Spectrophotometric determination of self-adducts of 4-methyl and 5-chloro-8-quinolinols with Nickel(II)

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Abstract. Shifts in the visible spectra of nickel chelates of 5-chloro- and 4-methyl-analogues of 8-quinolinol observed on addition of ligands to the chloroform solutions of the simple chelates were attributed to the formation of self-adducts. Formation constants for these adducts were evaluated from the spectrophotometric data.

1. Introduction

In the previous study (Bhatki *et al* 1977) nickel was found to extract with 8-quinolinol and its various analogues in chloroform over a wide range of pH and reagent concentration. The study was further extended to pyridine adducts (Bhatki *et al* 1978b and Rane and Bhatki 1979). Recently, however, the studies on adduct formation of nickel chelates were carried out in a monophase system employing a Cary 17D spectrophotometer. The structural changes observed on addition of the adducting bases and the steric hindrances noted due to typical ligands were discussed for both nickel and cobalt chelates of 8-quinolinols (Bhatki *et al* 1978 Bhatki and Rane 1979). The present study is the extension of the earlier investigation to the self adducts of 4-methyl and 5-chloro-8-quinolinols with nickel.

2. Experimental

A Cary 17D spectrophotometer was used for the absorbance measurements.

2.1. *Materials*

The 4-methyl-8-quinolinol was prepared and purified as described earlier (Bhatki *et al* 1977). The 5-chloro-8-quinolinol (Aldrich) was recrystallised from absolute

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alcohol. Preparation of nickel-4-methyl-8-quinolinate has also been described previously (Bhatki *et al* 1978a). The nickel complex of 5-chloro-8-quinolinol was prepared in a similar manner. The yellowish precipitate of Ni-5-Cl-8-quinolinate obtained was hydrated. It was made anhydrous by drying in an air oven at about 170° C for several hours.

2·2. *Equilibrium absorbance measurements*

Stock solutions were prepared afresh everytime by dissolving known amounts of anhydrous nickel complexes in dry chloroform. Specific amounts of chloroform solution of the nickel complex were then pipetted into 25 ml volumetric flasks containing varying amounts of 4-methyl or 5-chloro-8-quinolinol in chloroform and the volumes were adjusted to the mark with pure dry chloroform. The chloroform used was anhydrous, as the traces of moisture would render the nickel complex hydrated, resulting in its precipitation. The absorption spectra of the solutions were then taken in the visible and UV regions. One such set of spectra is shown in figure 1. The molar extinction coefficients were found to be $\epsilon_{455} = 43000$ (for Ni-4-Me-8-quinolinate) and $\epsilon_{480} = 11500$ (for Ni-5-Cl-8-quinolinate).

3. Results and discussion

The spectrum of the pure nickel chelate of 4-methyl-8-quinolinol in chloroform (figure 1) shows two absorption bands, one at 445 nm and the other at 340 nm. The band at 445 nm goes on decreasing gradually on the addition of the reagent and a large increase in absorbance is observed in the band at 340 nm, with isosbestic points located around 410 nm and 355 nm (the band at 340 nm is not shown in the figure).

The spectrum of pure nickel chelate of 5-chloro-8-quinolinol, in chloroform (not shown here) in the absence of the reagent gives three absorption bands at 480 nm, 410 nm and 350 nm. Only the band at 480 nm, though small, decreases gradually on the addition of 5-Cl-8-*HQ*. The band at 410 nm increases slightly, and a considerable increase in absorbance was observed in the band at 350 nm, with the isosbestic point centered around 410 nm. In the region between 450–500 nm, spectra were taken on an expanded scale (not shown here) for calculations.

The decrease in the absorbance that accompanies the addition of 4-methyl or 5-chloro-8-quinolinol has been used here to determine the adduct formation constants. It was shown previously (Bhatki *et al* 1978a) that the nickel chelates exist only as monomeric chelate-adducts.

The formation of an adduct is then represented by the following equation :

$$\text{Ni}Q_2 + n\text{HQ} \overset{K_{AD}}{\rightleftharpoons} \text{Ni}Q_2 \cdot n\text{HQ}. \tag{1}$$

Hence, as shown earlier (Bhatki *et al* 1978a)

$$\log K_{AD} = np\text{HQ} + \log \frac{A_0 - A}{A}, \tag{2}$$

where A_0 is the absorbance in the absence of the adducting ligand HQ and A, the absorbance in the presence of HQ whose concentration is given by its negative logarithm pHQ.

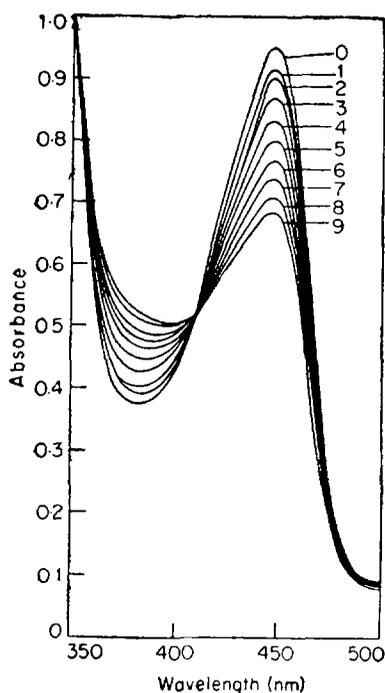**Figure 1.** Absorption spectra of Ni-4-Me-8Q + 4-Me-8-HQ in chloroform
$1 = 5\cdot728 \times 10^{-5}$, $2 = 8\cdot592 \times 10^{-5}$, $3 = 1\cdot145 \times 10^{-4}$, $4 = 1\cdot432 \times 10^{-4}$,
$5 = 1\cdot718 \times 10^{-4}$, $6 = 2\cdot004 \times 10^{-4}$, $7 = 2\cdot291 \times 10^{-4}$, $8 = 2\cdot577 \times 10^{-4}$,
$9 = 2\cdot864 \times 10^{-4}$ M 4-Me-8-*HQ*.

From the plot of $[\log (A_0 - A)/\log A]$ vs $\log HQ$, the value of adduct formation constant, $\log K_{AD}$ could be obtained directly from its intercept on y axis. The slope of the plots were found to be two (figure 2) thus indicating that two molecules of HQ were involved in the adduct formation : $NiQ_2\cdot2HQ$ giving rise to an hexacoordinate octahedral structure. The values of the adduct formation constants thus obtained are $\log K_{AD} = 6\cdot75$ for Ni-4-Me-8-quinolinate and $6\cdot60$ for Ni-5-Cl-8-quinolinate. The values evaluated thus are not strictly comparable to those obtained by solvent extraction for the following reasons : In solvent extraction, the organic solvent is invariably saturated with water, whereas in spectrophotometry, the solvent is strictly anhydrous. Secondly, in solvent extraction, the nickel chelates formed mono-adducts with 8-quinolinols, i.e. one molecule of ligand was attached to the nickel chelate as observed from the slope three of the plot of $\log D$ vs $\log HQ$ (Bhatki *et al* 1977) whereas, in a monophase system i.e. spectrophotometry, two additional molecules of the ligand were involved in the formation of the diadduct, as shown in figure 2.

This study reveals that nickel(II) exhibits two different coordination numbers, viz., five and six, during the add ct formation with the same ligand under different conditions. It is not uncommon, however, for a metal to show two different coordination numbers (Jones 1964). In the earlier spectrophotometric study of pyridine adducts of Ni-5-NO$_2$-8-quinolinate, pentacoordination was observed
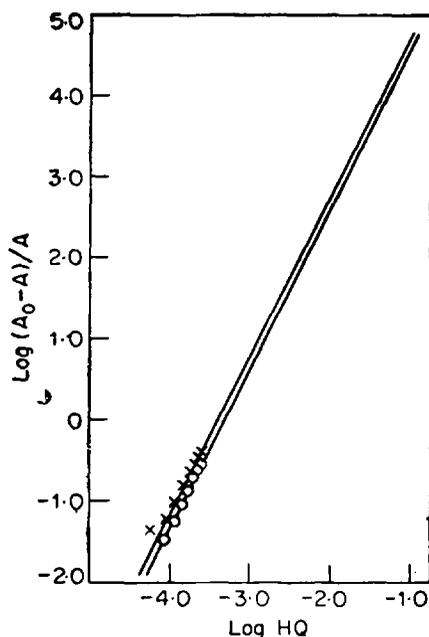
Figure 2. Plot showing self-adduct formation of Ni-4-Me-8-quinolinate and Ni-5-Cl-8-quinolinate. × Ni-4-Me-8-quinolinate; O Ni-5-Cl-8-quinolinate.

in the adducts of nickel chelates with pyridines of higher pK values and hexa-coordination was preferred in the adducts with the bases of lower pK values. The high basicity of both these ligands may be responsible to achieve hexacoordination, a stable configuration.

References

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