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Solvent Extraction of Cobalt(II) with 8-Quinolinol and its Analogues in the Presence of some Heterocyclic Nitrogen Bases

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Summary

Pyridine and its 2-methyl, 2,4-dimethyl and 2,4,6-trimethyl derivatives enhance the extraction of cobalt(II) into chloroform in the presence of 8-quinolinol and its 2-methyl, 4-methyl, 5-chloro and 5-nitro analogues. Adduct formation constants were determined for the cobalt(II) chelates, which formed diadducts with the pyridine bases. The special role of steric factors is discussed. The results are consistent with Lewis acid-base concepts.

Introduction

The synergistic effect of heterocyclic nitrogen bases in solvent extraction of neutral metal chelates has been extensively investigated. The mechanism of the effect is well explained by the formation of the base adducts.

Freiser and coworkers[1, 2] carried out extensive work on 8-quinolinols with copper and zinc ions. Nickel(II) was found to extract with 8-quinolinols in the form of a mono-adduct, $NiQ_2 \cdot HQ$, in which 8-quinolinol (HQ) was believed to be acting as a monodentate ligand involving the quinoline nitrogen[3]. Cobalt(II) was also found to extract with 8-quinolinols, forming a mono-adduct, $CoQ_2 \cdot HQ$, in a similar manner[4]. Pyridine and its methyl analogues were found to enhance the extraction of Zn^{II} [5] and Ni^{II} [6] from aqueous solution into chloroform with 8-quinolinol and its substi-

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tuted products. It has been reported that Zn^{II} formed 1 : 1 chelate-to-nitrogen base adducts whereas 1 : 2 chelate-to-nitrogen base adducts were observed[6] with Ni^{II}.

Adduct formation constants have also been evaluated spectrophotometrically in the monophase system of chloroform, of the pyridine base adducts of nickel chelates of 2-methyl- and 4-methyl-8-quinolinol. It was observed that pyridine bases formed diadducts with nickel chelates of 4-methyl-8-quinolinol whereas monoadducts were reported with 2-methyl-8-quinolinol[7]. Their formation was attributed to steric hindrance by the methyl group in 2-methyl-8-quinolinol.

An attempt is made here to investigate the behaviour of pyridine bases with regard to the extraction of cobalt(II) chelates of 8-quinolinol and its analogues and to see whether adduct formation could occur with a simple nitrogen base in a chelate having a potentially sterically hindering group and also with bases containing adjacent methyl groups.

Experimental

Apparatus

A Kahn type shaking machine, in which stoppered centrifuge tubes (10 cm^3) could be accommodated, was used to equilibrate the solutions at ambient temperatures.

Radioactivity was counted on a NaI(Tl) detector connected to a scintillation spectrometer, supplied by ECIL (India).

AR grade 8-quinolinol (Merck), 2-methyl-8-quinolinol (Fluka), 5-chloro-8-quinolinol (Aldrich) and 5-nitro-8-quinolinol (K & K) were recrystallised from absolute EtOH. 4-Methyl-8-quinolinol was synthesised from *o*-aminophenol and methyl vinyl ketone as described by Phillips *et al.*[8]. The crude product was purified by distillation *in vacuo* followed by two crystallisations from absolute EtOH to constant m.p., 140–142° (lit. m.p. 141°). Pyridine, B.D.H. AnalaR, collidine (2,4,6-trimethylpyridine), A. G. Fluka, α-picoline (2-methylpyridine) and lutidine (2,4-dimethylpyridine) were purified by distillation after drying over potassium hydroxide.

Carrier-free ^{58}Co ($t_{1/2}$ = 72d) was supplied by the Isotope Division, Bhabha Atomic Research Centre, Trombay, as $CoCl_2$. The activity was sufficiently diluted with distilled water and, every time, aliquots (0.2 cm^3) were taken for the distribution study. The solution was diluted with buffer to give *ca.* 1.2×10^5 counts/min.

A potassium hydrogen phthalate-sodium hydroxide buffer solution (pH 5.0) was prepared and the ionic strength was maintained at 0.25 M by sodium perchlorate.

The buffered ^{58}Co solution (5 cm^3) at 0.25 M ionic strength and the reagent solution (5 cm^3) in chloroform (8-quinolinol + varied amounts of heterocyclic base) was equilibrated by shaking for 30 min. The mixtures, after equilibration, were centrifuged and equal volumes of both the phases were pipetted out and counted separately at constant geometry.

Results and discussion

Consider a simple solvent extraction system containing a divalent metal ion M^{2+} and a chelating acid HQ. The overall extraction equilibrium can be written:

$$M^{2+} + 2HQ \rightleftharpoons MQ_2 + 2H^+ \quad (1)$$

The equilibrium constant K_{ex} is given by:

$$K_{ex} = [MQ_2]\,[H^+]^2 / [M^{2+}]\,[HQ]^2 \quad (2)$$

where the symbols in italics refer to the organic phase. At low [Q], when MQ_n complexes in the aqueous phase are negligible, the distribution ratio is:

$$D_0 = [MQ_2] / [M^{2+}] \quad (3)$$

From equations (2) and (3),

$$D_0 = K_{ex}\,[HQ]^2 / [H]^2 \quad (4)$$

for metal complex formation with chelating acid and neutral ligand, MQ_2L_n.

When the organic phase contains one chelating acid and one neutral ligand, L, and when the undissociated chelating acid does not react with the metal ion, the equilibrium, may then be written as follows:

$$M^{2+} + 2HQ + nL \rightleftharpoons MQ_2L_n + 2H^+ \quad (5)$$

with the equilibrium constant:

$$\beta_n K_{ex} = [MQ_2L_n][H^+]^2 / [M^{2+}][HQ]^2\,[L]^n \quad (6)$$

where

$$\beta_n = [MQ_2L_n] / [MQ_2]\,[L]^n \quad (7)$$

then:

$$\log D\,[H^+] / [HQ]^2 = \log K_{ex}\{1 + \beta_1\,[L] + \ldots \beta_n\,[L]^n\} \quad (8)$$

Substituting the value of K_{ex} from equation (4), then:

$$\log D/D_0 = \log\{1 + \beta_1\,[L] + \beta_2\,[L^2] + \ldots + \beta_n\,[L^n]\} \quad (9)$$

where D and D_0 are the distribution ratios in the presence and absence of L respectively. Thus, the curve of $\log D/D_0$ *vs.* $\log [L]$ has two asymtotes:

$$\text{(i) for } L \longrightarrow 0,\ \log D\,[H^+] / [HQ]^2 = \log K_{ex} \quad (10)$$

and $\log D/D_0 = 0$

$$\text{(ii) for } L \longrightarrow \infty,\ \log D\,[H]^2 / [HQ]^2 = \log K_{ex}\,\beta_n\,L^n \quad (11)$$

and

$$\log D/D_0 = \log \beta_n\,L^n = \log \beta_n + n \log L \quad (12)$$

At the point of intersection $\log D/D_0 = 0$, therefore:

$$\log \beta_n = -n \log L \quad (13)$$

The slope of the curves gives the ligand number, n, and β_n is the adduct formation constant in the organic phase of the 1 : 2 chelate and n moles of the adduct-forming base, L. In practice, a plot of log D *vs.* $\log [L]$ is plotted at constant

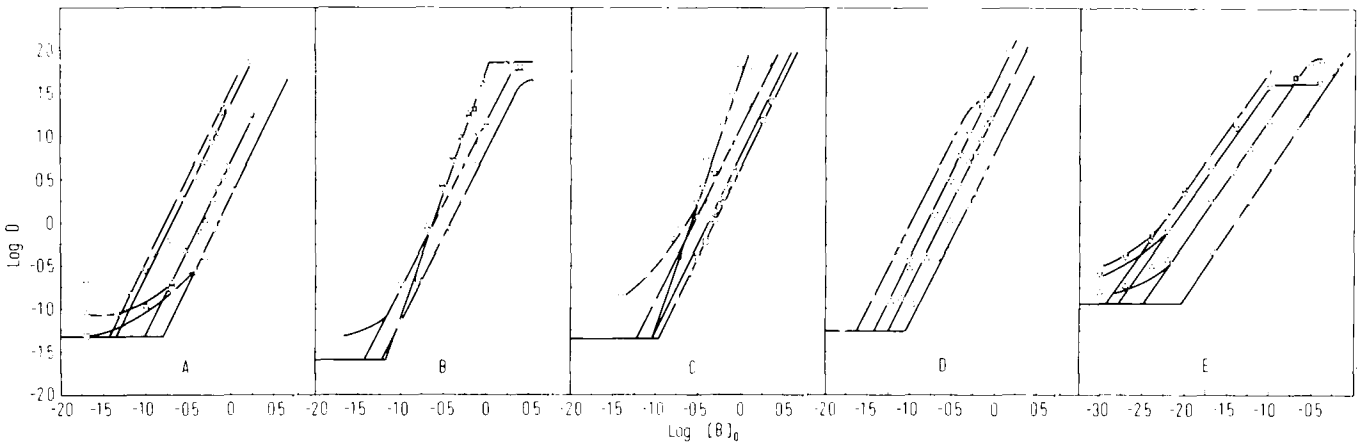

Figure 1. Distribution of pyridine adducts of cobalt-8-quinolinates between chloroform and water, pH = 5.0; ○ pyridine, △ 2,4,6-collidine, ▽ 2,4-lutidine and □ 2-picoline. A [*8-HQ*] = 1.25×10^{-3} M; B [*2-Me-8-HQ*] = 2×10^{-2} M; C [*4-Me-8-HQ*] = 1.0126×10^{-3} M; D [*5-Cl-8-HQ*] = = 1.0736×10^{-3} M; E [*5-NO_2-8-HQ*] = 8.18×10^{-5} M

[*HQ*] and constant pH giving two straight lines. The horizontal curve representing log D_0, in the absence of the neutral ligand, intercepts the other curve and the point of intersection gives directly the value of the adduct formation constant from equation (13).

Plots of log D *vs.* log [*B*] where B is the ligand L, are shown in Figure 1. The slope of most of these plots is two, indicating that two molecules of pyridine are attached to the cobalt chelate, thus forming an extractable diadduct. With 2-methyl- and 4-methyl-8-quinolinol, however, the slope of these plots with collidine is three, indicating that three molecules are involved in adduct formation instead of two as in other cases (Figures 1b and 1c). This might be due to oxidation of Co^{II} to Co^{III} in the presence of strongly basic chelating agents, such as collidine and 2-methyl- and 4-methyl-8-quinolinol. The pK values of collidine and 2-methyl- and 4-methyl-8-quinolinols are largest among all pyridines and oxines, respectively. It is not uncommon for cobalt ions to be extracted as Co^{III}. This was confirmed further by repeating the extractions in the presence of a strong reducing agent such as hydroxylamine hydrochloride, when the plots of slope two were obtained in these cases (not shown in the Figure).

During the course of extraction, two molecules of water, which would have remained attached to the metal chelate in the absence of excess of reagent HQ, were removed by pyridine molecules occupying the coordination sites of cobalt, leaving the extractable complex in the hexacoordinate state. The presence of two water molecules in the isolated cobalt chelate was confirmed earlier in the thermogravimetric study of the chelate.

The formation constants of pyridine : cobalt-8-quinolinate adducts are given in Table 1. From Table 1, it can be seen that these values are maximal for pyridine whereas for those of 2-picoline, they are minimal. Thus, the stabilities of the pyridine adducts are greater than those of the methylated pyridine adducts. All the methyl derivatives of pyridine contain a methyl group at position 2. The lower stabilities, for 2-picoline, lutidine and collidine are undoubtedly due to steric hindrance caused by the methyl group at position 2. Steric hindrance is maximal with 2-picoline. The order of adduct formation was found to decrease in the following order:

Pyridine > 2,4,6-collidine > 2,4-lutidine > 2-picoline

It would appear that the structure resulting from the introduction of methyl groups in the vicinity of the nitrogen atom should produce more steric hindrance towards the extraction of the complex as an adduct. Actually, the stabilities of the complexes instead of decreasing in the order: 2-picoline > lutidine > collidine were found to increase (*vide* Table 1) gradually with lutidine and collidine. This may be due to the presence of a methyl group at position 4, which also causes an increase in the basicity, *i.e.* the pK value of the base. The steric effect due to the methyl groups at the 2- and 6-positions is counteracted by the overall basicity of the base including the methyl group at position 4 resulting in a gradual stability increase. The methyl group at position 4 is more reactive, as was shown earlier[7] by the formation of a stronger adduct with 4-picoline. The pyridine adducts follow the order of the base strength in their reactivity with the exception of parent pyridine. This is shown by the gradual increase in the adduct formation constants and is maximal for pyridine, although its pK value is minimal. Thus, there is competition between the steric effect produced by

Table 1. Formation constants for various pyridine : cobalt-8-quinolinate adducts in $CHCl_3$

Base	pK[11, 12]	8-Quinolinol	2-Methyl-8-quinolinol	4-Methyl-8-quinolinol	5-Chloro-8-quinolinol	5-Nitro-8-quinolinol
Pyridine	5.20	2.85	2.85	2.43	3.26	5.86
2-Picoline	5.90	1.60	2.45	1.925	2.075	4.075
2,4-Lutidine	6.72	2.02	2.8[a]	2.075	2.60	4.975
2,4,6-Collidine	7.50	2.70	2.66[a]	2.60[a]	2.85	5.575

[a] Extractions performed in the presence of $NH_2OH \cdot HCl$.

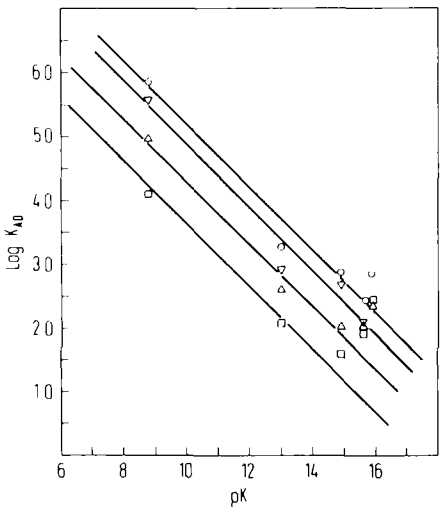

Figure 2. Correlation between adduct formation constants of cobalt pyridine adducts and the basicities of chelating agents; ○ pyridine, ▽ 2,4,6-collidine, △ 2,4-lutidine and □ 2-picoline

the methyl groups at the 2- and 6-positions and the synergistic effect produced by the increase in basicity due to methyl groups present. The adduct formation constant observed is, therefore, the resultant of these two effects. The influences of chelate stability of reagent basicity on adduct formation also counteract each other.

A linear correlation was observed when the logarithm of the adduct formation constants were plotted against the pK values of the 8-quinolinols (see Figure 2). This correlation indicates that the general trend is followed *i.e.*, the greater the stability of the metal chelate, the smaller the residual Lewis acidity and consequently the less favourable the conditions for adduct formation. Similar observations were made by Freiser and others[5, 6] during their studies of zinc(II) and nickel(II) adducts with 8-quinolinols and pyridine bases, respectively.

From our study, it is concluded that pyridine bases form diadducts with cobalt-8-quinolinates. X-ray diffraction studies[9, 10] of the 8-quinolinate chelate dihydrate show that the complexes of some metals possess a *trans*-coplanar arrangement of the two water molecules located at axial positions completing a hexacovalent octahedral structure. These metals form $MQ_2 \cdot 2\,H_2O$ compounds (M = Zn, Cd, Co, Ni and Pb) which are isomorphous, as investigated by Merritt *et al.*[9]. Diadduct formation for the pyridine : cobalt-8-quinolinate adduct, would just involve the replacement of axial water molecules by the pyridine molecules. Previous studies with zinc[5] and nickel[6] have indicated already the octahedral nature of the complex containing two apical pyridine molecules. The cobalt chelate, $CoQ_2 \cdot 2\,H_2O$, is isomorphous with the nickel and zinc chelates as suggested by Merritt *et al.*[9], and we conclude that the diadducts, $CoQ_2 \cdot 2P$, formed by pyridines with cobalt-8-quinolinates, are hexacoordinate, giving rise to an octahedral structure.

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