**Figure 3.** Comparison between calculated and observed values of $m_{Co(or)}$.

in which $m_{H_2R_2} = m_{H_2R_{2(init)}} - 2m_{Co(or)}$; subscript (init) refers to the initial concentration.

Inspection of Figure 2 shows that the $K_1^{11}$ is a function of $(m_{Co(or)}/m_{H_2R_2})$ and the initial concentration of extractant only.

It is convenient to express the initial concentration in terms of mole fraction, $X_{H_2R_{2(init)}}$. Thus we have

$$K_1^{11} = a + bX_{H_2R_{2(init)}} + c(X_{H_2R_{2(init)}})^2 + d(m_{Co(or)}/m_{H_2R_2}) +$$
$$e(m_{Co(or)}/m_{H_2R_2})^2 + fX_{H_2R_{2(init)}}(m_{Co(or)}/m_{H_2R_2}) +$$
$$gX_{H_2R_{2(init)}}(m_{Co(or)}/m_{H_2R_2})^2 \quad (36)$$

The best fit parameters were $a = 0.00488$, $b = 2.4089$, $c = -23.4329$, $d = 0.3090$, $e = 0.5607$, $f = 9.2910$, and $g = -17.4210$. The concentration of Co in the organic phase can then be calculated from the following second-order equation.

$$(m_{Co(or)}/m_{H_2R_2})^2 (e + gX_{H_2R_{2(init)}}) +$$
$$(m_{Co(or)}/m_{H_2R_2})(d + fX_{H_2R_{2(init)}} - K^{-1/2} (a_{H^+}^2/a_{Co(aq)})^{1/2}) +$$
$$a + bX_{H_2R_{2(init)}} + cX_{H_2R_{2(init)}}^2 = 0 \quad (37)$$

The comparison between calculated and observed values of $m_{Co(or)}$ is made in Figure 3. The standard deviation is 8.642 $\times$ 10$^{-3}$ which suggests a reasonable fit (although considerable scatter for some points is evident). In Figure 3 a few points, for which the $m_{Co(or)} > 0.05$, were not plotted since the scale of the plot would be too extended.

**Conclusion**

(1) The activity coefficient of $Co^{2+}$ in the multicomponent aqueous phase was calculated by using Pitzer's equation with the consideration of ion-pair $CoSO_4$. The correctness of this calculation was checked by our experiments.

(2) Thermodynamic extraction constant $K$ was estimated by using Petkovic's method. From five sets of initial extraction concentrations a reasonable constant value of $K$ was obtained.

(3) The activity coefficients of the organic phase were calculated, and the equivalent concentration scale was used to describe the extraction equilibria. It was shown that with the use of the equivalent scale the functions become much simpler than if the molality were used to express thermodynamic concentration.

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# Synergic Extraction of Mixed Adducts of Cobalt(II) 8-Quinolinates[†]

**Arvind T. Rane**

*Tata Institute of Fundamental Research, Bombay 400 005, India*

Cobalt(II) forms the strongest adduct with 5-nitro-8-quinolinol. Among all other oxines, the 5-NO$_2$ analogue was the least basic and its 2-methyl analogue was the most basic ligand investigated. An adduct of cobalt 2-methyl-8-quinolinate chelate as an acceptor and 5-nitro-8-quinolinol as a donor forms the strongest adduct, whereas that of cobalt 5-nitro-8-quinolinate as an acceptor and 2-methyl-8-quinolinol as a donor forms the weakest adduct. Synergic enhancement was observed in the extraction of Co(II) on the addition of small amounts of 5-nitro-8-quinolinol due to the formation of the most stable adduct, Co(2-Me-8-Q)$_2$·(5-NO$_2$-8-HQ). Relatively less stable adducts were observed when 5-NO$_2$-8-HQ was used as a chelating agent and other oxines as adducting ligands. Synergy coefficients of Co(II) adducts of the mixed ligands were evaluated.

**Introduction**

In the solvent extraction studies of nickel (*1*) and cobalt(II) (*2*) with 8-quinolinol and its substituted analogues, it was observed that the adduct formation constants increase with the decrease in the basicity of the ligands. Similar trend was observed in the extraction of pyridine adducts of nickel (*3*) and cobalt 8-quinolinates (*4*). The value of the adduct formation constant was found to be maximum with 5-nitro-8-quinolinol whose p$K$ value was the least, i.e., 8.79, among the oxines studied. This was attributed to the dual function of the reagents which act both as an acceptor-chelating agent and as a donor base. As a result the increase in the donor basicity was compensated, to a certain extent, by the ability to form with a weaker acceptor a more stable metal adduct.

Among the oxines studied, the 5-nitro-8-quinolinol ligand was the least basic and its 2-methyl analogue was the most basic ligand investigated. An adduct of cobalt 2-methyl-8-quinolinate chelate as an acceptor and 5-nitro-8-quinolinol as a donor would be the strongest adduct or an adduct of cobalt-5-nitro-8-

**Table I. 5-Nitro-8-quinolinol ($pK$ = 8.79) as Adducting Agent**

| chelating ligand | $pK$ | $\beta_2$ |
|---|---|---|
| 8-quinolinol | 14.9 | 8.40 |
| 2-methyl-8-quinolinol | 15.9 | 9.06 |
| 4-methyl-8-quinolinol | 15.66 | 8.30 |
| 5-chloro-8-quinolinol | 13.0 | 7.95 |

**Table II. 5-Nitro-8-quinolinol as Chelating Ligand**

| adducting agent | $\beta_2$ |
|---|---|
| 8-quinolinol | 5.35 |
| 2-methyl-8-quinolinol | 4.30 |
| 4-methyl-8-quinolinol | 5.75 |
| 5-chloro-8-quinolinol | 4.95 |

quinolinate chelate as an acceptor and 2-methyl-8-quinolinol as a donor would be the weakest adduct. In the spectrophotometric investigation of nickel 5-nitro-8-quinolinate, it was observed that nickel could form such a mixed adduct between two substituted ligands having different $pK$ values (5). The value of the formation constant of such an adduct of mixed ligands was found to be much more than the normal self-adduct. If such considerable difference in the adduct formation constant was observed with substituted ligands having different $pK$ values, it would be possible to increase the extent of extraction through the formation of a mixed adduct due to synergic enhancement. Earlier it was thought that the chelate-forming ligand might interfere with the adducting ligand, i.e., donor. This difficulty could be overcome by keeping the chelating ligand concentration just sufficient enough to form chelate at low pH and varying donor ligand's concentration.

An attempt is made here to investigate the extraction of mixed cobalt(II) chelates of parent and the substituted analogues of 8-quinolinol in two ways: (1) 5-nitro-8-quinolinol acting as a donor and chelates of other substituted 8-quinolinols as acceptor and (2) chelate of 5-nitro-8-quinolinol as an acceptor and other 8-quinolinols as donor. The synergy coefficients of these ligands were also evaluated.

## Experimental Section

Carrier-free $^{58}$Co ($t_{1/2}$ = 72 days) was supplied by the Isotope Division, B.A.R.C., Trombay, as $CoCl_2$. A few drops of saturated solution of hydroxylamine hydrochloride were added to prevent the oxidation of Co(II).
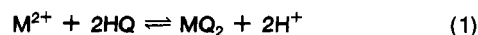
A potassium hydrogen phthalate buffer solution (pH 4.0) was prepared and ionic strength was maintained constant at 0.25 M by sodium perchlorate.

All the oxines were recrystallized from ethyl alcohol.

*Procedure.* The buffered $^{58}$Co(II) solution (5 mL) at pH 4.0 with 0.25 ionic strength and the reagent solution in chloroform (chelating agent + varied amount of adducting agent) was equilibrated by shaking for 30 min in a shaking machine. The mixtures, after equilibration, were centrifuged and equal volumes of both the phases were pipetted out and counted separately on a scintillation spectrometer at constant geometry.

## Results and Discussion

For a simple extraction system containing a divalent metal ion $M^{2+}$ and a chelating acid HQ, the extraction equilibrium may be written as

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

and

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

the distribution coefficient is

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

$$\therefore D_0 = K_{ex}[HQ]^2/[H^+]^2 \qquad (4)$$

For mixed adduct formation with chelating acid HQ and adducting ligand HQ', the equilibrium may then be written as

$$M^{2+} + 2HQ + nHQ' \rightleftharpoons MQ_2 \cdot nHQ' + 2H^+ \qquad (5)$$

with equilibrium constant

$$\beta_n K_{ex} = [MQ_2 \cdot n HQ'][H^+]^2/[M^{2+}][HQ]^2[HQ']^n \qquad (6)$$

where

$$\beta_n = [MQ_2 \cdot n HQ']/[MQ_2][HQ']^n \qquad (7)$$

$$\therefore \log D[H^+]^2[HQ]^2 =$$
$$\log K_{ex}\{1 + \beta_1[HQ'] + ... + \beta_n[HQ']^n\} \qquad (8)$$

Substituting the values of $K_{ex}$

$$\log D/D_0 =$$
$$\log \{1 + \beta_1[HQ'] + \beta_2[HQ']^2 + ... + \beta_n[HQ']^n\} \qquad (9)$$

where $D$ and $D_0$ are the distribution coefficients in the presence and absence of HQ', respectively. Thus, the plot of $\log D/D_0$ vs. $\log [HQ']$ has two asymptotes

(i) $\qquad$ for HQ' $\rightarrow$ 0, $\log D/D_0 = 0$ $\qquad (10)$

(ii) $\qquad$ for HQ' $\rightarrow \infty$, $\log D/D_0 = \log \beta_n[HQ']^n$

$$= \log \beta_n + n \log [HQ'] \qquad (11)$$

At the point of intersection, i.e., the intercept on the $x$ axis
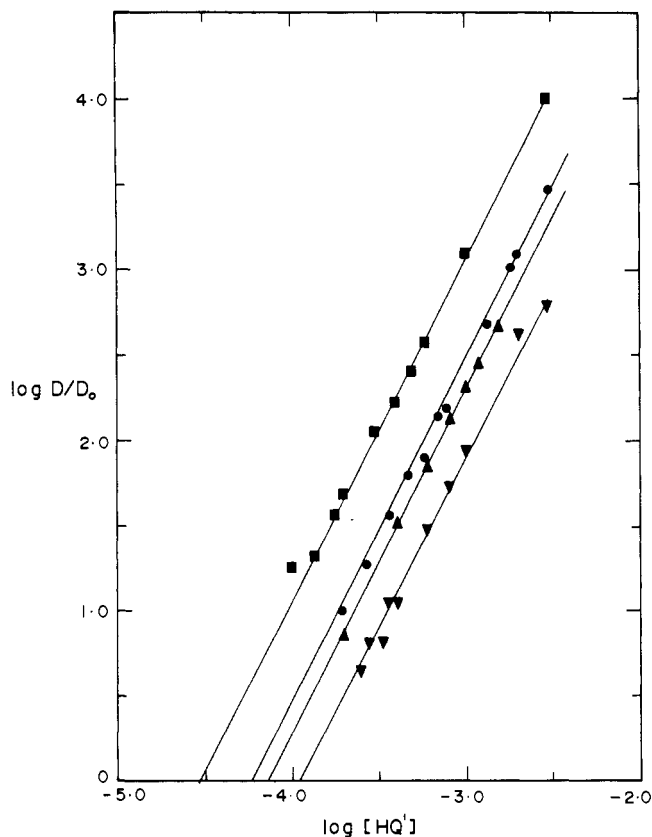
$$\log \beta_n = -n \log [HQ'] \qquad (12)$$

The slope of asymptote (ii) gives the number of adducting ligands, $n$, attached, and $\beta_n$ is the adduct formation constant in the organic phase.
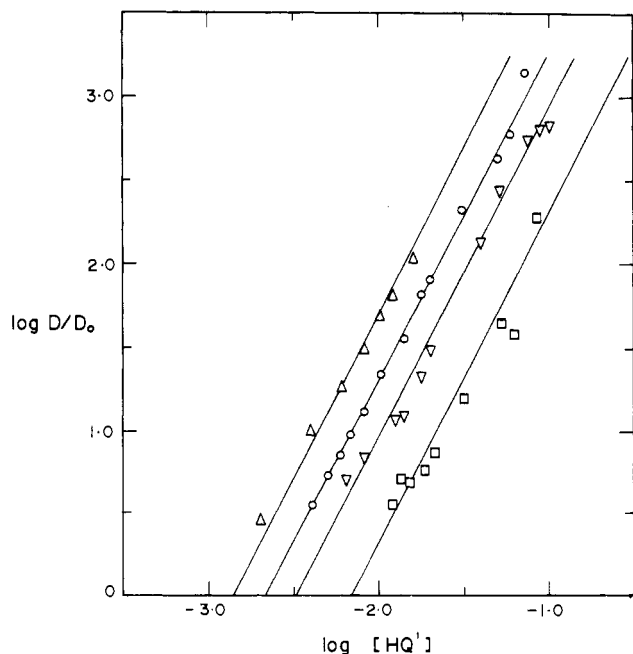
Plots of $\log D/D_0$ vs. $\log [HQ']$ are shown in Figures 1 and 2. In Figure 1, 5-nitro-8-quinolinol is acting as a donor, i.e., adduct-forming base, and parent and other substituted oxines are chelate-forming acids, i.e., acceptors, and in Figure 2 vice versa. The slope of all these plots is two, indicating that two molecules of adduct-forming ligand are attached to the cobalt chelate, thus forming a diadduct having an empirical formula, $CoQ_2 \cdot 2HQ'$. Presence of reducing agent like hydroxylamine hydrochloride was very essential to prevent the oxidation of Co(II) to Co(III), particularly during the extraction with excess of ligands of higher $pK$ values. A similar observation was reported earlier in the extraction of Co(II) with oxines and heterocyclic nitrogen bases (4).

The formation constants of adducts of cobalt 8-quinolinates with 5-NO$_2$-8-HQ as adducting agent, i.e., donor, are given in Table I, and those of 5-NO$_2$-8-HQ as chelating agent or acceptor are given in Table II. From these results, it could be seen that the values of formation constant with 5-NO$_2$-8-HQ as adducting agent are much higher than those with 5-NO$_2$-8-HQ as chelating agent. It is interesting to note that these values are maximal with the cobalt chelate of 2-methyl-8-quinolinol as acceptor and minimal with 2-methyl-8-quinolinol as donor. This confirms the earlier assumption that the adduct formation constant would be maximum with chelates of ligands having higher $pK$ values adducting with ligands having lower $pK$ values (5). The adducting oxine is acting as a neutral ligand.

*The Influence of Extractant Concentration.* The equilibrium experiments of buffered cobalt(II) solution at pH 4.0 were carried out between the organic phases having concentrations from 4 × 10$^{-4}$ M to 1 × 10$^{-2}$ M of mixtures of 5-NO$_2$-8-HQ and

**Figure 1.** Influence of 5-NO$_2$-8-HQ concentration on Co(II) extraction with mixture of other oxines at pH 4.0. Final oxine concentrations, 5-NO$_2$-8-HQ varying, are as follows: (●) [8-HQ]$_0$ = 10$^{-3}$ M; (■) [2-Me-8-HQ]$_0$ = 2 × 10$^{-2}$ M; (▲) [4-Me-8-HQ]$_0$ = 4 × 10$^{-2}$ M; (▼) [5-Cl-8-HQ]$_0$ = 2 × 10$^{-3}$ M.



**Figure 2.** Influence of oxine concentration on Co(II) extraction with a mixture of 5-NO$_2$-8-HQ at pH 4.0. Final [5-NO$_2$-8-HQ]$_0$ = 2 × 10$^{-4}$ M, other oxines varying: (O) 8-HQ; (□) 2-Me-8-HQ; (△) 4-Me-8-HQ; (▽) 5-Cl-8-Hq.

Table III. Influence of Extractant Concentration on Co(II) Extraction with a Mixture of 8-HQ and 5-NO$_2$-8-HQ at pH 4.0

| organic phase compn | $D$ | $D_1 + D_2$ | $S$ |
|---|---|---|---|
| 0.0004 M 8-HQ | 0.0107 | | |
| 0.0004 M 5-NO$_2$-8-HQ | 0.0237 | 0.0344 | 0.7446 |
| 0.0004 M 8-HQ + 0.0004 M 5-NO$_2$-8-HQ | 0.191 | | |
| 0.0008 M 8-HQ | 0.008856 | | |
| 0.0008 M 5-NO$_2$-8-HQ | 0.1884 | 0.1972 | 0.7315 |
| 0.0008 M 8-HQ + 0.0008 M 5-NO$_2$-8-HQ | 1.063 | | |
| 0.001 M 8-HQ | 0.0113 | | |
| 0.001 M 5-NO$_2$-8-HQ | 0.4467 | 0.4580 | 0.5709 |
| 0.001 M 8-HQ + 0.001 M 5-NO$_2$-8-HQ | 1.7053 | | |
| 0.002 M 8-HQ | 0.0116 | | |
| 0.002 M 5-NO$_2$-8-HQ | 2.5344 | 2.5460 | 0.5980 |
| 0.002 M 8-HQ + 0.002 M 5-NO$_2$-8-HQ | 10.09 | | |
| 0.004 M 8-HQ | 0.0256 | | |
| 0.004 M 5-NO$_2$-8-HQ | 18.84 | 18.8656 | 0.2621 |
| 0.004 M 8-HQ + 0.004 M 5-NO$_2$-8-HQ | 34.50 | | |
| 0.005 M 8-HQ | 0.0304 | | |
| 0.005 M 5-NO$_2$-8-HQ | 36.3211 | 36.3515 | 0.1566 |
| 0.005 M 8-HQ + 0.005 M 5-NO$_2$-8-HQ | 52.13 | | |
| 0.008 M 8-HQ | 0.0737 | | |
| 0.008 M 5-NO$_2$-8-HQ | 78.730 | 78.8037 | −1.1027 |
| 0.008 M 8-HQ + 0.008 M 5-NO$_2$-8-HQ | 6.2195 | | |
| 0.01 M 8-HQ | 0.1084 | | |
| 0.01 M 5-NO$_2$-8-HQ | 298.50 | 298.608 | −1.8773 |
| 0.01 M 8-HQ + 0.01 M 5-NO$_2$-8-HQ | 3.9608 | | |

Table IV. Influence of Extractant Concentration on Co(II) Extraction with a Mixture of 2-Me-8-HQ and 5-NO$_2$-8-HQ at pH 4.0

| organic phase compn | $D$ | $D_1 + D_2$ | $S$ |
|---|---|---|---|
| 0.0002 M 2-Me-8-HQ | 0.00166 | | |
| 0.0002 M 5-NO$_2$-8-HQ | 0.00335 | 0.00501 | 0.7124 |
| 0.0002 M 2-Me-8-HQ + 0.0002 M 5-NO$_2$-8-HQ | 0.02584 | | |
| 0.0004 M 2-Me-8-HQ | 0.0044 | | |
| 0.0004 M 5-NO$_2$-8-HQ | 0.0237 | 0.0281 | 0.4194 |
| 0.0004 M 2-Me-8-HQ + 0.0004 M 5-NO$_2$-8-HQ | 0.0738 | | |
| 0.0008 M 2-Me-8-HQ | 0.00449 | | |
| 0.0008 M 5-NO$_2$-8-HQ | 0.1884 | 0.19289 | 0.2413 |
| 0.0008 M 2-Me-8-HQ + 0.0008 M 5-NO$_2$-8-HQ | 0.3362 | | |
| 0.001 M 2-Me-8-HQ | 0.00246 | | |
| 0.001 M 5-NO$_2$-8-HQ | 0.4467 | 0.44916 | 0.2584 |
| 0.001 M 2-Me-8-HQ + 0.001 M 5-NO$_2$-8-HQ | 0.8143 | | |
| 0.002 M 2-Me-8-HQ | 0.00352 | | |
| 0.002 M 5-NO$_2$-8-HQ | 2.50 | 2.50352 | −0.1875 |
| 0.002 M 2-Me-8-HQ + 0.002 M 5-NO$_2$-8-HQ | 1.6258 | | |
| 0.004 M 2-Me-8-HQ | 0.00473 | | |
| 0.004 M 5-NO$_2$-8-HQ | 18.844 | 18.84873 | −0.9953 |
| 0.004 M 5-NO$_2$-8-HQ + 0.004 M 5-NO$_2$-8-HQ | 1.905 | | |
| 0.01 M 2-Me-8-HQ | 0.6108 | | |
| 0.01 M 5-NO$_2$-8-HQ | 298.50 | 299.11 | −1.6487 |
| 0.01 M 2-Me-8-HQ + 0.01 M 5-NO$_2$-8-HQ | 6.7159 | | |

other substituted oxines. The synergy coefficient, $S$, was calculated from the formula $S = \log D/(D_1 + D_2)$, where $D$, $D_1$, and $D_2$ are distribution coefficients of the mixture of extractants and individual extractants, respectively (6). These

results are given in Tables III–VI.

It is very interesting to note that the synergy constant, $S$, goes on decreasing with the increase in extractant concentration. The experiments were repeated twice, particularly in the cases where the values of $S$ were found negative when consistent and reproducible results were obtained. The synergism produced is undoubtedly due to a change in the composition of

**Table V. Influence of Extractant Concentrations on Co(II) Extraction with a Mixture of 4-Me-8-HQ and 5-NO$_2$-8-HQ at pH 4.0**

| organic phase compn | $D$ | $D_1 + D_2$ | $S$ |
|---|---|---|---|
| 0.0004 M 4-Me-8-HQ | 0.00942 | | |
| 0.0004 M 5-NO$_2$-8-HQ | 0.0237 | 0.03312 | 0.8794 |
| 0.0004 M 4-Me-8-HQ + 0.0004 M 5-NO$_2$-8-HQ | 0.2509 | | |
| 0.0008 M 4-Me-8-HQ | 0.0094 | | |
| 0.0008 M 5-NO$_2$-8-HQ | 0.1884 | 0.1978 | 1.2761 |
| 0.008 M 4-Me-8-HQ + 0.0008 M 5-NO$_2$-8-HQ | 3.7354 | | |
| 0.001 M 4-Me-8-HQ | 0.0582 | | |
| 0.001 M 5-NO$_2$-8-HQ | 0.4467 | 0.5049 | 1.0892 |
| 0.001 M 4-Me-8-HQ + 0.001 M 5-NO$_2$-8-HQ | 6.20 | | |
| 0.002 M 4-Me-8-HQ | 0.0616 | | |
| 0.002 M 5-NO$_2$-8-HQ | 2.50 | 2.5616 | 1.0420 |
| 0.002 M 4-Me-8-HQ + 0.002 M 5-NO$_2$-8-HQ | 28.10 | | |
| 0.004 M 4-Me-8-HQ | 0.1032 | | |
| 0.004 M 5-NO$_2$-8-HQ | 18.840 | 18.9432 | 0.3006 |
| 0.004 M 4-Me-8-HQ + 0.004 M 5-NO$_2$-8-HQ | 37.850 | | |
| 0.008 M 4-Me-8-HQ | 0.3317 | | |
| 0.008 M 5-NO$_2$-8-HQ | 78.73 | 79.0617 | −0.2732 |
| 0.008 M 4-Me-8-HQ + 0.008 M 5-NO$_2$-8-HQ | 42.15 | | |
| 0.01 M 4-Me-8-HQ | 0.4311 | | |
| 0.01 M 5-NO$_2$-8-HQ | 298.50 | 298.9311 | −0.7955 |
| 0.01 M 4-Me-8-HQ + 0.01 M 5-NO$_2$-8-HQ | 47.87 | | |

**Table VI: Influence of Extractant Concentration on Co(II) Extraction with a Mixture of 5-Cl-8-HQ and 5-NO$_2$-8-HQ at pH 4.0**

| organic phase compn | $D$ | $D_1 + D_2$ | $S$ |
|---|---|---|---|
| 0.0004 M 5-Cl-8-HQ | 0.003343 | | |
| 0.0004 M 5-NO$_2$-8-HQ | 0.02371 | 0.02705 | 0.3144 |
| 0.0004 M 5-Cl-8-HQ + 0.0004 M 5-NO$_2$-8-HQ | 0.0558 | | |
| 0.0008 M 5-Cl-8-HQ | 0.008656 | | |
| 0.0008 M 5-NO$_2$-8-HQ | 0.1884 | 0.1970 | 0.4601 |
| 0.0008 M 5-Cl-8-HQ + 0.0008 M 5-NO$_2$-8-HQ | 0.5684 | | |
| 0.001 M 5-Cl-8-HQ | 0.008065 | | |
| 0.001 M 5-NO$_2$-8-HQ | 0.4467 | 0.4547 | 0.1352 |
| 0.001 M 5-Cl-8-HQ + 0.001 M 5-NO$_2$-8-HQ | 0.6209 | | |
| 0.002 M 5-Cl-8-HQ | 0.01288 | | |
| 0.002 M 5-NO$_2$-8-HQ | 2.7935 | 2.8063 | 0.02552 |
| 0.002 M 5-Cl-8-HQ + 0.002 M 5-NO$_2$-8-HQ | 2.9762 | | |
| 0.004 M 5-Cl-8-HQ | 0.01729 | | |
| 0.004 M 5-NO$_2$-8-HQ | 18.840 | 18.8573 | −0.6054 |
| 0.004 M 5-Cl-8-HQ + 0.004 M 5-NO$_2$-8-HQ | 4.678 | | |
| 0.008 M 5-Cl-8-HQ | 0.05675 | | |
| 0.008 M 5-NO$_2$-8-HQ | 78.736 | 78.7867 | −1.1238 |
| 0.008 M 5-Cl-8-HQ + 0.008 M 5-NO$_2$-8-HQ | 5.9244 | | |
| 0.01 M 5-Cl-8-HQ | 0.129 | | |
| 0.01 M 5-NO$_2$-8-HQ | 298.80 | 298.929 | −1.7175 |
| 0.01 M 5-Cl-8-HQ + 0.01 M 5-NO$_2$-8-HQ | 5.729 | | |

the compound extracted with the mixture of extractants as compared to that extracted with the individual oxine of the mixture. All the oxines, except the 2-methyl analogue, when extracted alone give a slope of 3 for log $D$ vs. log [HQ] plots in contrast to the slope 2 obtained in the log $D/D_0$ vs. log [HQ'] plots in the present study. The advantage of plotting log $D/D_0$ instead of log $D$ in these plots is that all the plots of different adducting ligands are normalized and brought on the same base line, irrespective of the final chelating ligand's concentration. In the extraction of self-adducts, monoadducts are formed, whereas diadducts are obtained in the mixed adduct system giving rise to an octahedral bipyramidal hexacoordinated structure in contrast to the pentacoordinated square base pyramidal structure exhibited in the self-adducts. This has been inferred from the earlier findings of Merritt et al. (7) and Palenik (8) who determined the crystal structure of the dihydrates of zinc and copper 8-quinolinates, by X-ray crystallography, the chelates of which are isomorphous with those of Co(II) and Ni(II) oxinates. The possibility of formation of self-adducts before the formation of mixed adduct is ruled out because of the low concentration of the chelating ligand, which favors the formation of a simple 1:2 chelate as shown in the previous studies (1, 2). The slope of 2 obtained in the present study clearly indicates two additional molecules of adducting ligand joined to the chelate. If any self-adduct formation had taken place before the addition of adducting ligand it would have saturated the coordination number of Co$^{2+}$ and there would not have been synergic extraction. In that case the value of log $D/D_0$ would remain zero irrespective of the adducting ligand's concentration. The concentration of the chelating oxine was just optimum enough to form a simple chelate with the metal

ion, whereas, the concentration of the adducting donor ligand was comparatively too low to compete with the chelating ligand to form a chelate but sufficient enough to form an adduct.

The pH of the extraction system was maintained at 4.00 as Co(II) gets appreciably extracted with 5-NO$_2$-8-HQ at pH $\geqslant$ 4 whereas, at the same pH, with other oxines, the extraction is very low (2). Another interesting fact is that 2-methyl-8-quinolinol can extract synergistically with 5-NO$_2$-8-HQ and form an adduct, Co(2-Me-8-Q)$_2$·(5-NO$_2$-8-HQ), in spite of the methyl group present at 2-position, because of its high p$K$ value as compared to other oxines as seen from the tables. The negative values of synergy coefficients obtained at higher concentrations may be due to a decrease in the activity of the extractants caused by their interaction because of difference in the p$K$ values. Thus it is possible to produce synergism with the use of similar ligands having different p$K$ values.

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