Self-adduct Formation in the Extraction of Nickel(II) Chelates of Certain 8-Quinolinols

KASHINATH S. BHATKI & ARVIND T. RANE

Tata Institute of Fundamental Research, Bombay 400005

and

HENRY FREISER

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Equilibrium distribution ratios have been determined for the extraction of nickel(II) with 8-quinolinol and 2-methyl-, 4-methyl-, 5-chloro- and 5-nitro-8-quinolinols into chloroform as a function of pH and reagent concentration at ambient temperature. Except in the case of 2-methyl-8-quinolinol, which forms a simple 1:2 chelate, the extractable complexes are mono self-adducts, that is, 1:2 chelates to which a third molecule of the reagent is coordinated. The overall formation constants of the nickel chelates in aqueous solutions have been determined. A linear correlationship is observed between the formation constants, adduct formation constants and the basicity of the reagent. This dependence can be used to predict, based on known data, the stabilities of not yet experimentally studied complexes. The distribution coefficients of the chelates and the chelate adducts are discussed in terms of structural influences. A penta-coordinate, square base pyramidal structure has been proposed for the self-adducts of nickel(II) with 8-quinolinols (except 2-methyl analogue).

MUCH work has been done on the metal chelate systems in which only one kind of ligand is involved in chelation. The effect of such factors as ligand basicities, sizes of the chelate rings, steric factors and metal ion acidity have been evaluated in the formation of a chelate from the aquated metal ion and the chelating agent. Very little is known, however, about the factors affecting the formation of a complex from a complexing agent and a metal ion that has some of its coordinated water molecules replaced by a strong complexing agent, e.g. a chelating agent. One approach to study more about the relevant factors is through a systematic study of adduct formation.

Adduct extraction systems previously investigated are almost exclusively those involving the β-diketones and 8-quinolinols as chelating agents, and either oxygen-containing solvents, e.g. alcohols, ketones, organophosphorous compounds or nitrogen-containing bases, such as pyridine, quinoline, or alkylamine as the donor; the work has been reviewed by several authors[1-4].

The coordination saturated chelates, e.g. thenoyltrifluoroacetone (TTA) complexes of Ce(III), Fe(III) and Th(IV) and the 8-quinolinates of La(III), Tl(III) and W(IV) are extracted well by both the oxygen-containing and non-oxygen-containing solvents[5].

The extraction of coordination-unsaturated chelates can, in some cases, be favoured by the use of an excess chelating agent. For example, Dyrssen[6] succeeded in extracting Sr(II) as the species, $SrQ_2.2HQ$ (where HQ represents the 8-quinolinol molecule). Stary[7] studied the use of 8-quinolinol in the extraction of some 32 metal ions and reported

the extraction of the species $MQ.HQ$; $MQ_2.HQ$; $MQ_2.2HQ$ and $MQ_3.HQ$. Among these 32 metal ions, he reported that Co^{2+} got extracted as an adduct, $CoQ_2.2HQ$ while Ni^{2+} was extracted as a simple chelate NiQ_2. Chou *et al.*[8] have studied the adducts of Zn^{2+} with 8-quinolinol and its analogues wherein Zn^{2+} was found to be extracted in chloroform by the reagent in the form $ZnQ_2.HQ$, termed as self-adduct, in which the HQ was believed to be acting as a monodentate ligand involving the quinoline nitrogen atom.

Oki[9] reported the distribution of U(IV) with oxine in chloroform and concluded that the extractable species is $UO_2Q_2.HQ$. He extended the study to the extraction of Zn(II)[10], Ni(II)[11] and Co(II)[12] systems and showed that it is possible to extract the adducts of these metal ions from perchlorate solutions. The extractable adducts were $ZnQ_2.$ $2HQ$, $NiQ_2.HQ$ and $CoQ_2.HQ$ respectively. Oki and Terada[13] reported the extraction of zinc adduct from perchlorate solutions as a binuclear complex $Zn_2Q_3.3HQ.ClO_4$. However, no extraction from either nitrate or chloride solution was reported in the case of cobalt and zinc. As an extension Oki and Terada[13] isolated two different types of nickel adducts of oxine with chloroform from perchlorate and sulphate solutions[14]. The adduct $Ni_2Q_3.3HQ.$ ClO_4 was reported from perchlorate solution at low pH and the adduct $Ni_2Q_4.2HQ$ was extracted from perchlorate solution at high pH or from sulphate solution. The nickel adducts extracted from the perchlorate solutions and from aqueous solutions containing various common inorganic alkali metal salts were found to be the same.

The present study attempts to resolve some of the controversies raised in the extraction of nickel with oxine[7,11] and extends the study of the adduct formation to the extraction of nickel oxinate with heterocyclic bases.

Materials and Methods ·

A Kahn type Box Shaker in which a dozen 10 ml centrifuge tubes with stoppers could be accommodated was used to equilibrate solutions at $28° \pm 1°$.

Radioactivity counting was carried out on NaI(Tl) detector system connected to a scintillation spectrometer (Electronics Corporation, Hyderabad).

A Beckman model G pH meter with a glass and saturated calomel electrode pair was calibrated with known buffer solutions of pH 4·00 and 7·00 and was used for all pH measurements.

8-Quinolinol (E. Merck, AR), 2-methyl-8-quinolinol (Fluka), 5-chloro-8-quinolinol (Aldrich) and 5-nitro-8-quinolinol (K and K) were recrystallized from absolute ethyl alcohol; melting points 73°, 74°, 126° and 179° respectively.

4-Methyl-8-quinolinol was synthesized from o-aminophenol and methyl vinyl ketone as described by Phillips et al.[16] and purified by vacuum distillation followed by two recrystallizations from absolute ethanol; m.p. 140° (lit.[16] m.p. 141°).

For every irradiation, a sample of accurately weighed ($\sim$0·1 mg) enriched nickel-64 (Union Carbide, USA) was used. It was irradiated in pneumatic rabbit facility of CIRUS (reactor), Trombay, to get nickel-65 ($t\frac{1}{2} = 2·56$ hr). The irradiated target was dissolved in hydrochloric acid, acid was carefully removed under infrared lamp and the residue, which was almost invisible (with high specific activity) was dissolved in pure distilled water and made up to a known volume in a standard measuring flask. The final concentration of nickel in the solution was $\sim$6·2×10^{-6}M.

Hydrochloric acid-potassium biphthalate buffer solutions were used in the acidic pH range and potassium dihydrogen phosphate-sodium hydroxide buffers in the pH range 6-8. In a few cases ammonia-ammonium chloride buffer was employed for pH >8·0. Sodium perchlorate was added to the buffers to maintain a constant ionic strength at 0·25.

All other chemicals were of AR grade and were used without further purification.

Procedure — Buffered nickel-65 solution (5 ml) at a constant ionic strength (0·25) and reagent solution (10^{-4} to 1·0M, 5 ml) in chloroform, were equilibrated for 15 min. It was separately ascertained that this period of shaking was adequate for the attainment of equilibrium in the pH range employed. After shaking was over, the mixtures were centrifuged and equal volumes of both the phases were pipetted out in suitable counting glass tubes and counted for activity separately, at a constant and reproducible geometry. The pH value of the aqueous phase after extraction was taken as the equilibrium pH value.

Results and Discussion

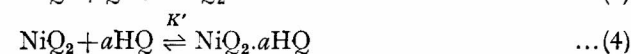In Fig. 1 are shown the extraction curves (log D vs pH) for nickel(II) at different concentrations of the reagents, viz. 8-quinolinol (HQ) and its four substituted compounds: 2-methyl, 4-methyl, 5-chloro and 5-nitro. Each curve has a slope of 2 which shows that in each of these extractions two protons are released on the formation of the extractable complex. A plot of log D vs pH at constant [reagent] in the organic phase, generally describes the extraction of a simple chelate. These plots essentially consist of two linear portions; the log D increasing initially in the lower pH region with a slope of n (the number of protons released) and then eventually reaching a constant, pH-independent value, determined by K_{DC}, the distribution coefficient of the chelate. The increase in [reagent] shifts the entire curve to the left, i.e. to a region of lower pH, without alteration of either the slope or the value of the maximum log D, which remains equal to log K_{DC}. This situation changes when the extractable complex is not a simple chelate but an adduct. The adduct reagent concentration then influences the entire extraction curve. An increase in [reagent] then causes the plateau portion of the curve to shift to a higher log D, the initial linear portion of the curve shifting to a lower pH, without changing its slope. This is exactly what is observed in Figs. 1A, C, D and E. In the case of 2-methyl-8-quinolinol (Fig. 1B) all the curves in the higher pH region merge indicating the absence of the adduct in the extraction system.

Plots of log D versus log [reagent] were constructed for the extraction of Ni(II) with the 8-quinolinols, and are shown in Fig. 2. The slopes of these plots show the number of reagent molecules incorporated in the extractable complex. The behaviour of the 2-methyl-8-quinolinol extraction indicates that the extractable complex is simple 1:2 chelate since, two reagent molecules per nickel ion are involved in the extraction. Whereas, in other cases (Figs. 2A, C, D and E) the slope three of these plots indicate the formation of a self-mono adduct, e.g. NiQ$_2$.HQ.

These plots in Fig. 2 show a number of curves in each portion A, B, C, etc. These have been drawn for various pH values from the data in plots of Fig. 1. It is interesting to observe from these curves that at the lower [reagent], the slopes (Figs. 2A, C, D, E) approach a value of two indicating the absence of the adduct. The slopes subsequently increase to three with increase in [reagent] showing that the formation of adduct has taken place. This is not the case with 2-methyl-8-quinolinol (Fig. 2B). Here the slope remains two throughout, confirming the absence of any adduct in this system.

A theoretical description of such an extraction system can be given as follows:

In the aqueous phase we have (i) the dissociation of reagent (Eq. 1) (ii) the formation of the chelate (Eqs. 2 and 3) and (iii) the formation of the adduct (Eq. 4).
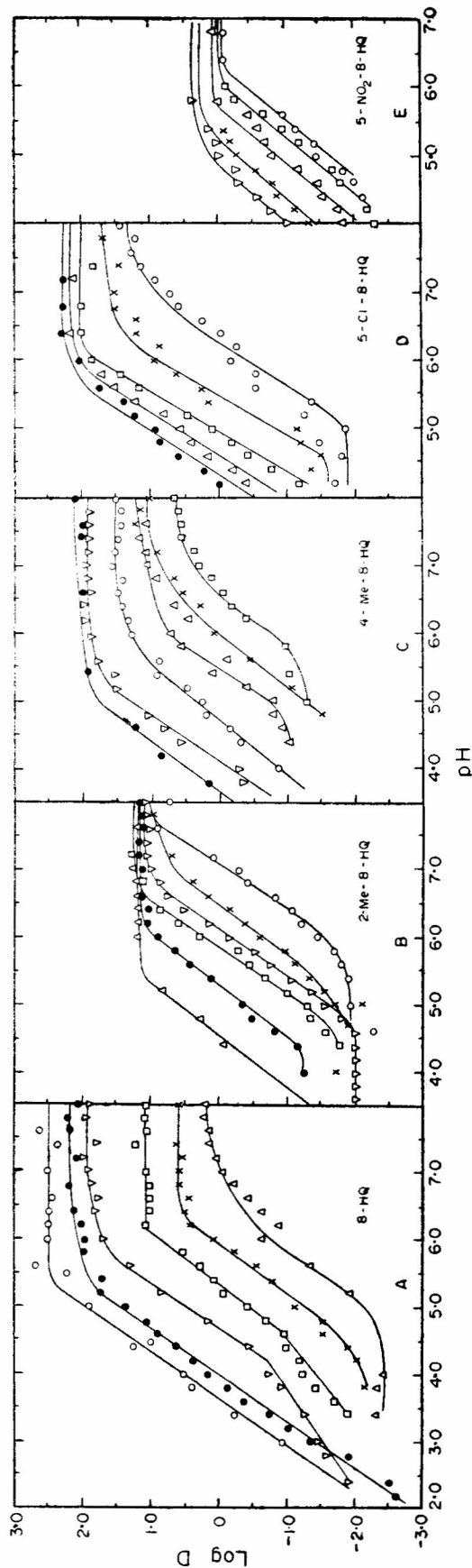
$$HQ \overset{Ka}{\rightleftharpoons} H^+ + Q^- \qquad \ldots(1)$$

$$Ni^{2+} + Q^- \overset{K_1}{\rightleftharpoons} NiQ^+ \qquad \ldots(2)$$

$$NiQ^+ + Q^- \overset{K_2}{\rightleftharpoons} NiQ_2 \qquad \ldots(3)$$

$$NiQ_2 + aHQ \overset{K'}{\rightleftharpoons} NiQ_2.aHQ \qquad \ldots(4)$$

Fig. 1 — Extraction of Ni(II) with 8-quinolinols at different concentration of the reagent (log D vs pH) [(△) 8-Quinolinol: (○) 10^{-2}; (●) 7.449×10^{-3}; (▽) 4.238×10^{-3}; (□) 2.0×10^{-3}; (×) 10^{-3}; and (△) $5.235 \times 10^{-4}M$. (B) 2-Methyl-8-quinolinol: (△) 4.111×10^{-1}; (●) 2.005×10^{-1}; (▽) 1.035×10^{-1}; (×) 8.185×10^{-2}; (○) $2.151 \times 10^{-2}M$. (C) 4-Methyl-8-quinolinol: (●) 6.407×10^{-3}; (▽) 4.304×10^{-3}; (○) 2.203×10^{-3}; (△) 1.076×10^{-3}; (×) 5.5×10^{-4}; and (□) $3.518 \times 10^{-4}M$. (D) 5-Chloro-8-quinolinol: (●) 8.137×10^{-3}; (△) 6.022×10^{-3}; (×) 4.068×10^{-3}; (○) 1.953×10^{-3}; and (○) 8.137×10^{-4}; (▽) $5.754 \times 10^{-4}M$. (E) 5-Nitro-8-quinolinol: (▽) 3.889×10^{-4}; (△) 1.866×10^{-4}; (□) 1.011×10^{-4}; and (○) $7.7 \times 10^{-5}M$]

In the organic phase:

$$K_{DR} = \frac{[HQ]_0}{[HQ]} \qquad \ldots(5)$$

$$K_{DC} = \frac{[NiQ_2]_0}{[NiQ_2]} \qquad \ldots(6)$$

$$K'_{DC} = \frac{[NiQ_2.aHQ]_0}{[NiQ_2.aHQ]} \qquad \ldots(7)$$

The distribution ratio D is then given by Eq. (8)

$$D = \frac{[Ni]_0}{[Ni]} = \frac{[NiQ_2]_0 + [NiQ_2.aHQ]_0}{[Ni^{2+}] + [NiQ^+] + [NiQ_2] + [NiQ_2.aHQ]} \qquad \ldots(8)$$

Eq. 8 may be modified when adduct formation predominates by incorporating the assumption that the simple chelate NiQ_2 is not extracted to a significant extent and that, of the possible adduct complexes $a = 1$ to $a = a$, only the last is of importance. The value of a can then be determined from a plot of log D, for the nickel extraction, vs log $[HQ]_0$. Since two reagent molecules are involved in the formation of a simple 1:2 chelate, the slope of the resulting line should be $(2+0)$. It is seen from Fig. 2, that the value of a for 8-quinolinol, 4-methyl-, 5-chloro- and 5-nitro-8-quinolinols is unity and for the 2-methyl-8-quinolinol it is zero, i.e. no adduct formation is involved in the extraction of the nickel chelate of 2-methyl-8-quinolinol.

At lower $[HQ]$, when formation of simple 1:2 chelate cannot be ignored, and at the lower pH range where Ni^{2+} predominates in the aqueous phase, the distribution ratio D is then given by Eq. (9).

$$D = \frac{[NiQ_2]_0 + [NiQ_2.aHQ]}{[Ni^{2+}]} \qquad \ldots(9)$$

Substituting appropriate equilibrium expression in Eq. (9) we get Eq. (10).

$$D = \frac{K_{ex}[HQ]_0^2}{[H]^2}[1 + K_{AD_0}[HQ]_0^a] \qquad \ldots(10)$$

where

$$K_{ex} = K_1 K_2 K_{DC} K_a^2 / K_{DR}^2 \qquad \ldots(10a)$$

The plot of log D vs log $[HQ]_0$ consists of two linear portions (i) for $[HQ]_0 \to 0$

$$\log D = \log K_{ex} + 2 \log [HQ]_0 + 2p\text{H} \qquad \ldots(11)$$

and (ii) for $[HQ]_0 \to \infty$

$$\log D = \log K_{ex} + \log K_{AD} + 2p\text{H} + (2+a) \log [HQ]_0 \qquad \ldots(12)$$

The intersection of these two linear curves gives the value for the adduct formation constant in the organic phase

$$\log K_{AD} = a \log [HQ]_0, \text{ intersection} \qquad \ldots(13)$$

Eq. (10) can also be written as

$$D \frac{[H]^2}{[HQ]^2} = K_{ex}(1 + K_{AD}[HQ]_0^a) \qquad \ldots(14)$$

Letting $Y = D[H]^2/[HQ]^2$ we may write Eqs. (11) and (12) as

$$\log Y = \log K_{ex} \text{ (for } [HQ]_0 \to 0) \qquad \ldots(11a)$$

and

$$\log Y = \log K_{ex} + (2+a) \log [HQ]_0 \text{(for } [HQ]_0 \to \infty) \qquad \ldots(12a)$$

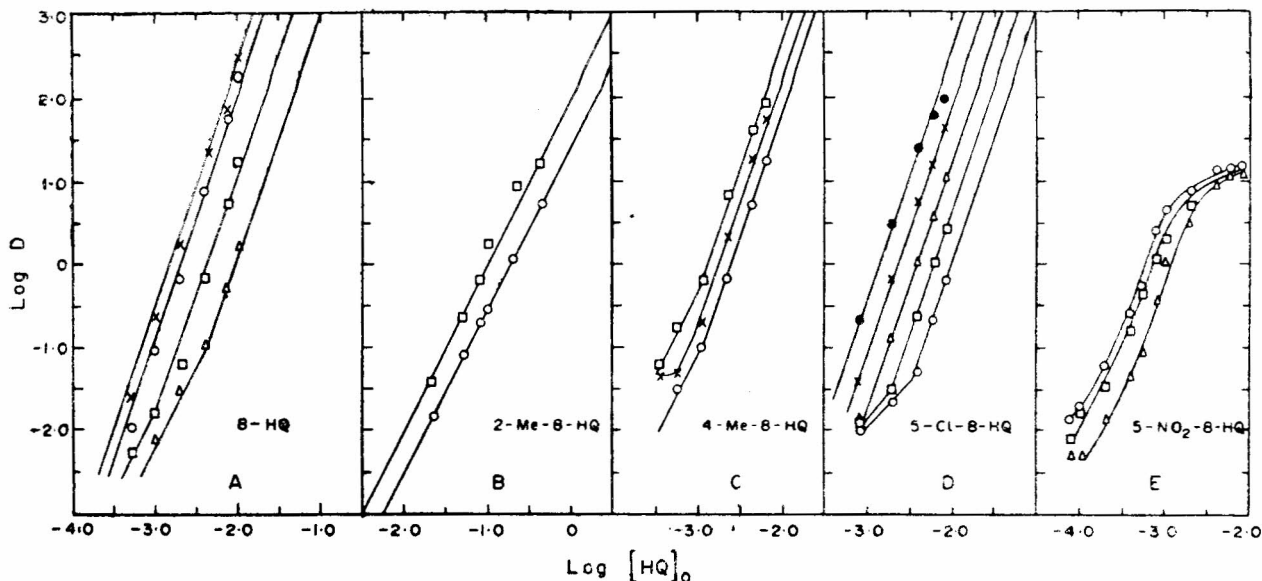Fig. 2 — Extraction of Ni(II) with 8-quinolinols at different pH values (log D vs log $[HQ]_0$) [(A) 8-Quinolinol: Slope = 3·0; (×) 5·5 pH; (○) 5·2; (□) 4·5; and (Δ) 3·8. (B) 2-Methyl-8-quinolinol: Slope = 2·0; (□) 6·0 pH and (○) 5·5. (C) 4-Methyl-8-quinolinol: Slope = 3·0; (○) 4·6 pH; (×) 5·0; and (□) 5·4. (D) 5-Chloro-8-quinolinol: Slope = 3·0; (●) 5·8 pH; (×) 5·4; (Δ) 5·0; (□) 4·6; and (○) 4·2. (E) 5-Nitro-8-quinolinol: Slope = 3·0; (○) 4·8 pH; (□) 4·6; and (Δ) 4·0]
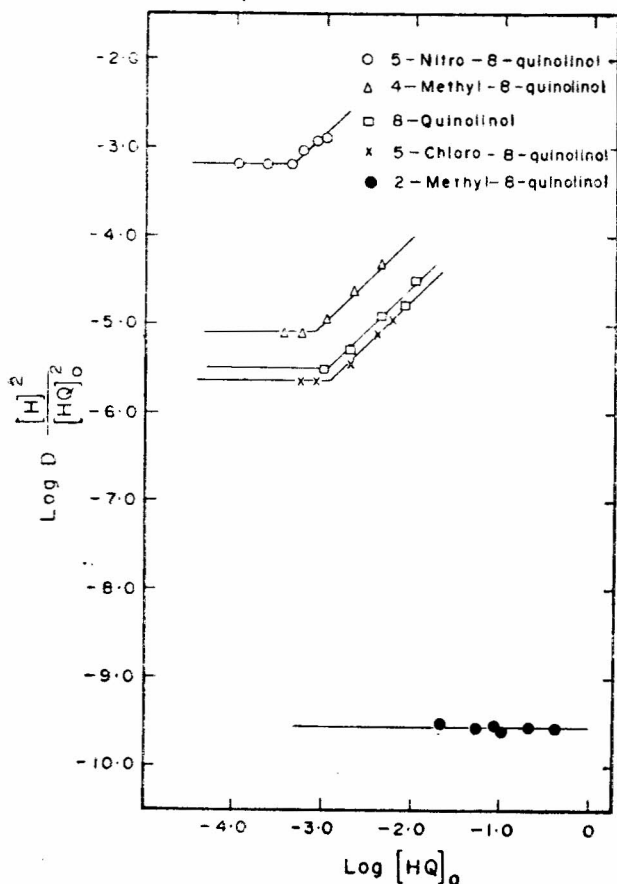
Fig. 3 — Plots of log D $[H]^2/[HQ]^2_0$ vs log $[HQ]_0$ [(○) 5-NO$_2$-8-HQ; (Δ) 4-Me-8-HQ; (□) 8-HQ; (×) 5-Cl-8-HQ; and (●) 2-Me-8-HQ]

A plot of log $D[H]^2/[HQ]^2_0$ against log $[HQ]_0$ takes into account the variations both in pH and in the reagent concentrations simultaneously[17]. Such a plot gives two linear intersecting curves. The horizontal line corresponds to log D = log K_{ex} and the line of slope a shows the number of neutral reagent molecules involved in the self-adduct. The intersection of these lines gives the adduct formation constant, K_{AD_0} (Eqs. 11a and 12a) (Fig. 3). Results for 2-methyl-8-quinolinol are also given in Fig. 3. The entire curve in the case of 2-methyl is parallel to log $[HQ]_0$ axis indicating that no adduct is formed in this case.

In the plots of log D against pH (Fig. 1) we have seen that for a given [reagent] at higher pH values log D reaches a plateau, D_{max} which is a constant value if the extractable species is the simple 1:2 chelate (Fig. 1B) and is, however, proportional to the [reagent] if the extractable species is a self-adduct. Such plots of log D_{max} versus log $[HQ]_0$ are shown in this Fig. 4 for 8-quinolinol and its substituted products 4-methyl-, 5-chloro-, and 5-nitro-8-quinolinols. The intercept of the log D_{max} vs log $[HQ]_0$ plot gives the value of $K_{AD}K'_{DC}/K_{DR}$. This group of constants in combination with the adduct formation constants in the organic phase, K_{AD_0} gives the value of K_{DC} from Eq. (15),

$$\frac{K'_{DC}K_{AD}}{K^a_{DR}} = K_{AD_0}K_{DC} \qquad ...(15)$$

The overall formation constant, K_f of the 1:2 chelate may be evaluated from the extraction constant, K_{ex}, according to Eq. (10a), the K_{DR} and K_a values being obtained from the literature.

Alternatively, a plot of log $D - a$ log $[HQ]_0$ vs $-$log $[Q^-]$ which takes into account the variations
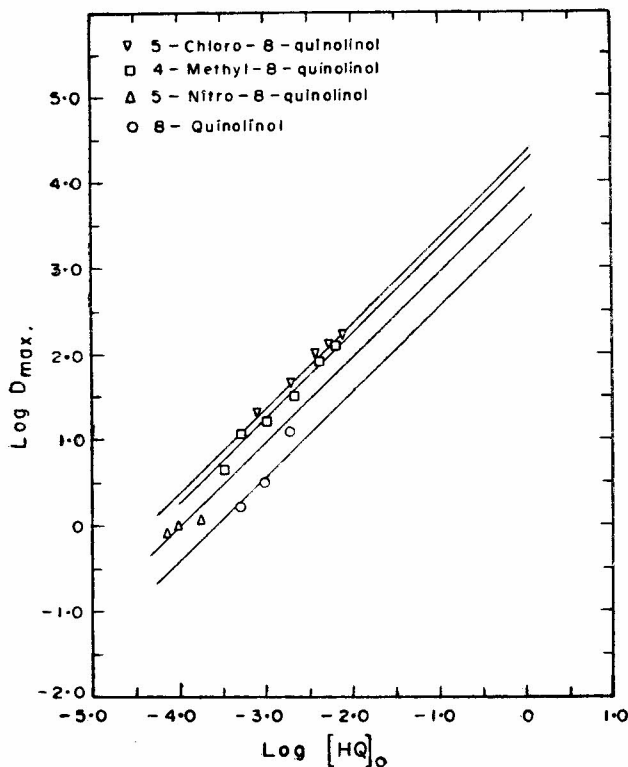
Fig. 4 — Plots of log D_{max} vs log $[HQ]_0$ [($\triangledown$) 5-Cl-8-HQ; ($\square$) 4-Me-8-HQ; ($\triangle$) 5-NO$_2$-8-HQ; and ($\bigcirc$) 8-HQ]

Fig. 5 — Plots of log D —log $[HQ]_0$ vs —log $[Q]$ [(A) 8-Quinolinol; (B) 4-methyl-8-quinolinol; (C) 5-chloro-8-quinolinol; and (D) 5-nitro-8-quinolinol]

in the *p*H and the [reagent] simultaneously gives two linear intersecting curves. The K_f values may be obtained from the intersections of the two linear curves, i.e. —log $[Q^-] = \frac{1}{2}(\log K_f)$.

Such plots were constructed for 8-quinolinol, for 4-methyl-, 5-chloro- and for 5-nitro-8-quinolinols and are shown in Fig. 5, whereas, a plot for 2-methyl-8-quinolinol is given in Fig. 6. In these plots (except 2-methyl) the value of $a = 1$ and $[Q^-]$ represents the corresponding quinolinol anion concentration in the aqueous phase. As the value of a for a simple 1:2 chelate, such as that formed by Ni(II) with 2-methyl-8-quinolinol, is zero, Fig. 6 shows a plot of log D vs —log $[Q^-]$ instead of log D—log $[HQ]_0$ vs —log $[Q^-]$.

Table 1 gives the summary of equilibrium constants for nickel chelates of 8-quinolinol and its substituted products such as 2-methyl-, 4-methyl-, 5-chloro- and 5-nitro-8-quinolinols.

This study has revealed an important difference between the behaviour of Ni(II) with 2-methyl-8-quinolinol from that of the other reagents. A similar observation was made earlier by Chou and coworkers[8] in their study of Zn(II). The reason for this difference, the extraction of the simple chelate, results from the steric hindrance to adduct formation presented by the substituent in the 2-position. This steric hindrance must extend to the hydration of the chelate as well since the results indicate that the extracted chelate is not hydrated. If the extracted chelate were hydrated, it would be expected that the 8-quinolinol, or certainly the 4-methyl-8-quinolinol extractions at lower [reagent]
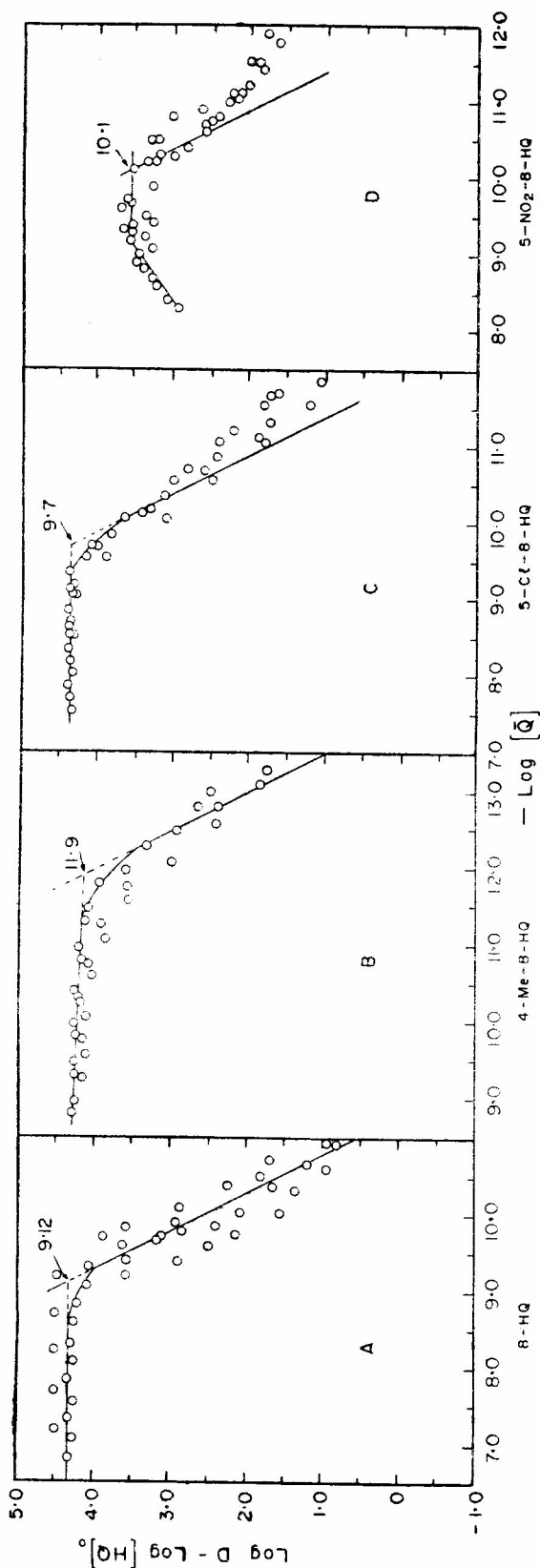
TABLE 1 — SUMMARY OF EQUILIBRIUM CONSTANTS FOR NICKEL CHELATES OF 8-QUINOLINOL AND
SUBSTITUTED 8-QUINOLINOLS AT $28° \pm 1°C$

| Substituted 8-quinolinol	Species extracted	Log K_{ex}	Log K_{AD_0}	Log K_{DC}	$pKa_1 + pK_{a_2}^*$	Log $K_{DR}^\dagger$	Log K_f
8-Quinolinol	NiQ$_2$.HQ	−5·5	2·95	0·58	14·9	2·64	18·24
2-Methyl-	NiQ$_2$	−9·55	No adduct formation	1·25	15·9	3·22	18·1
4-Methyl-	NiQ$_2$.HQ	−5·1	3·1	1·14	15·66	3·27	23·8
5-Chloro-	do	−5·65	2·85	1·40	13·00	3·32	19·4
5-Nitro-	do	−3·2	3·4	0·55	8·79	2·64	20·2

*Fa-chun Chou & H. Freiser, *Analyt. Chem.*, **40** (1968), 34.
†A. J. Fresco & H. Freiser, *Analyt. Chem.*, **36** (1964), 631.
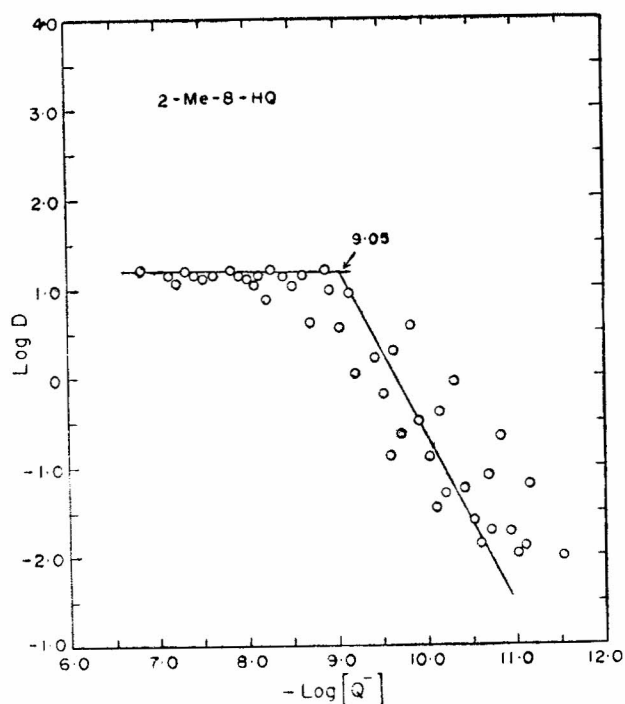
Fig. 6 — Plots of log D vs −log [Q⁻] for 2-methyl-8-quinolinol

would have resembled those of the 2-methyl-8-quinolinol, but this is not so.

Most common example of steric inhibition of complex formation can be cited when a bulky group is attached either to the donor atom or very near to it, enough to cause mutual repulsion between ligands. This results in weakening of the metal-ligand bonds, thus, making a sterically crowded complex unstable. Steric hindrance was also observed in the extraction of Zn(II) with 5-iodo-8-quinolinol, but no steric hindrance was observed in the extraction of Zn(II) with 5-chloro- and 5-nitro-8-quinolinols[8]. Merely blocking the reagent at 5-position does not produce any steric hindrance is also confirmed in the present study. The steric hindrance due to 5-iodo- analogue is attributed, therefore, to the bulky nature of the reagent. Substitution in the chelating molecule may not only alter its basic strength and alter the stability of the complex it forms as well, but, it may also introduce

steric effects. This is very well shown by difference in the extraction behaviour of Ni(II) with 2-methyl-and 4-methyl-8-quinolinols.

Healy in his review[18] suggested that during adduct formation some of the bidentate chelate links can become monodentate. The simplest and the most direct way for the formation of adduct is to join the metal chelate either by direct addition to the metal, increasing N, its coordination number or by substitution from water[18,19]. The first observation of this phenomenon was that one molecule of ligand (S) when added to the established species $UO_2(HX)_2$ formed a highly extractable adduct $UO_2(HX)_2S$ with an increase in the coordination number of uranium from 6 to 7. Similarly zinc also forms extractable adduct with TTA and tri-n-octyl phosphate (TOP) in carbon tetrachloride by the displacement of water molecules as shown by the NMR studies[20]. Thus,

$$Zn(TTA)_2.2H_2O + \overline{TOP} \rightleftharpoons \overline{Zn(TTA)_2TOP} + 2H_2O$$
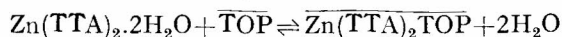
The results presented in Fig. 2, where a slope of three is obtained when log D is plotted against log $[HQ]_0$, indicate that to each atom of nickel are attached three molecules of the reagent HQ. Whereas, only two protons are liberated in the course of extraction, as seen from the log D vs pH plot (Fig. 1). This is obvious from the fact that 8-quinolinol exhibiting a dual role, firstly, by coordinating with nickel, as a bidentate ligand, forming a 1:2 chelate, and secondly as an unidentate ligand in the adduct formation. This is shown by Eqs. (2)-(4).

In aqueous solution, Ni(II) forms a dihydrate, $NiQ_2.2H_2O$ with 8-quinolinol. X-ray diffraction studies of $ZnQ_2.2H_2O$ (refs 21, 22) and $CuQ_2.2H_2O$ (ref. 23) show that these complexes possess trans-coplanar arrangement of the two water molecules located at axial position, completing an hexavalent octahedral structure. The compounds of Zn, Cd, Co, Ni and Pb are isomorphous as $MQ_2.2H_2O$ (ref. 21). The data obtained in the present study leads to the conclusion that two molecules of 8-quinolinol form the square base of a pyramid. The water molecules are pushed out of the coordination sphere and are replaced by the third molecule of the excess ligand present. Thus, for bonding and steric reasons the highest symmetry is generally the energetically preferred one; that is, the unidentate ligand is in the axial position of a square base pyramid (point
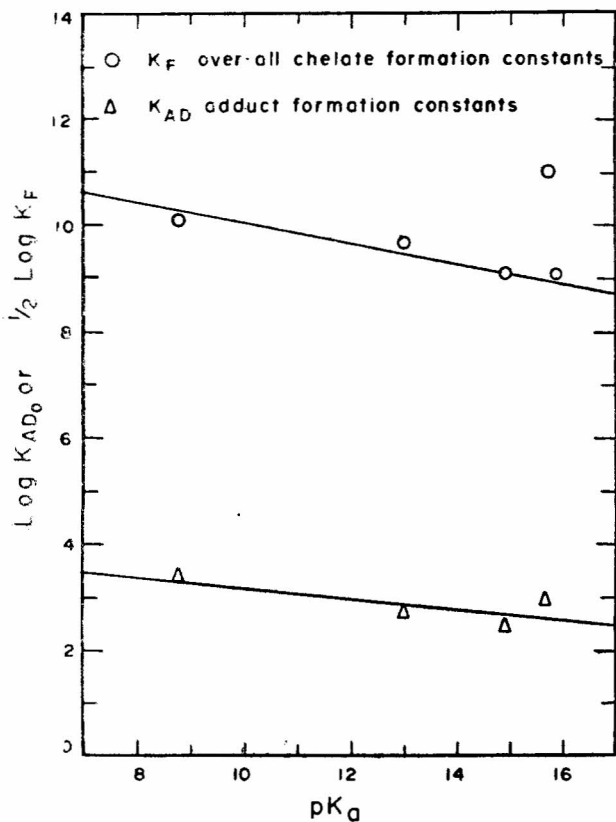
Fig. 7 — Correlation between adduct formation constants or chelate formation constants and the basicities of the chelating agents

group C_{3v}[24]. The extracted species are, thus, the anhydrous pentacoordinate adducts having a square base pyramidal structure.

In order to ascertain the pentacoordinated structure of the nickel adduct of 8-quinolinol, the nickel adduct was isolated in solid state as described by Oki[12,13]. Nickel (II) was extracted from a neutral solution of nickel chloride with excess of oxine in chloroform. The organic extract was filtered through a filter paper to remove organic suspension. Benzene was then added, with constant stirring, to the filtered extract until greenish precipitate of the adduct appeared. The precipitate was filtered off on a filter paper and washed with benzene and dried in a desiccator. The isolated nickel adduct was then subjected to thermogravimetric analysis which gave the formula of the adduct as $NiQ_2.HQ$.

The values of the overall formation constants obtained from the log D—log $[HQ]_0$ vs pQ^- plots are in good agreement with those obtained by potentiometric titration in aqueous dioxane (50%, v/v), allowing for the difference in medium. When the logarithm of the chelate formation constants were plotted against pKa values of the 8-quinolinols (where $pKa = pKa_1 + pKa_2$), the overall basicity of the donor atoms, the expected linear relationship is observed as seen in Fig. 7.

In the same figure (Fig. 7), a similar plot was constructed between the adduct formation constants and the pKa values of the reagents. In this case

also a linear dependence was observed. In the latter case the slope is, however, much smaller. In other words, the self-adduct formation constants are almost constant over a wide range of pKa values. This can be explained on the following basis.

An adduct is formed between a Lewis acid and a Lewis base, its stability depends, therefore, on the Lewis basicity of the donor as well as the Lewis acidity of the acceptor, the metal chelate. To a first approximation, the Lewis acidity of the metal chelate, after chelation, decreases with increasing stability of the chelate. On forming a self-adduct, 8-quinolinol acts both as chelating agent and as an adducting base. The enhancement in the adduct formation constant due to an increase in the reagent basicity is compensated to a certain extent by its ability to form a more stable chelate, i.e. a weaker acceptor. The overall effect would be a much smaller net increase in the adduct formation constants for a relatively large increase in the reagent basicity. This dependence may be used to estimate, based on known data, the stabilities of not yet experimentally studied complexes.

Similar linear correlationship is observed between the formation constants, adduct formation constants, distribution coefficients of Ni(II) chelates of 8-quinolinol analogues and the molecular weights of the chelates (see Fig. 8). The formation constants and the adduct formation constants are plotted against the molecular weights of the nickel chelates. These two plots are parallel to each other and increase steadily with the increase in molecular weights. The formation constant of 8-quinaldine is much higher and deviates from the linear plots. All other points lie on the linear curve.

In the same Fig. 8, are plotted the distribution coefficients of the nickel chelates against the molecular weights of the chelates. The distribution coefficients of the nickel chelates of 8-quinolinol
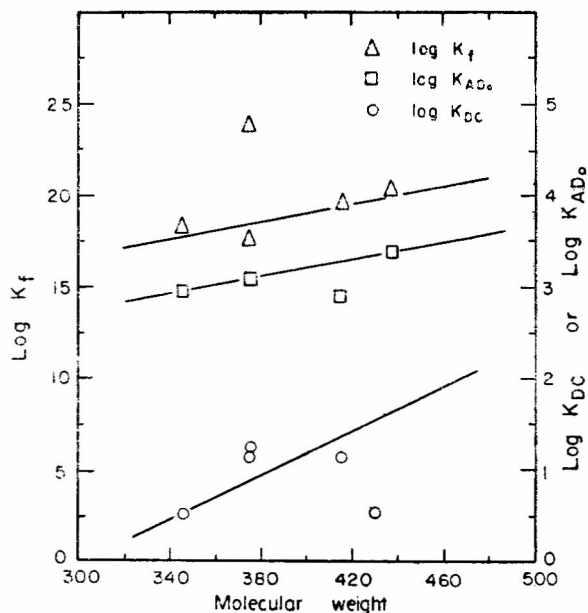

Fig. 8 — Correlation between distribution coefficients, adduct formation constants, formation constants and molecular weights of the chelates

analogues, except for 5-nitro-, increase linearly with the molecular weight of the chelates. The K_{DC} value of Ni(II)-5-NO$_2$-8-quinolinol is much below the linear plot. Probably the effect of the solvation by water on the larger polar nitro group compensates for the large increase in the molecular weight.

Similar experiments, as described in the foregoing, were done for higher concentrations of nickel(II), using inactive nickel (e.g. 10^{-4} to $10^{-5}M$). Essentially the same curves were obtained, indicating no dependence in metal ion concentration and, thus, giving confidence that no appreciable metal ion polymerization was occurring.

References

1. MARCUS, Y., *Chem. Rev.*, **63** (1963), 139.
2. HEALY, T. V., *Nucl. Sci. Engng*, **16** (1963), 413.
3. FREISER, H., *Analyt. Chem.*, **38** (1966), 131R.
4. FERNANDO, Q., *Sep. Sci.*, **1** (1966), 575.
5. ALIMARIN, I. P. & ZOLOTOV, Y. A., *Talanta*, **9** (1962), 891.
6. DYRSSEN, D., *Svensk Kem. Tidskr.*, **67** (1955), 311.
7. STARY, J., *Anal. chim. Acta*, **28** (1963), 132.
8. CHOU, FA-CHUN, FERNANDO, Q. & FREISER, H., *Analyt. Chem.*, **37** (1965), 361.
9. OKI, S., *Talanta*, **16** (1969), 1153.
10. OKI, S., *Bunseki Kagaku*, **18** (1969), 822.
11. OKI, S., *Anal. chim. Acta*, **49** (1970), 455.
12. OKI, S., *Anal. chim. Acta*, **50** (1970), 465.
13. OKI, S. & TERADA, I., *Anal. chim. Acta*, **61** (1972), 49.
14. OKI, S. & TERADA, I., *Anal. chim. Acta*, **66** (1973), 201.
15. OKI, S. & TERADA, I., *Anal. chim. Acta*, **69** (1974), 220.
16. PHILLIPS, J. P., ELBINGER, R. L. & MERRITT, L., *J. Am. chem. Soc.*, **71** (1949), 3987.
17. SEKINE, T. & DYRSSEN, D., *J. inorg. nucl. Chem.*, **26** (1964), 1727.
18. HEALY, T. V., in *Solvent extraction research*, edited by A. S. Kertes & Y. Marcus (John Wiley, New York), 1969, 257-279.
19. FERNANDO, Q., in *Separation techniques in chemistry and biochemistry*, edited by R. A. Keller (Marcel Dekker, New York), 1967, 357-376.
20. WALKER, W. R. & LI, W. C., *J. inorg. nucl. Chem.*, **27** (1965), 411.
21. MERRITT, L. L., *Analyt. Chem.*, **25** (1963), 718.
22. MERRITT, L. L., CADY, R. T. & MUNDY, B. W., *Acta Cryst.*, **7** (1954), 473.
23. KRUN, R. & DIGGINS, C. W., *J. Am. chem. Soc.*, **77** (1955), 806.
24. WOOD, J. S., in *Progress in inorganic chemistry*, Vol. 16, edited by S. J. Lippard (Interscience, New York), 1972, 227-486.