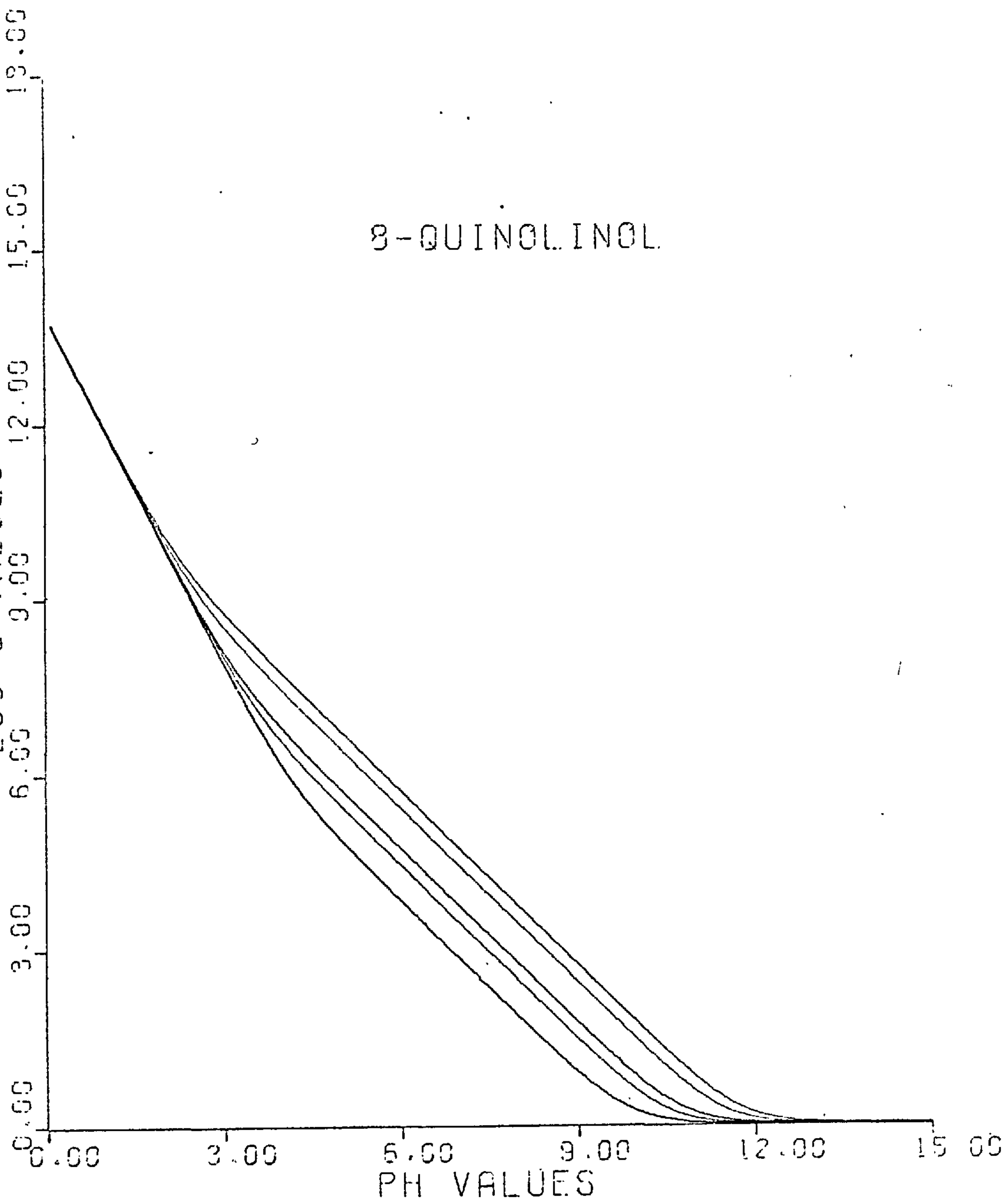
Slopes and intercepts, with errors of linear graphs of log extraction ratio versus pH or log β for metal chelates of 8-quinolinol and 2-alkyl homologues.

Metal ion: Indium (111)	Intercept		Slope		-	-
Chelating agent	vs pH	vs log β	vs pH	vs log β	$pH_{E=0.5}$	$\log \beta_{E=0.5}$
8-quinolinol	-2.92±0.38	4.74±0.37	0.82±0.12	-0.68±0.05	3.50±0.16	6.93±0.10
2-methyl-8-quinolinol	-3.80±0.43	7.96±0.98	1.10±0.12	-0.90±0.11	3.44±0.10	8.85±0.14
2-ethyl-8-quinolinol	-	-	-	-	-	-
2-isopropyl-8-quinolinol	-4.35±0.37	13.60±0.76	1.47±0.12	-1.47±0.08	2.96±0.05	9.23±0.04
2-tert-butyl-8-quinolinol	-2.39±0.39	7.35±1.07	0.72±0.11	-0.72±0.11	3.35±0.15	10.25±0.15

Graphs of

(i) log Q vs pH of 8-quinolinol and 2-alkyl homologues. at V_o/V_A = 1.0, 0.5, 0.1, 0.05 and 0.01

(ii) log extraction ratio vs log β or pH for 8-quinolinol chelates of copper (II), nickel (II) and iron (III) at V_o/V_A = 1.0, 0.5, 0.1 and 0.05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3.00
6.00
9.00
12.00
15.00
18.00
PH VALUES
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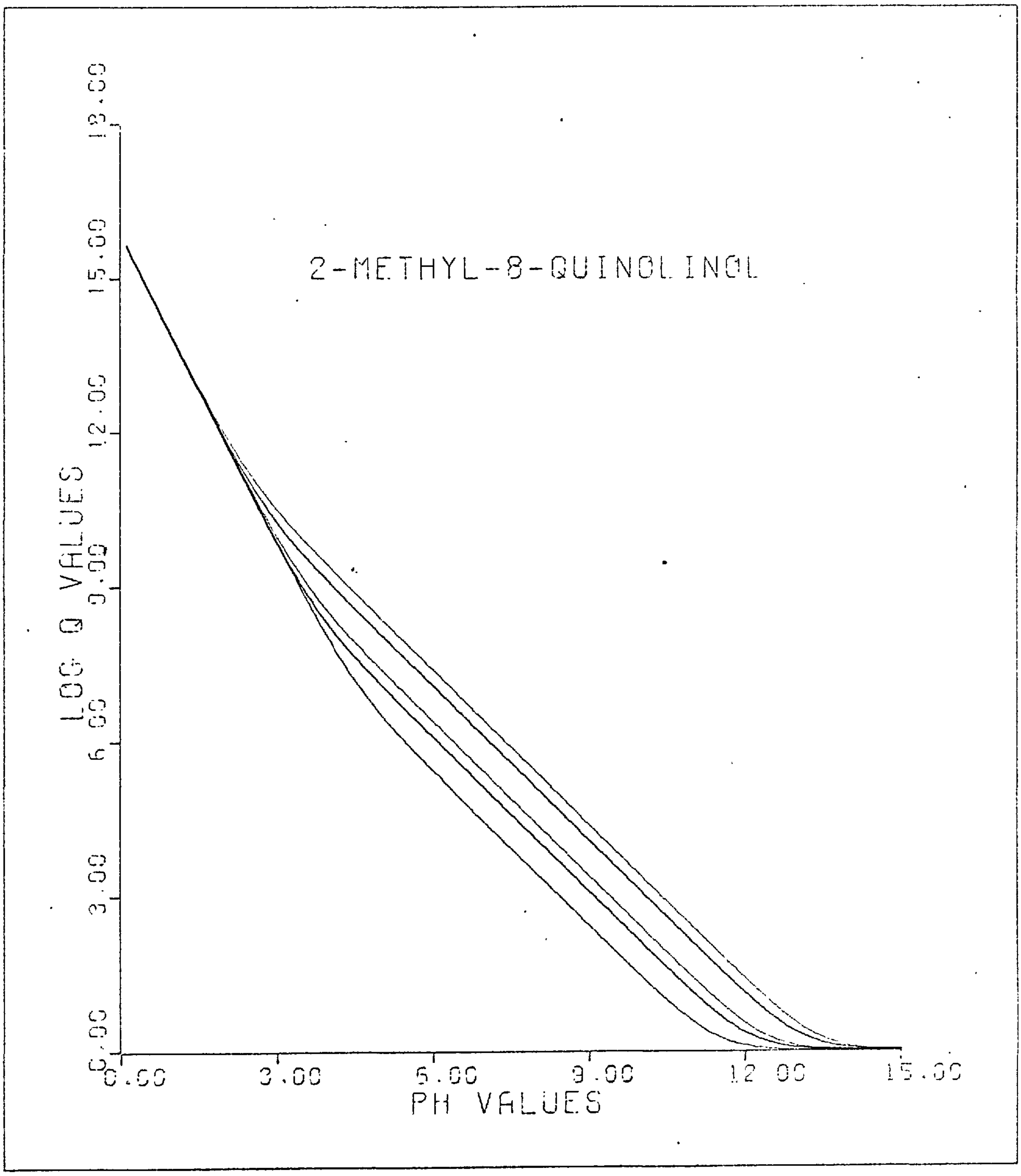
3.00
6.00
9.00
12.00
15.00


2-METHYL-8-QUINOLINOL
LOG Q VALUES
0.00
3.00
6.00
9.00
12.00
15.00
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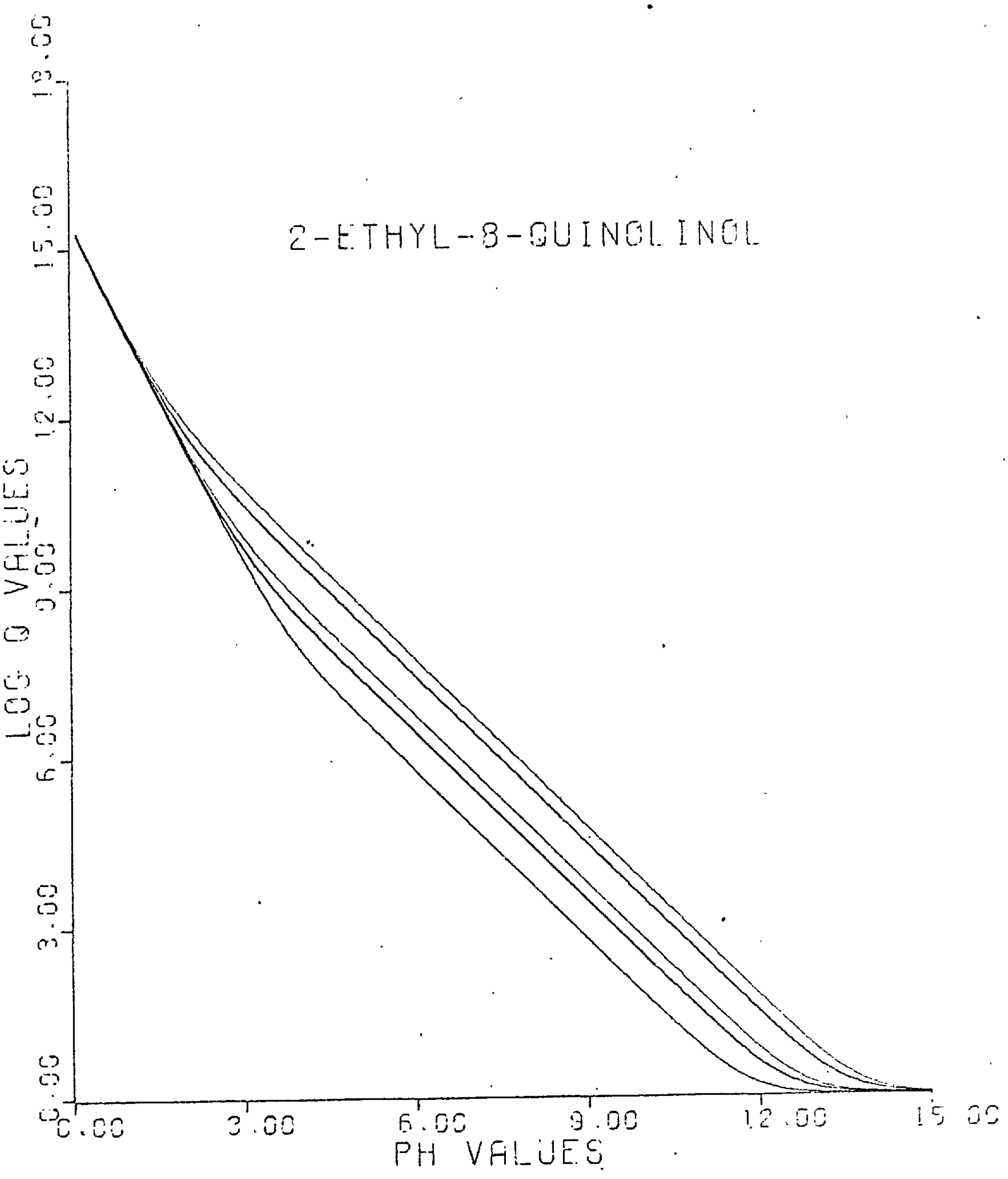
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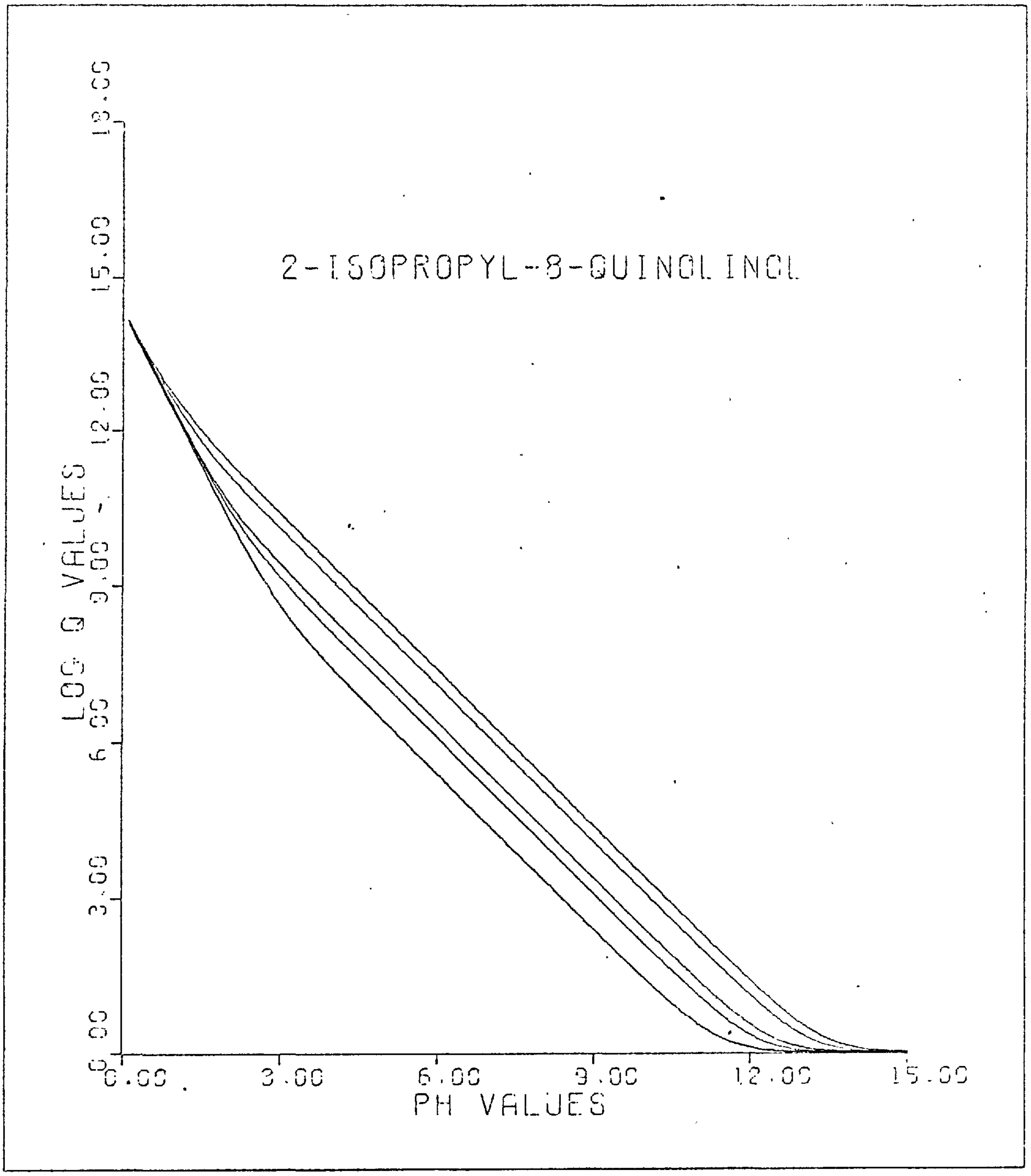
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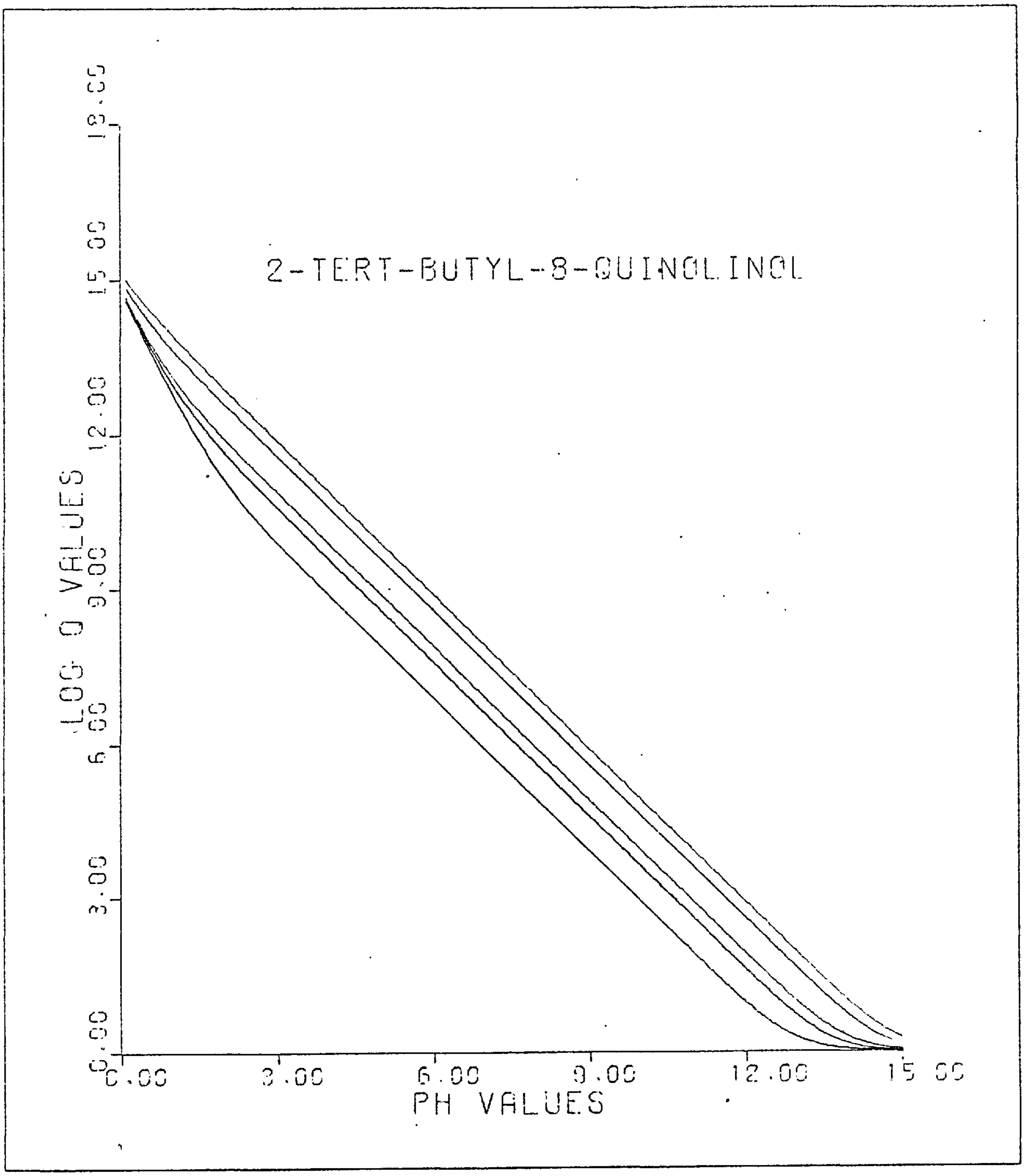
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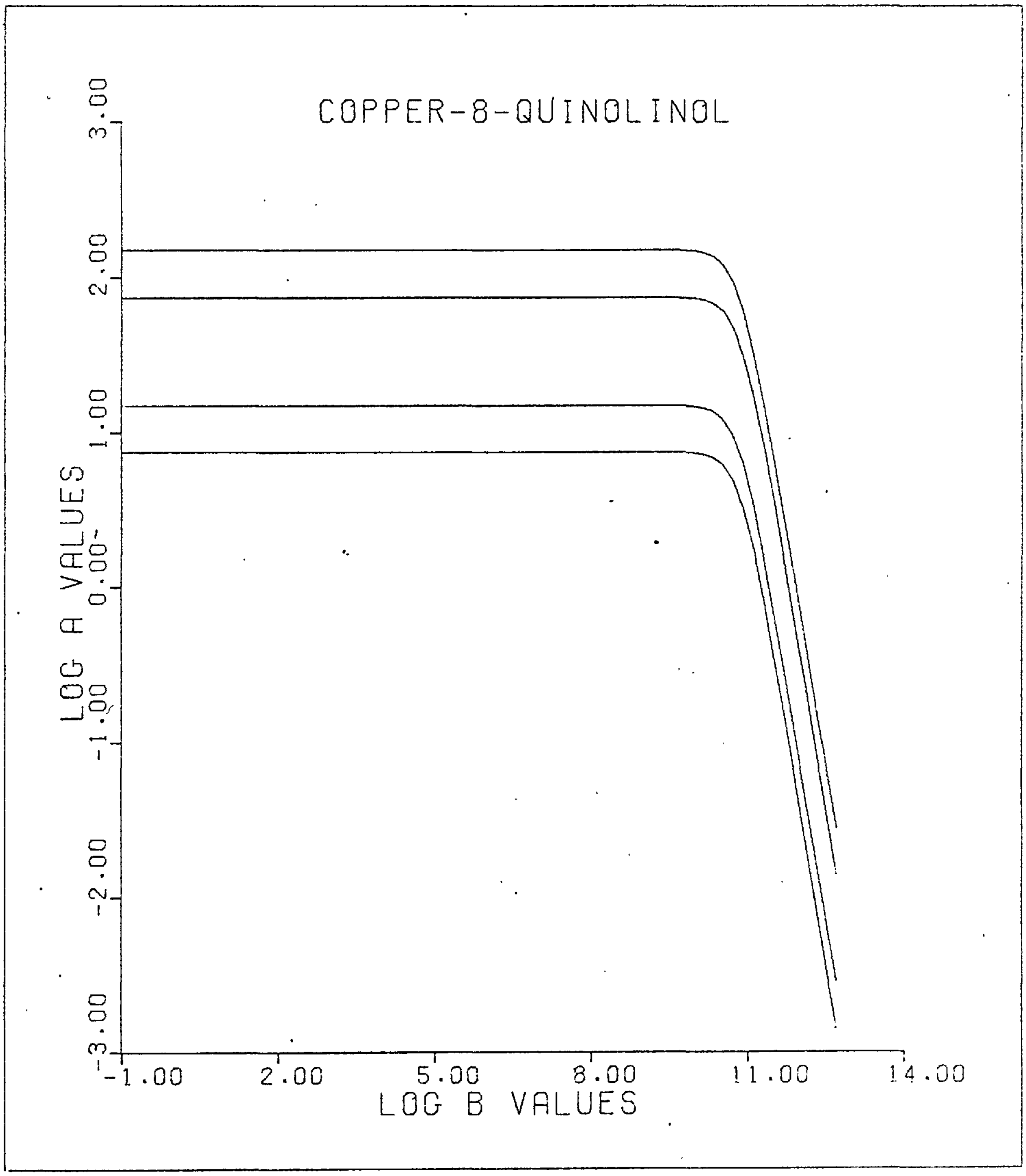
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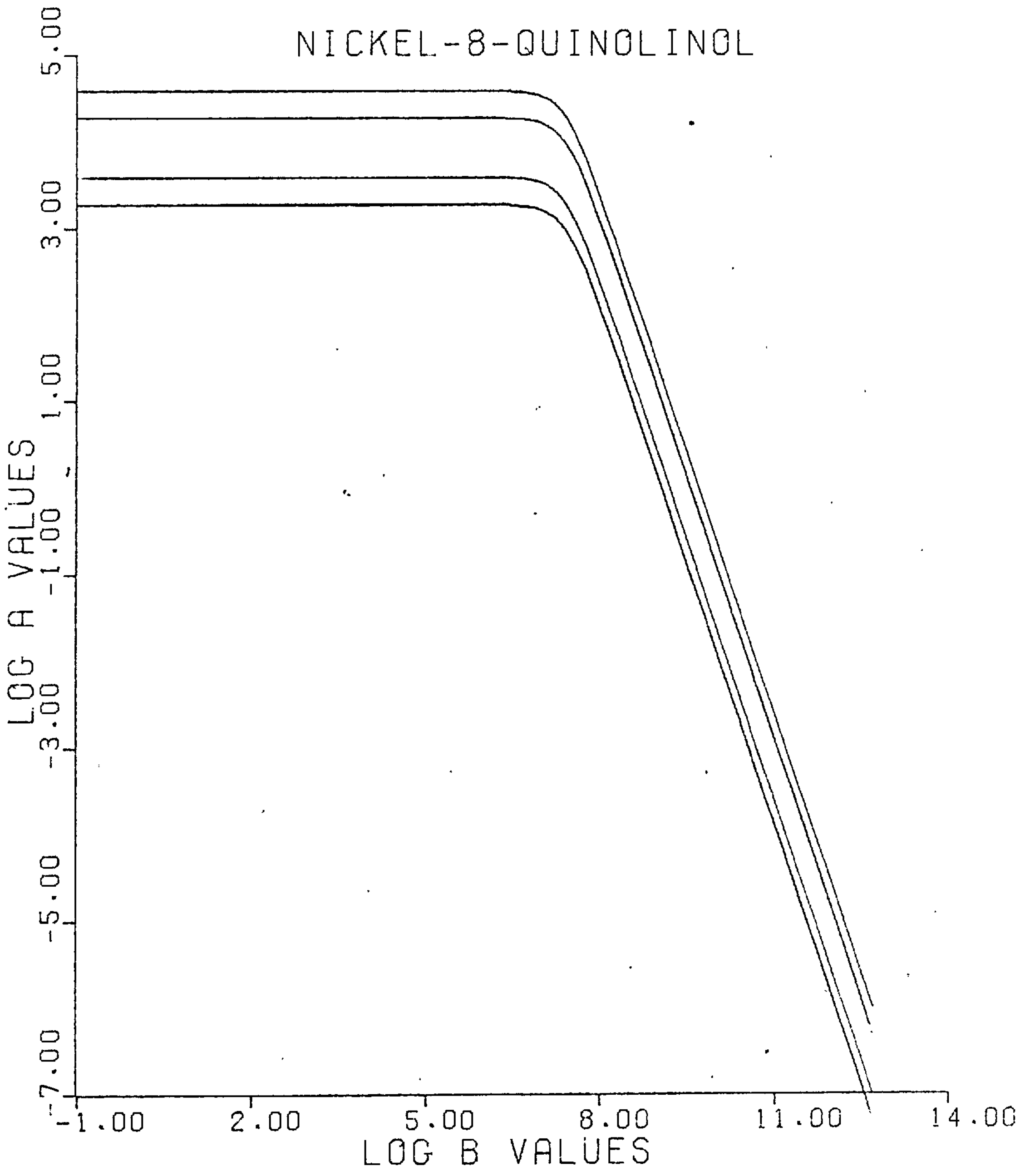
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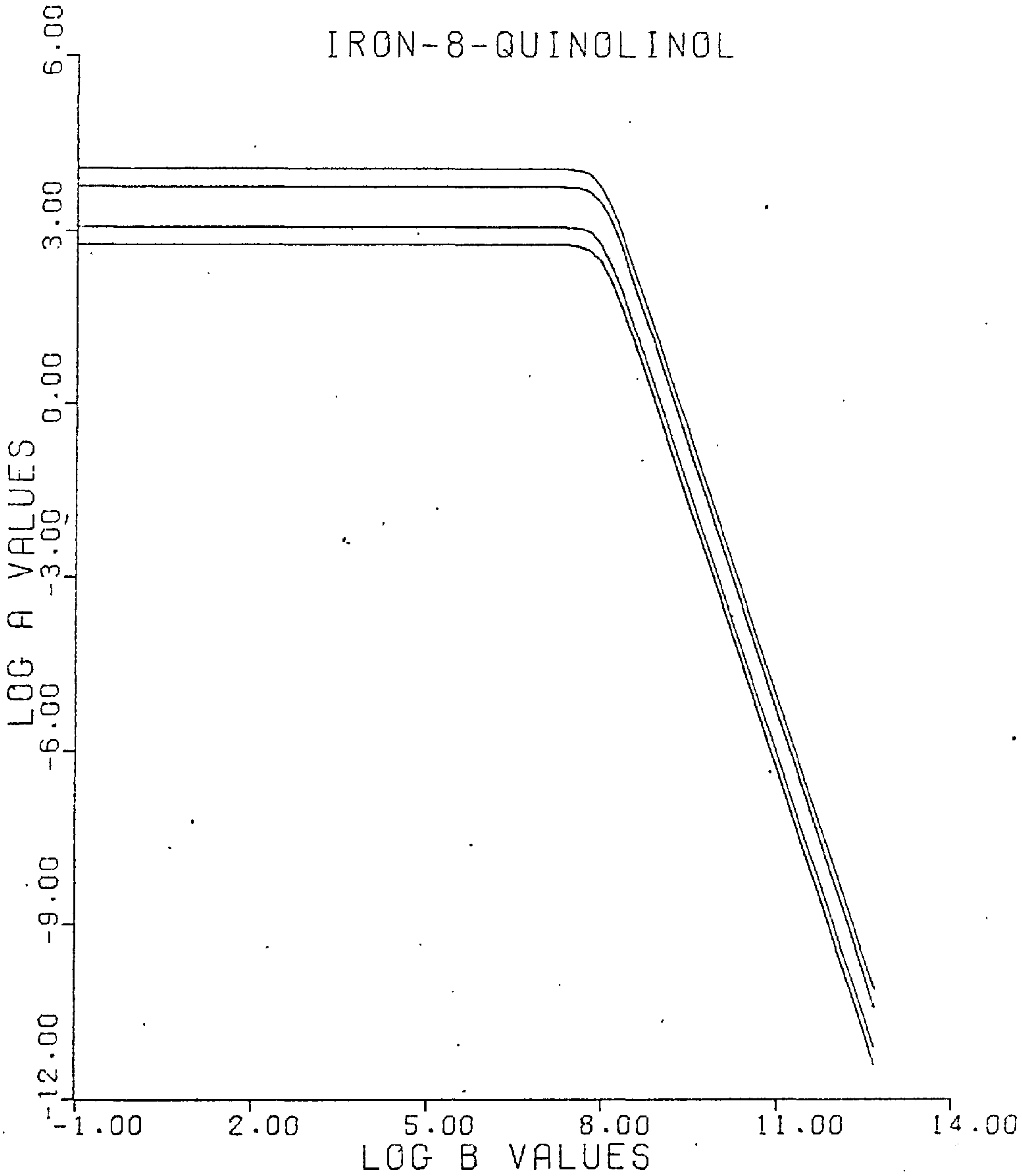
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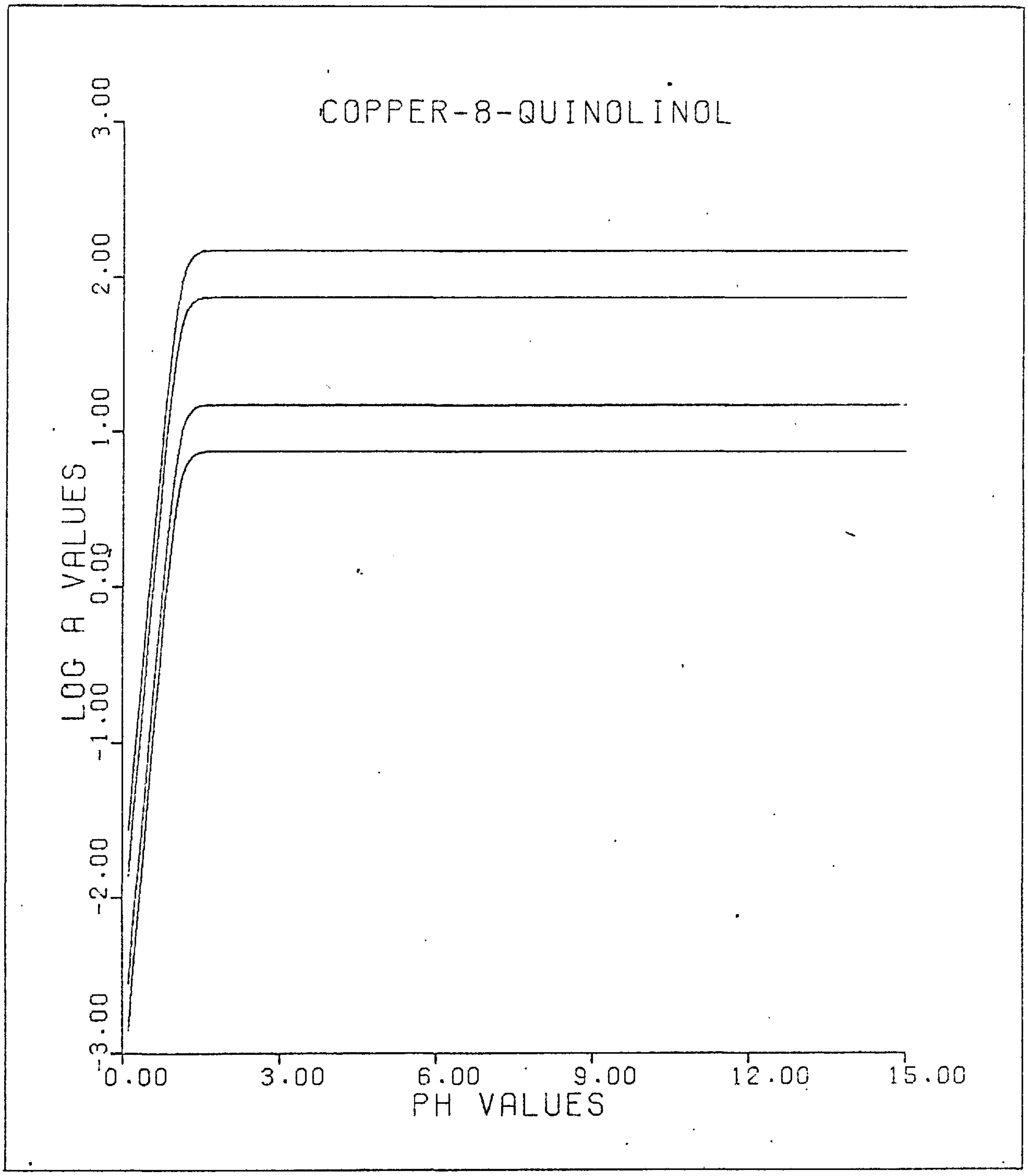
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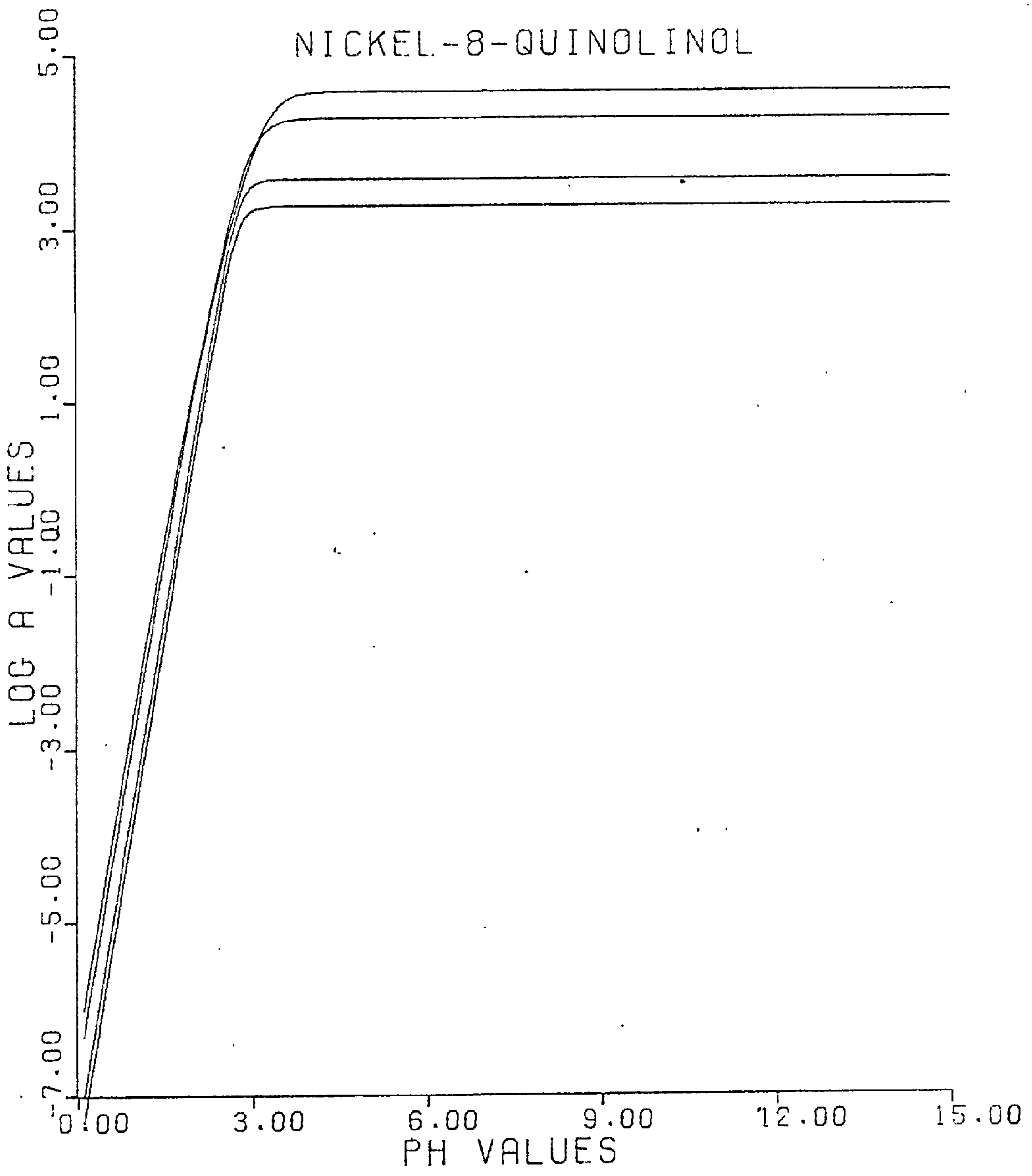
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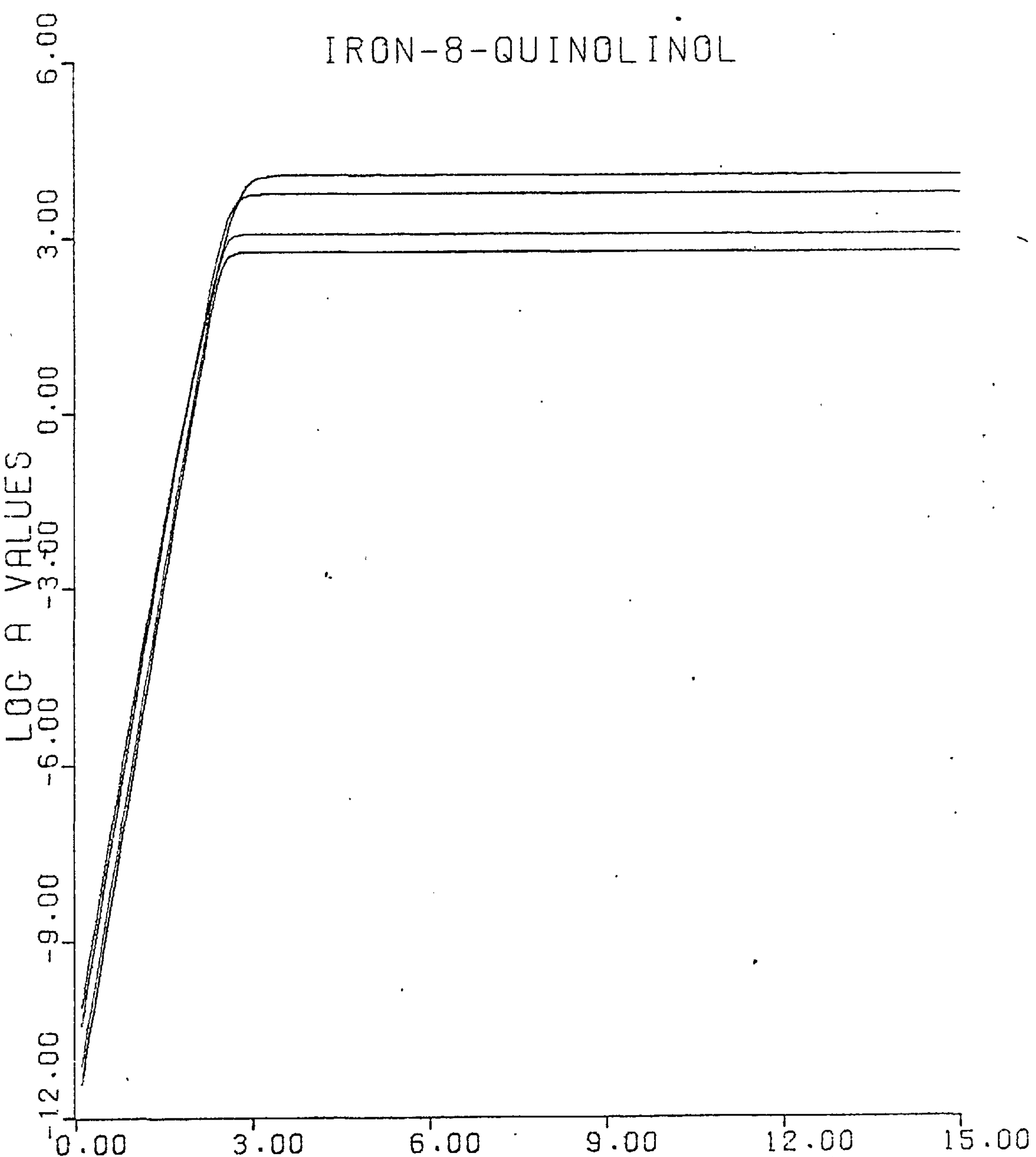
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9.00
12.00
15.00
PH VALUES

6.6.3 Calculation of the Stability Constants.

The stability constants of the chelates formed by copper (11), nickel (11), iron (111) gallium (111) and indium (111) with 8-quinolinol and its 2-alkyl homologues have been calculated using the extractability formula:

$$\log D = \log \frac{P_C V_o}{V_A K_C} - \log \left[\frac{1}{K_C} + \frac{\beta^m}{T_R^m} + \frac{\beta^{m-1}}{T_R^{m-1} K_{C_1}} + \frac{\beta^{m-2}}{T_R^{m-2} K_{C_1} K_{C_2}} + \ldots\ldots \right]$$

where D, P_C, T_R, β, V_o and V_A were obtained separately from experimental data and using values of m (valency) = 2 and 3 for divalent and trivalent metal ions respectively. The value of the slope obtained in practice for most of the metal chelate systems was unity, indicating that MR^+ and MR_2^+ species were predominant in the aqueous phase in the case of divalent and trivalent metal ions respectively. Therefore, the equation reduces to

$$\log D = \log \frac{P_C V_o}{V_A K_C} - \log \left[\frac{1}{K_C} + \frac{\beta^{m-1}}{K_{C_1} T_R^{m-1}} \right]$$

$$\text{and } \log D = \log \frac{P_C V_o}{V_A K_C} - \log \left[\frac{1}{K_C} + \frac{\beta^{m-2}}{K_{C_1} K_{C_2} T_R^{m-2}} \right]$$

for divalent and trivalent metal ions respectively. Thus, at log D = 0, the value of $K_{C_2} = \frac{K_C}{K_{C_1}}$ for metal chelates of divalent ions and $K_{C_3} = \frac{K_C}{K_{C_1} K_{C_2}}$ for trivalent ions have been calculated. However, the slope value of two obtained, particularly in the case of copper-8-quinolinol chelate, indicated that either the chelate may be considered to be fully dissociated in aqueous phase:

$$MR_2 \quad \overset{K_C}{\rightleftharpoons} \quad M^{2+} + 2R^-$$

or it may be due to association of the three ligand molecules with one cupric ion, which dissociated:

$$MR_3 \quad \overset{K_{C_2}\,K_{C_3}}{\rightleftharpoons} \quad MR^{2+} + 2R^-$$

The continuous variation experiment using cupric chloride and 8-quinolinol at pH = 4.0, in o-dichlorobenzene did not substantiate the latter view, although Haba[3] showed that the slope was 3 at high pH values. Therefore, it has been considered that sparingly water soluble $Cu(OX)_2$ dissociated fully in the aqueous phase and the relationship

$$\log D = \log \frac{P_C V_o}{V_A K_C} - \log \left\{ \frac{1}{K_C} + \frac{\beta^m}{T_R^m} \right\}$$

has been used to calculate K_C values of copper-8-quinolinol. A slope value of unity for the remaining copper-2-alkyl-8-quinolinol chelates was used. Therefore, $K_{C_2} = \frac{K_C}{K_{C_1}}$ values were calculated.

The K_C data has also been presented table XXI-XXV for the copper-2-alkyl homologue chelates assuming the full dissociation of the chelates in aqueous phase i.e. considering the slope value equal to oxidation state of the metals. However, the data so obtained may be considered only an exercise for comparison purposes. As it happens, the values turn out to be near the published[69] values of K_C, but little significance should be attributed to this. Similarly, most of the experimental values of the slopes for the chelate systems which were either slightly less or above unity have been employed to calculate stability data of the chelates. The K_C or K_C/P_C values so obtained, may be considered due to partial dissociation. This explains the presence of complex species predominant in aqueous phase with a single ligand residue in the chelate in the case of the divalent metal ions. But there is possibly a significant proportion of other M species e.g. M^{2+} or MR_2 depending on whether the slope is greater or less than unity.

However, a comparative data of the K_C or K_C/P_C values calculated on the basis of full dissociation, taking the slope value of unity as discussed above is given in table XXl-XXV.

The slope value of approximately unity in most of the cases substantiated the view that the species of the type $MR^{+}_{(m-1)}$ were predominant in aqueous phase. Hence, the data based on the slope value of unity has been considered to be valid and preferred for further calculations. Nevertheless, the experimental values of the slope of the log D versus log Q graphs is of interest. A glance at table XV-XX and at values given by Haba showed that considerable variation exists. Eventually this depends on the 8-quinolinol homologue, on the exact values of the pH ranges of extraction and on other conditions of experimentation. With the hindsight of many experiments it has become clear that experimental slopes of exactly integral values of one or perhaps two could be guaranteed by suitable choice of test conditions. Under these circumstances better values of stability constants of individual species could have been obtained. Although this is a criticism of the present work and that of Haba, it should be realised that differences from values given in Table XX1-XXV will be small since it seems that use of experimental slopes or their nearest integral values leads to actually the same results in most cases. In any case, the values are adequate for analytical application.

Also, taking into consideration the identical solvent extraction properties of the chelates of different metals with similar oxidation state and other physical properties, some empirical relationships[75-80] have been used to predict some stability constants or K_C/P_C ratios. For example,

$$\frac{\log K\,(MR'_2)}{\log K\,(MR''_2)} = \frac{\log K\,(M'R'_2)}{\log K\,(M'R''_2)} = \frac{\log K\,(M''R'_2)}{\log K\,(M''R''_2)}$$

Similarly $$\frac{P_C(MR'_2)}{P_C(MR''_2)} = \frac{P_C(M'R'_2)}{P_C(M'R''_2)} = \frac{P_C(M''R'_2)}{P_C(M''R''_2)}$$

where M, M', M'' etc. represent different metal ions and R', R'' .... etc. represent 8-quinolinol and 2-alkyl homologues along the series $-H \longrightarrow -CH_3 \longrightarrow -C_2H_5 \longrightarrow -CH(CH_3)_2 \longrightarrow -C(CH_3)_3$.

The calculated K_C and K_C/P_C values have been found to be in agreement with those reported by Haba[3]. The method seemed reasonable to be adopted in the absence of detailed experimental data of each metal chelate studied. The results have been given in table XX1-XXV.

Table XXI

Stability constants and K_C/P_C data for metal chelates of 8-quinolinol and 2-alkyl homologues. (Figures in parentheses indicate predicted values)

Chelating agent: 8-quinolinol

Metal ion	Slope*			Species in aqueous phase	$-\log K_C$	$-\log K_{C_2}$	$-\log K_{C_3}$	K_C/P_C	K_{C_2}/P_C	K_{C_3}/P_C
	I	II	III							
Copper (II)	2	-	-	M^{2+}	23.5			2.3×10^{-26}		
		2		M^{2+}	23.5			2.3×10^{-26}		
			1.7	M^{2+}	19.6			1.7×10^{-22}		
Nickel (II)	2			M^{2+}	(16.8)			6.0×10^{-20}		
		1		MR^{+}		(7.3)			1.7×10^{-10}	
			0.9	MR^{+}		(6.3)			1.5×10^{-9}	
Iron (III)	3			M^{3+}	(35.1)			6.4×10^{-40}		
		1		MR_2^{+}			9.2			5.4×10^{-14}
			1.14	MR_2^{+}			11.2			1.9×10^{-15}
Indium (III)	3			M^{3+}				1.2×10^{-27}		
		1		MR_2^{+}						6.7×10^{-10}
			0.68	MR_2^{+}						4.5×10^{-7}
Gallium (III)	3			M^{3+}				2.0×10^{-34}		
		2		MR^{2+}					2.7×10^{-23}	
			1.77	MR^{2+}					1.0×10^{-20}	

*I = oxidation state of the metal ion

II = experimental slope value rounded to the nearest whole number

III = experimental slope value.

Table XXII

Stability constants and K_C/P_C data of metal chelates. (Contd)

Chelating agent: 2-methyl-8-quinolinol

Metal ion	Slope I	Slope II	Slope III	Species in aqueous phase	$-\log K_C$	$-\log K_{C_2}$	$-\log K_{C_3}$	K_C/P_C	K_{C_2}/P_C	K_{C_3}/P_C
Copper (II)	2			M^{2+}	21.1			$7.0\text{x}10^{-26}$		
		1		MR^+		8.7			$1.9\text{x}10^{-13}$	
			1	MR^+	8.8				$1.9\text{x}10^{-13}$	
Nickel (II)	2			M^{2+}	(17.3)			$2.4\text{x}10^{-22}$		
		1		MR^+		(6.7)			$1.1\text{x}10^{-11}$	
			0.65	MR^+		(2.9)			$5.9\text{x}10^{-8}$	
Iron (III)	3			M^{3+}				$6.3\text{x}10^{-41}$		
		2		MR^{2+}					$5.1\text{x}10^{-26}$	
			1.65	MR^{2+}					$2.1\text{x}10^{-22}$	
Indium (III)	3			M^{3+}				$1.6\text{x}10^{-33}$		
		1		MR_2^+						$7.4\text{x}10^{-12}$
			0.9	MR_2^+						$9.0\text{x}10^{-11}$
Gallium (III)	3			M^{3+}				$7.7\text{x}10^{-35}$		
		1		MR_2^+						$2.7\text{x}10^{-12}$
			1.07	MR_2^+						$4.4\text{x}10^{-13}$

Table XXIII

Stability constants and K_C/P_C data of metal chelates. (Contd.)

Chelating agent: 2-ethyl-8-quinolinol.

Metal ion	Slope I	Slope II	Slope III	Species in aqueous phase.	$-\log K_C$	$-\log K_{C_2}$	$-\log K_{C_3}$	K_C/P_C	K_{C_2}/P_C	K_{C_3}/P_C
Copper (II)	2			M^{2+}	22.9			2.4×10^{-27}		
		1		MR^+		9.7			3.7×10^{-14}	
			0.98	MR^+		9.5			6.4×10^{-13}	
Iron (III)	3			M^{3+}				7.7×10^{-41}		
		1		MR_2^+						2.1×10^{-13}
			0.78	MR_2^+						1.9×10^{-11}

Table XXIV

Stability constants and K_C/P_C data of metal chelates. (Contd).

Chelating agent: 2-isopropyl-8-quinolinol.

Metal ion	Slope I	Slope II	Slope III	Species in aqueous phase.	$-\log K_C$	$-\log K_{C_2}$	$-\log K_{C_3}$	K_C/P_C	K_{C_2}/P_C	K_{C_3}/P_C
Copper (II)	2			M^{2+}	20.3			$4.5x10^{-26}$		
		1		MR^+		7.8			$1.4x10^{-13}$	
			1.1	MR^+		9.4			$3.5x10^{-15}$	
Nickel (11)	2			M^{2+}	(14.6)			$9.9x10^{-20}$		
		1		MR^+		(4.8)			$7.1x10^{-11}$	
			0.34	MR^+					$2.3x10^{-6}$	
Iron (III)	3			M^{3+}				$2.6x10^{-41}$		
		1		MR_2^+						$1.9x10^{-14}$
			1.1	MR_2^+						$8.6x10^{-15}$
Indium (III)	3			M^{3+}				$1.6x10^{-33}$		
		1		MR_2^+						$7.4x10^{-12}$
			1.47	MR_2^+						$9.7x10^{-18}$
Gallium (III)	3			M^{3+}				$1.5x10^{-36}$		
		1		MR_2^+						$7.2x10^{-13}$
			1.45	MR_2^+						$3.4x10^{-18}$

Table XXV

Stability constants and K_C/P_C data of metal chelates (Contd).

Chelating agent: 2-tert-butyl-8-quinolinol.

Metal ion	Slope			Species in aqueous phase	$-\log K_C$	$-\log K_{C_2}$	$-\log K_{C_3}$	K_C/P_C	K_{C_2}/P_C	K_{C_3}/P_C
	I	II	III							
Copper (II)	2			M^{2+}	(22.9)			$4.5x10^{-26}$		
		1		MR^+		8.9			$1.8x10^{-14}$	
			0.83	MR^+		6.7			$2.7x10^{-12}$	
Nickel (II)	2			M^{2+}	(18.6)			$1.5x10^{-24}$		
		1		MR^+		(7.8)			$8.6x10^{-13}$	
			0.81	MR^+		(4.6)			$1.5x10^{-10}$	
Iron (III)	3			M^{3+}				$1.6x10^{-42}$		
		2		MR^{2+}					$2.9x10^{-29}$	
			1.78	MR^{2+}					$2.5x10^{-26}$	
Indium (III)	3			M^{3+}				$5.4x10^{-38}$		
		1		MR_2^+						$2.4x10^{-13}$
			0.72	MR_2^+						$6.6x10^{-10}$
Gallium (III)	3			M^{3+}				$9.2x10^{-39}$		
		1		MR_2^+						$1.3x10^{-13}$
			1.08	MR_2^+						$1.3x10^{-14}$

6.6.4 Influence of steric and inductive effects

It has been noted that the pK_{R_1} and pK_{R_2} values of the reagents along the series $-H \longrightarrow -CH_3 \longrightarrow -C_2H_5 \longrightarrow -CH(CH_3)_2 \longrightarrow -C(CH_3)_3$ are affected due to the steric[84] and inductive effects operating in the ligand molecules Fig V This also affects the formation of the metal chelates. For example, the inductive effect due to the increased number of methyl groups at the 2-position increases the electron density of nitrogen atom and in turn of oxygen by transmission of the effect through the aromatic ring system. This increases the bonding character of the oxygen and nitrogen atoms with hydrogen as well as cations of the metals[85,86]. Therefore, the release of the phenolic protons decreases along the series due to 2 - alkylation. But the co-ordination bond-forming capacity of the nitrogen with metal ions increases correspondingly.

Similarly, for the same metal ion, the steric hindrance along the series is of the order of tert-butyl- > isopropyl- > ethyl- > methyl > unsubstituted. But this decrease is not necessarily regular. Also, the chelates of trivalent metal ions were obtained with 8 - quinolinol and the 2-alkyl homologues except 2-tert-butyl homologue. This could be explained taking into consideration arbitrary values of the inductive and steric effects Fig III-IV. The former increased steadily from zero to two in case of unsubstituted to 2-tert-butyl homologue respectively.

However, it is suggested that the steric effect increases sharply in moving from zero at 8-quinolinol to importance at 2-methyl - 8 - quinolinol, but then shows no change sgnificantly untill there is another sharp rise at the 2-tert-butyl homologue. This is evidenced by non-formation of aluminium (III) 2-methyl - 8 - quinolinol chelate and by metal (III) 2-tert-butyl-8-quinolinol chelates.

The increased steric effect in the 2-tert-butyl homologue, may also be explained by the fact that upto 2-isopropyl -8-quinolinol homologue, the rotation of an alkyl group along the single bond was possible to allow three ligand molecules to pack around trivalent cations except aluminium (III) i.e. only those trivalent cations whose ionic radii are greater than 0.5°A. But in the case of bulky tert-butyl group in 2-position of the ligand, the rotation would be restricted due to bulkiness of the group and steric repulsion of the protons of the three adjacent methyl groups. These effects can be elegantly and clearly understood by use of atomic models. Therefore, in the case of the trivalent metal ions an octahedral chelate may be formed with unfavourable disposition of the organic ligands around the metal ion. To acquire a strain free structure, it may break up into charged complexes in aqueous solutions.

The results show an abnormal shift in $pH_E = 1.00$ values in the case of the metal chelates of 2-methyl- and 2-tert-butyl homologues. In the former case increase of inductive effect from zero to 0.5 (arbitrary units) due to replacement of 2-hydrogen atom by a methyl group occurs. Simaltenously the steric effect due to methyl group also comes into operation in the molecule. The inductive and steric effects operating in the molecule oppose each other. For example, the inductive effect increases bond-forming capacity of nitrogen and oxygen atoms as described above, but the steric effect prevents octahedral packing of the three ligand residues around a trivalent metal ion. The latter effect is predominant. This is clear from the fact that aluminium (III) with ionic radius 0.5 Å does not react with the 2-methyl homologue. Even in the case of other trivalent metal ions with greater ionic radii, the tren towards lower stability of the chelates confirmed the above view. Similarly, in case of 2-tert-butyl homologue the increase in inductive effect is equal to 0.5 when 2-isopropyl group is replaced by 2-tert-butyl group in the 8-quinolinol. But the steric effect increases sharply as confirmed from non-precipitation of chelates of all the trivalent metal ions which under similar conditions reacted with the rest of the 2-alkyl homologues. Such increase in magnitude of steric effect was also expected from stereochemical point of view. The fig II-IV explain diagrammatically operation of inductive and steric effects in the ligand molecules. Although an arbitrary scale has been chosen to correlate the two effects, it is satisfactory to describe qualitatively the predominance of the steric effect in case of the 2-tert-butyl homologue. This explains further that the formation of chelates depends simaltaneously on the properties of the ligands and the metal ions used. For example, the free energy of formation of a chelate between a metal ion and an organic ligand may be expressed by the relationship[81,82]:

$$-\ \Delta G = \frac{m}{r} \times \text{constant}$$

where r = crystal radius of the metal ion

m = valency

Therefore, it may be reasonable to mention that it is extremely difficult to describe quantitatively the magnitude to which any individual factor affects the chelate formation and solvent extraction work. However, a rational qualitative argument as presented above is likely to explain the behaviour of the ligands and metal chelates and help to interpret the physicochemical data obtained experimentally.

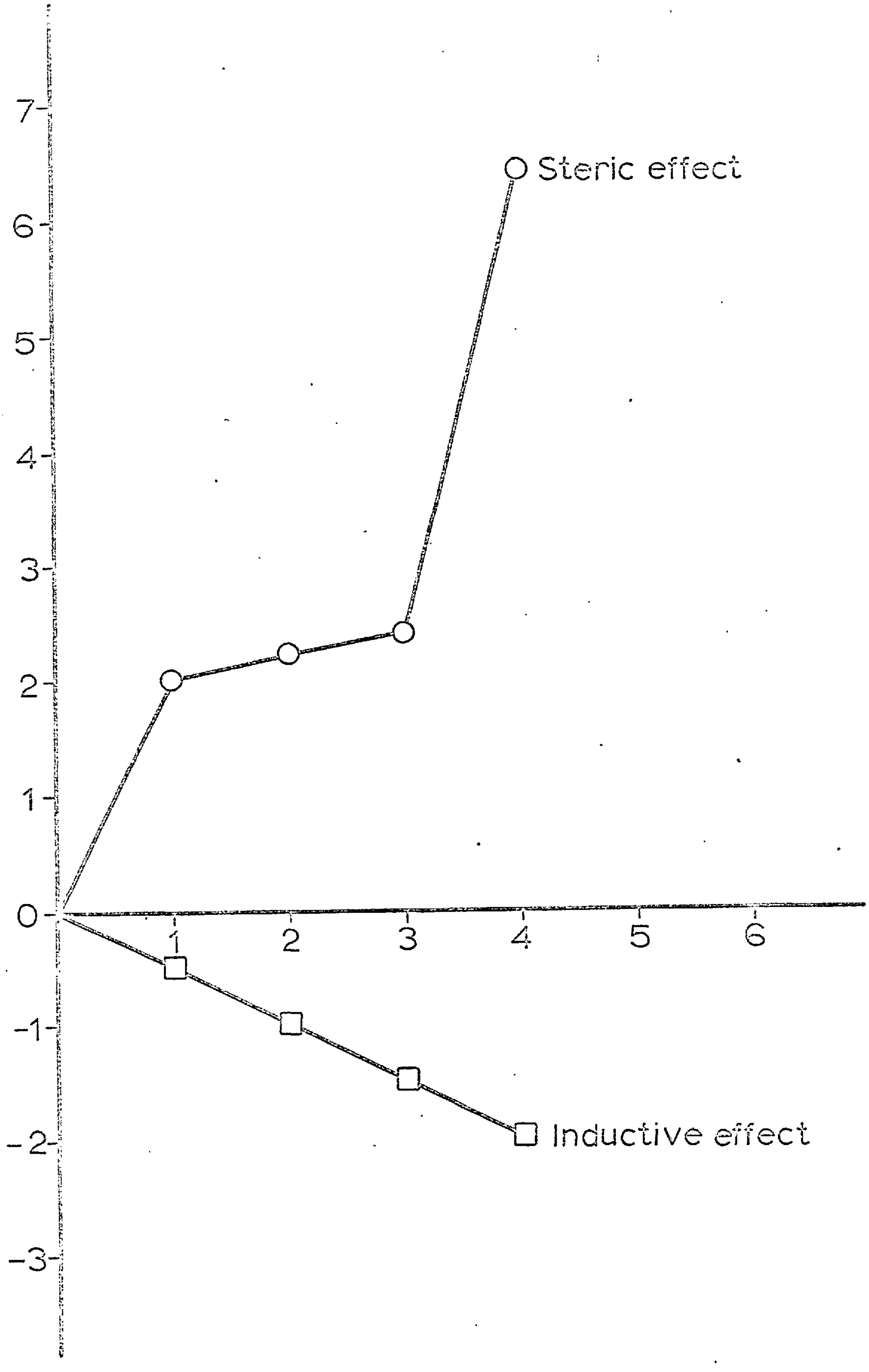

Fig. III ——No. of C-atoms in 2-substituent——→

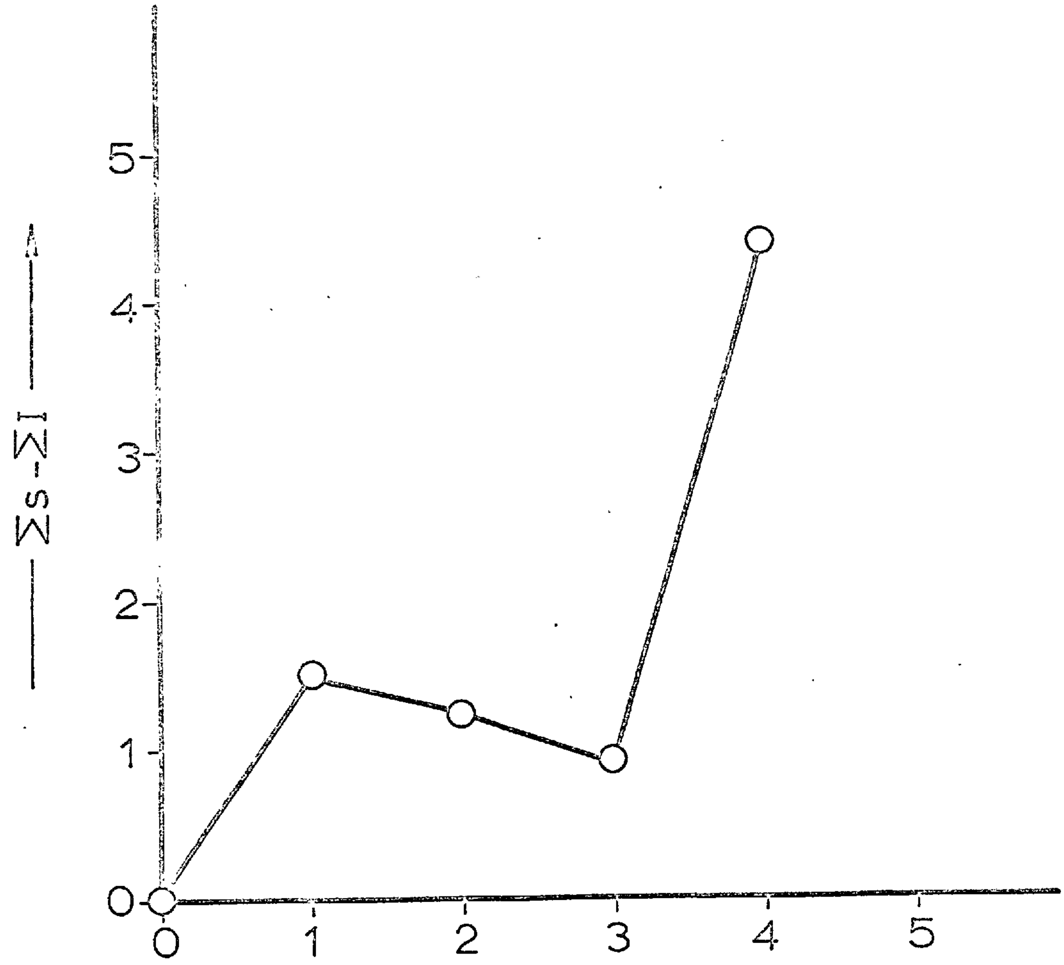

Fig. IV —No. of C-atoms in 2-substituent——→

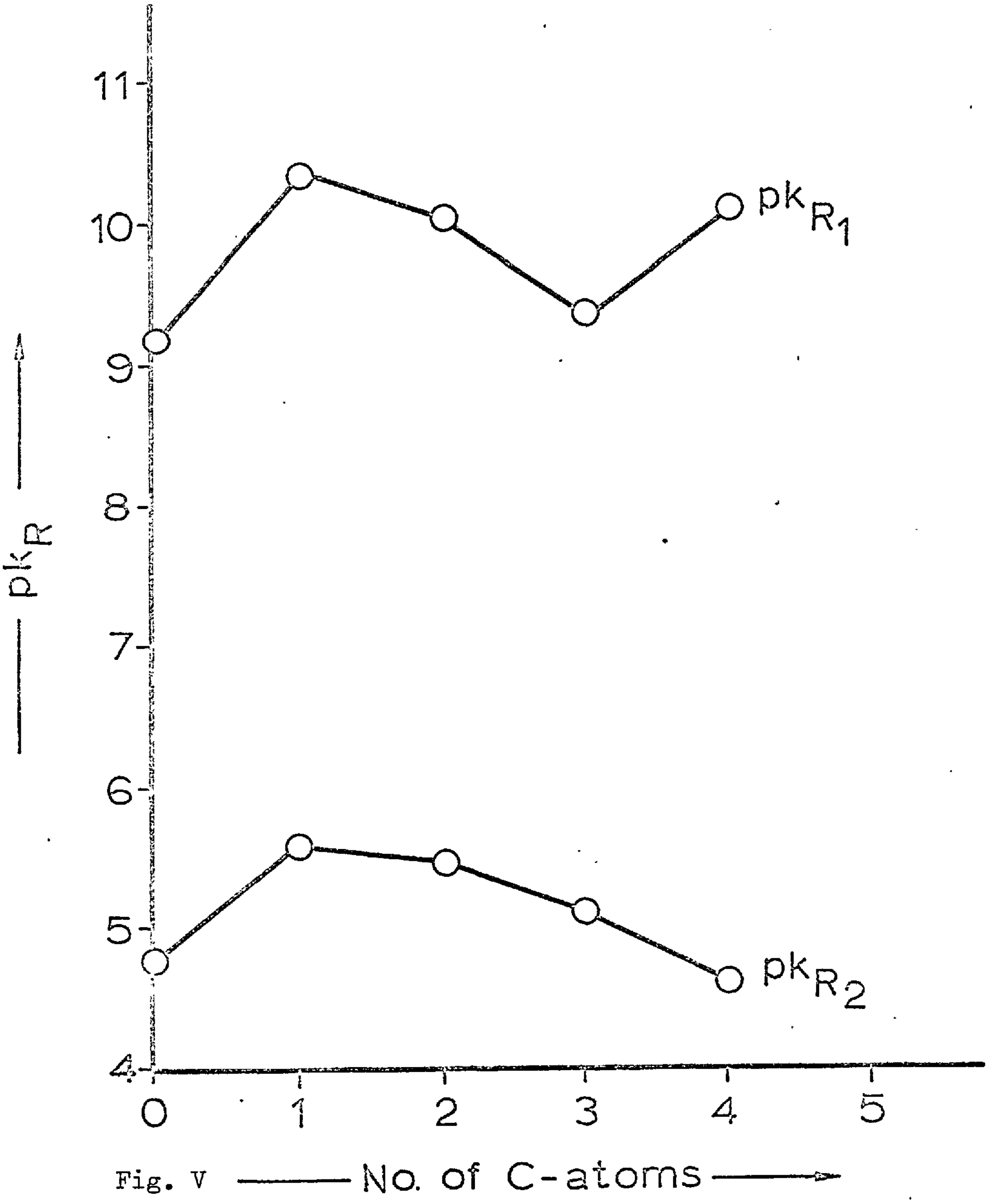

Fig. V

6.6.5 Separation of mixtures.

An investigation of the estimation of aluminium content of the permanent magnet alloy BCS 233 using the 2-isopropyl- and 2-tert-butyl-8-quinolinols was carried out.

Use of o-dichlorobenzene as solvent and adaptation of equilibrium conditions as described by Haba[3] gave high results. This showed that the interfering metals, especially, nickel were not removed quantitatively from the mixture under the analytical conditions used. o-Dichlorobenzene was employed in phase equilibrium studies due to low dielectric constant, low volatility and high immiscibility with water. This helped extraction of fully chelated metal chelate from aqueous solutions, eliminated extraction of ion pairs of the type $MR^{x+}_{(m-x)}(ClO_4^-)_x$ in the organic phase and maintained constant ionic strength in two phases. However, the slow attainment of equilibrium, for which allowance was made in the physico-chemical studies, was the main disadvantage which prevented adoption of o-dichlorobenzene in solvent extraction work for analytical purposes.

CHAPTER SEVEN

7. Conclusions.

The project as described in this thesis was consolidation and extension of an earlier novel approach to chelate solvent extraction[3]. The principle aim was to synthesise 2-ethyl-, 2-*iso*propyl- , and 2-*tert*-butyl-8-quinolinol reagents in efficient yields, to study their solvent extraction properties and to test the validity of the extraction equilibria relationships.

These aims have largely been achieved as summarized below:

(i) The synthesis of all the required reagents was successfully accomplished by direct condensation of 8-quinolinol and appropriate lithium alkyl. The method used was simple and economical. The yield of the products ranged from 30 to 50%. The 2-ethyl- and 2-*iso*propyl homologues were identified with those prepared by Haba[3]. Also, an extensive study of the physical properties, relative to structure and for identification and analytical purposes, of all the 8-quinolinols was carried out using instrumental techniques. These included ultraviolet, infrared and mass spectroscopy, proton magnetic resonance, X-ray powder diffraction and electron spectroscopy for chemical analysis, "ESCA". The chelates of a wide selection of metals with the five quinolinols were prepared. Additional parameters such as dissociation and protonation constants and solubility ratio of the quinolinols and their metal chelates were also determined experimentally.

The cumulative physicochemical data so obtained have been used to estimate the operation of steric hindrance and inductive effects due to 2-alkylation in the quinolinols. It has been concluded that a quantitative interpretation of the above mentioned effects is not possible due to significant contributions by other factors due to metal ion used. However, the experimental data such as dissociation and protonation of the reagents and $pH_{E=1.00}$ for extraction of the metal chelates have been correlated with increased inductive and steric effects with introduction of bulky alkyl group in the 2-position of the 8-quinolinol, becoming a maximum in case of 2-tert-butyl homologue. For example, 2-tert-butyl homologue did not react with any tried trivalent metal ions to give insoluble chelates of stiochiometric composition. The difficulty of arranging around a trivalent metal ion of small ionic radius, three ligand residues with 2-tert-butyl group, to obtain a strain-free octahedral chelate has been considered the main factor in this situation, overriding all other effects whether related to ligand molecule or metal ion. However, the precipitation of chelates of similar trivalent metal ions, using the rest of the 2-alkyl homologues has been considered due to possible rotation of an alkyl group along the single bond so as to allow three ligand molecules to pack around the cation.

A remarkable feature of alternation, instead of gradation of some physical properties such as, m.p. of the reagents and P_C values of the corresponding copper chelates has been noted. Obviously, these affect the overall equilibrium data. Therefore, generalization of the experimental results and their extension to other systems could not be done. However, some empirical relationships have been used with caution to calculate K_C and P_C data of some chelates.

(ii) At the latter stage, the phase equilibrium relationships derived by Haba[3] were extended, introducing two new parameters, β and Q both of which are functions of pH. Also, the equations have been refined by considering activities and activity coefficients of the ions in aqueous phase. It has also been shown that in phase equilibria studies, involving transfer of molecular species from aqueous into organic phase at constant ionic strength, the activities could be replaced by concentrations without significant effect on the treatment of the results. Hence, simpler equations could be used. To test the validity of equilibria relationships, a detailed and comparative solvent extraction work was carried out using the five quinolinols and copper (11), nickel (11), iron (111), gallium (111) and indium (111) metal ions. These studies were carried out at $25 \pm 0.1^{\circ}C$ and in o-dichlorobenzene, a nonvolatile, highly water-immiscible and low dielectric constant solvent, to resolve fine differences in the phase equilibrium studies. Also, most of the other parameters, used in the equilibrium equations were determined by separate experimentation. The best values of the parameters were obtained by statistical analysis and used in subsequent calculations of stability data of the metal chelates. The results have been compared with those obtained by other workers and found in good agreement. The slope value of approximately unity in most of the experimental data indicated that the predominant species in aqueous phase were of the type $MR^{+}_{(m-1)}$. Hence, the equilibria relationships as derived have been found valid. It has been established that the species extracted into the organic phase is the fully chelated species and not a mixed chelate.

(iii) A detailed and comparative data of K_C and K_C/P_C values was compiled for the metal chelates, where the slope value was

(a) equal to oxidation state of the metal ion,

(b) the experimental slope value and

(c) the latter value rounded to nearest whole number.

However, the slope of unity has been preferred and the best calculations are based on it, thus considering predominance of $MR^{+}_{(m-1)}$ species in the aqueous phase.

(iv) The K_C or K_C/P_C data showed that the metal chelates of lower stability were produced with higher 2-alkylated-8-quinolinols. For example, a monoligand species of iron-2-tert-butyl-8-quinolinol chelate was predominant in aqueous phase. Similarly, in case of gallium, K_{C_3}/P_C for 2-isopropyl- and 2-tert-butyl-homologues were 3.4×10^{-18} and 1.3×10^{-14} respectively, which confirmed the trend towards lower stability of the chelates along the series $-H \longrightarrow -CH_3 \longrightarrow -C_2H_5 \longrightarrow -CH(CH_3)_2 \longrightarrow -C(CH_3)_3$. However, the differences in the stability of the chelates of the same metal ions along the series were smaller in magnitude than expected. In general, from the solvent extraction and gravimetric work it has been concluded that the specificity of the reagents has not improved. However, in gravimetric work, the 2-tert-butyl homologue showed greater selectivity as it did not react with most of the trivalent metal ions.

Also, the solvent extraction data predicted that the desired value of unity for the slope could be obtained by fixing the extraction parameters like T_R and pH. For example, by decreasing reagent: metal concentration ratio from 300:1 to 100: 1 and working at low pH ranges, the slope value was nearly halved. This also proved that a large excess of the reagent caused physical interference in the extraction of stiochiometric chelates into organic phase. Therefore, such undesired effects could easily be minimised varying the reagent: metal concentration ratio and ideal equilibrium conditions could be established. The integral slope value obtained under such conditions could be used to evaluate accurate stability data.

In view of the amount of experimental work involved to obtain a detailed and comparative data for all the 8-quinolinols and corresponding metal chelate systems, the solvent extraction studies were limited to equilibrium studies carried out at low pH and in absence of masking agents. Therefore, the equilibria relationships derived for the hydrolysis and presence of masking agents have not been dealt with in this work. In practice, effects of hydrolysis are expected to be small[3] at the working pH values used in this work.

A satisfactory solution has been found for most of the problems set forth in this project in that, with refinements predicted it should be possible to determine with reasonable accuracy stability constants of chelates and to apply results in analytical processes.

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