Effects of the Anion on the Extraction of Cobalt with 8-Quinolinol into Chloroform

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The effects of the anions, especially the perchlorate ion, on the extraction of cobalt into chloroform with 8-quinolinol (Hql) were examined. Two kinds of cobalt(II) 8-quinolinol complexes, species A and B, are extracted into the chloroform phase from the aqueous cobalt(II) solution containing perchlorate ions. Species A contains no perchlorate ion and is extracted above pH 7.7; species B is an ion-pair complex containing a perchlorate ion and is predominantly extracted below pH 5.1. The compositions of species A and B were estimated to be $Co_2ql_4(Hql)_2$ and $Co_2ql_3(Hql)_3ClO_4$, respectively. These dimer complexes are related by the following equilibrium, with $\log K_{AB} = -7.2$:

$$[Co_2ql_3(Hql)_3]^+ClO_{4(o)}^- \rightleftharpoons Co_2ql_4(Hql)_{2(o)} + ClO_4^- + H^+$$

The species extracted into the chloroform phase from the aqueous cobalt(II) solution containing sulfate ions does not contain any sulfate ions. The formation of the species containing anions increases in the order: $ClO_4^- > NO_3^- > Cl^- > SO_4^{2-}$, which is also the general order of the extent of forming the ion-pair compounds. The ion-pair complex tends to prevent the oxidation from cobalt(II) 8-quinolinol complex to cobalt(III) 8-quinolinol complex.

The stoichiometric behavior of the extraction of cobalt into chloroform containing 8-quinolinol (Hql) has been studied by several investigators.[1-4] In these studies it was reported that the species extracted into chloroform is not the simple cobalt 8-quinolinol chelate, $Coql_2$, but the self-adduct, such as $Coql_2(Hql)_2$,[1,2] or $Coql_2Hql$.[3,4] These stoichiometric studies, of course, were carried out under the condition of a constant ionic strength, which was adjusted by the addition of a salt such as sodium perchlorate or potassium chloride. On the other hand, Ōki *et al.* recently reported that an ion-pair complex is extracted into chloroform when a zinc solution containing perchlorate ions is shaken with a chloroform solution containing 8-quinolinol.[5] They suggested the formation of an ion-pair complex for nickel as well as for zinc.[6] Moreover, Sekido *et al.* studied the effects of various kinds of anions on the extraction of zinc with the chloroform solution of 8-quinolinol;[7] the compositions of the zinc 8-quinolinol complexes extracted were also determined.[8] Consequently, it will be assumed that the extraction of cobalt with chloroform containing 8-quinolinol may also be affected by the kind of anion contained in the aqueous solution. Thus, in this study, the extraction behavior of the cobalt with the chloroform solution of 8-quinolinol from an aqueous solution containing one of such anions as the perchlorate, nitrate, sulfate, or chloride ion have been reexamined.

Experimental

Reagents. 8-Quinolinol was recrystallized twice from ethanol (mp 73—73.5 °C). The chloroform was shaken with dilute hydrochloric acid solution, sodium hydroxide solution, and demineralized water, dried with anhydrous sodium sulfate, and then distilled twice. Cobalt perchlorate and nitrate in analytical-reagent grade were used to prepare stock solutions of cobalt; their concentrations were determined by chelatometric titrations. Carrier-free ^{60}Co radiotracer was added to the stock solutions when the distribution ratio of cobalt was determined. The sodium salts of perchlorate, nitrate, sulfate, and chloride and the buffer components were all of analytical-reagent grade.

Apparatus. Extraction was carried out in a Taiyo M incubator at 25±0.1 °C. A Japan Radio well-type NaI(Tl) scintillation detector connected with a Toshiba UDS-24202 B universal scalar was used for the radioactivity counting. Ultraviolet and visible absorption spectra of the chloroform phase were taken with a Hitachi 124 double beam spectrophotometer and the pH of the aqueous phase was measured with a Hitachi-Horiba M-5 pH meter.

Extraction of Cobalt. Into a 50 ml glass cylindrical tube with a glass stopper was introduced 1.00 ml of 1×10^{-3} M cobalt(II) perchlorate or nitrate solution, adjusted to the desired pH with a small amount of a buffer solution. Then the sodium salt solution of the appropriate anion, whose effect was to be examined, was added, so that 10.00 ml of the final cobalt solution could be kept at the ionic strength of 0.1 or 1.0. The buffer solution was made with the mineral acid having the appropriate anion, sodium hydroxide, or such a small amount of acetic acid or boric acid that we could ignore the effect of the acetate or borate anion. After the addition of 10 ml of 0.1 M chloroform solution of 8-quinolinol, the mixture was completely equilibrated by shaking for 10 min at 200 strokes/min at 25±0.1 °C. After the mixture was centrifuged for 2 min, 5 ml of the aqueous and of the chloroform phases were taken in order to measure the radioactivity. The residual aqueous phase was used for the measurement of pH. The absorption spectra of the chloroform phase, which was extracted by the procedure described above using the cobalt solution which does not contain ^{60}Co, were measured in the range of 300 to 500 nm.

Determination of the Perchlorate Ion in the Chloroform Extract. The extracted chloroform phase was shaken for 2 min with 8 ml of 0.01 M EDTA solution adjusted to pH 5.8 and then the amount of perchlorate ion back-extracted in the aqueous solution was absorptiometrically determined by Uchikawa's method.[9]

Estimation of Cobalt(II) and (III) 8-Quinolinol Complexes in the Chloroform Phase. It is important to determine the oxidation state of cobalt in the cobalt 8-quinolinol complexes extracted into the chloroform phase. The oxidation state of cobalt was judged by the following manner as proposed by Ōki.[3] 1) Cobalt(II) 8-quinolinol complexes in the chloroform solution are readily back-extracted into aqueous EDTA solution, while cobalt(III) complexes are not. 2) The absorption spectrum of cobalt(III) 8-quinolinol complex in the chloroform solution has an absorption maximum at 420 nm. The practical procedure is as follows: Cobalt(II) and (III) 8-quinolinol complexes which might be contained in a chloroform phase are shaken for one min with 0.001 M EDTA solution at a pH in the range of 4.0 to 5.0. The cobalt(II) 8-quinolinol complexes are completely back-extracted into the aqueous solution, whereas cobalt(III) 8-quinolinol complex remains in the chloroform phase. The absorbance of the chloroform phase back-extracted at 420 nm is measured by using the calibration curve made from the chloroform solutions of known amounts of cobalt(III) 8-quinolinol complex.

Results and Discussion

Extraction of Cobalt into Chloroform with 8-Quinolinol from an Aqueous Solution Containing Perchlorate, Nitrate, or Sulfate Ions. The relationship between the logarithm of the distribution ratio, log D, and the pH of the aqueous phase containing 0.1 M perchlorate, nitrate, or sulfate ion is shown in Fig. 1. In the part where $D < K_{\mathrm{Dc}}$ in the acidic region (K_{Dc}: distribution coefficient of cobalt 8-quinolinol complexes), the distribution curve for sulfate ion gives a straight line with the slope +2, but for perchlorate or nitrate ions, especially for perchlorate ions, the data do not give a linear relationship. Furthermore, it is observed that their distribution ratios decrease in the order of $ClO_4^- > NO_3^- > SO_4^{2-}$ at an arbitrary pH below 5. On the other hand, the distribution curves for the three anions start to overlap in the region above pH 8.

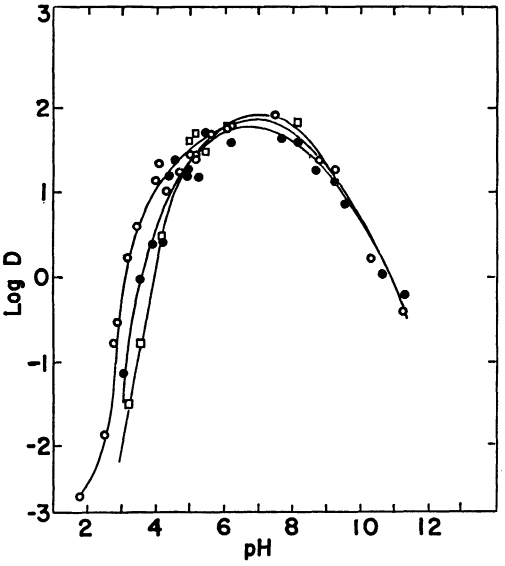


Fig. 1. Plots of log D *vs.* pH.
Initial concentration; cobalt 1.15×10^{-4} M, 8-quinolinol 0.1 M.
—○—; 0.1 M ClO_4^-, —●—; 0.1 M NO_3^-, —□—; 0.1 M SO_4^{2-}.

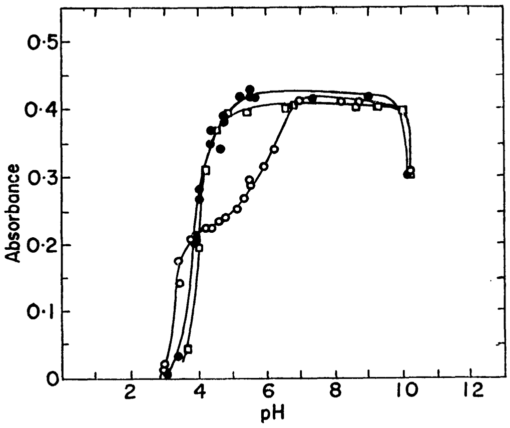


Fig. 2. Absorbance of the chloroform extracts as a function of pH. Wavelength; 410 nm, —○—; 0.1 M ClO_4^-, —●—; 0.1 M NO_3^-, —□—; 0.1 M SO_4^{2-}.

Values of the absorbance at 410 nm of the extracted chloroform phase as a function of pH of the aqueous phase containing 0.1 M perchlorate, nitrate, or sulfate ion are shown in Fig. 2. The absorbance change in the range of pH 4 to 7 for perchlorate ion shows significant differences from those for sulfate and nitrate ions, although the total concentrations of cobalt in the chloroform phase for three anions are not so appreciably different in this pH range, as seen in Fig. 1. Actually, the apparent molar absorptivity at 410 nm of the species extracted at various pH values can be calculated from the values of the distribution ratio and the absorbance. The results are shown in Table 1. The values of the

Table 1. Apparent molar absorptivity of chloroform extract at 410 nm

pH[a]	0.1M ClO_4^-			0.1M NO_3^-			0.1M SO_4^{2-}		
	$[Co]_0\times10^4$ [b]	Abs.[c]	E_{410}[d]	$[Co]_0\times10^4$ [b]	Abs.[c]	E_{410}[d]	$[Co]_0\times10^4$ [b]	Abs.[c]	E_{410}[d]
3.5	0.816	0.175	2150	0.306	0.075	2450	—	—	—
4.0	0.908	0.210	2310	0.816	0.220	2700	0.569	0.230	4140
4.5	0.938	0.225	2400	0.918	0.350	3810	0.891	0.370	4150
5.0	0.985	0.240	2440	0.959	0.400	4170	0.969	0.390	4020
5.5	1.00	0.260	2600	0.980	0.420	4290	0.993	0.400	4030
6.0	1.01	0.310	3070	0.980	0.425	4340	1.00	0.410	4100
6.5	1.02	0.350	3430	1.00	0.430	4300	1.00	0.410	4100
7.0	1.02	0.415	4070	1.02	0.430	4220	1.01	0.410	4060
8.0	1.02	0.420	4120	1.02	0.425	4170	1.00	0.410	4100
9.0	0.979	0.420	4290	0.979	0.420	4290	0.979	0.410	4190

a) pH of the aqueous phase after extraction. b) Total concentration of cobalt in chloroform extract.
c) Absorbance at 410 nm. d) Apparent molar absorptivity at 410 nm $\left(=\frac{\mathrm{Abs}}{[\mathrm{Co}]_0}\right)$.

apparent molar absorptivity for perchlorate ion seem to vary in two steps with pH. These facts suggest that two species of cobalt 8-quinolinol complexes exist in the chloroform phase: one is species A with $\varepsilon=4.1$—4.2×10^3 extracted in the range of pH 7.0 to 9.0, and the other is species B with $\varepsilon=\approx2.4\times10^3$, extracted in the range of pH 4.0 to 9.0 for sulfate ions and in the range of pH 5.0 to 9.0 for nitrate ions, this species may be identical to species A extracted into the chloroform in the range of pH 7.0 to 9.0 for perchlorate ions. It was confirmed that no cobalt(III) 8-quinolinol complex, $Coql_3$, exists in the chloroform phase immediately after the extraction from an aqueous cobalt(II) solution below pH 7.0 containing 0.1 M perchlorate, nitrate, or sulfate ion, although several percents of cobalt are also extracted as a cobalt(III) 8-quinolinol complex at a pH above 7.0.

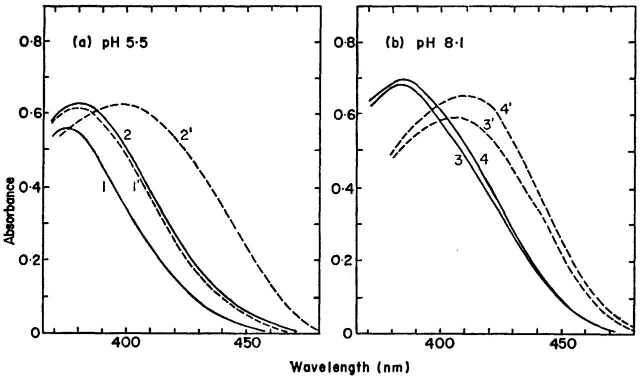


Fig. 3. Absorption spectra of the chloroform extracts from the aqueous solutions containing 0.1 M anion.
(*a*); pH 5.5, 1 and 1′; 0.1 M ClO_4^-, 2 and 2′; 0.1 M NO_3^-, Standing time; 1 and 2: 0 h, 1′ and 2′: 20 h.
(*b*); pH 8.1, 3 and 3′; 0.1 M ClO_4^-, 4 and 4′; 0.1 M NO_3^-, Standing time; 3 and 4: 0 h, 3′ and 4′: 16 h.

Absorption Spectra of Cobalt 8-Quinolinol Complexes Extracted into Chloroform. When the chloroform phase, which has been separated with a centrifuge from the aqueous phase, is allowed to stand in the dark at room temperature, its absorption maximum around 380 nm shifts to longer wavelengths and finally reaches 420 nm. The changes of the absorption spectra with time at pH 5.5 and 8.1 are shown Figs. 3a and 3b respectively. It is considered that the shift to the longer wavelength is due to the oxidation of the cobalt(II) 8-quinolinol complex to the cobalt(III) 8-quinolinol complex for the following reasons: 1) the wavelength of the finally reached absorption maximum, 420 nm is in accord with that for the cobalt(III) 8-quinolinol complex oxidized by hydrogen peroxide; 2) when the chloroform extracts were allowed to stand for an appropriate time, followed by back-extraction with the EDTA solution, the absorption maximum of the back-extracted chloroform phase was located at 420 nm; and 3) when nitrogen gas is passed through the chloroform phase, the shift to longer wavelengths is prolonged with time. The solid lines in Figs. 3a and 3b show absorption spectra of the chloroform phase immediately after the extraction at pH 5.5 and 8.1 from the cobalt(II) solution containing 0.1 M perchlorate or nitrate ion. These absorption spectra have their absorption maxima at 380 nm or below. This fact indicates that species A and species B extracted into the chloroform phase are not the normal 1 : 2 cobalt(II) 8-quinolinol complex, $Coql_2$, because its absorption maximum is located at 400 nm in chloroform.[10,11] The broken lines in Figs, 3a and 3b indicate the absorption spectra after the chloroform extracts were allowed to stand for a fixed time. When the chloroform phase extracted at pH 5.5 for perchlorate ions is allowed to stand for 20 h, no appreciable shift to longer wavelengths is observed. On the other hand, an appreciable shift to longer wavelengths is observed for nitrate ions at pH 5.5 as well as for perchlorate and nitrate ions at pH 8.1. These results lead to the conclusion that species A is apt to be oxidized in air, while species B is difficult to oxidize.

Tendency of the Formation of Species A or Species B with the Kind of Anions. The effect of the anion on the formation of species A and species B in the chloroform phase was examined by using various kinds of anions, such as perchlorate, nitrate, chloride, and sulfate ions, in 1.0 M solutions. The relationships of the standing time and the change of the absorption spectra of the chloroform phases extracted at pH 6.5 and 8.1 from the cobalt solution containing an anion in 1.0 M concentration are shown in Figs. 4 and 5 respectively. The

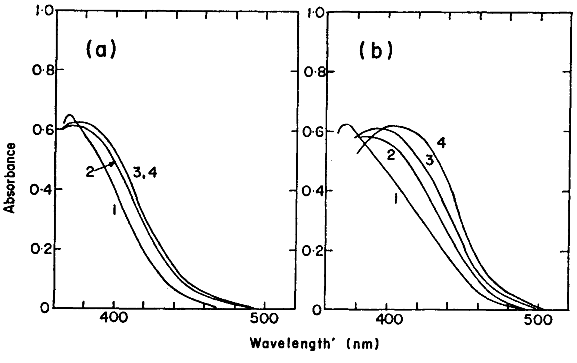


Fig. 4. Absorption spectra of the chloroform extracts from the aqueous solutions containing 1 M anion at pH 6.5.
(*a*); Immediately after extraction. (*b*); after standing for 20 h. 1; ClO_4^-, 2; NO_3^-, 3; Cl^-, 4; SO_4^{2-}.

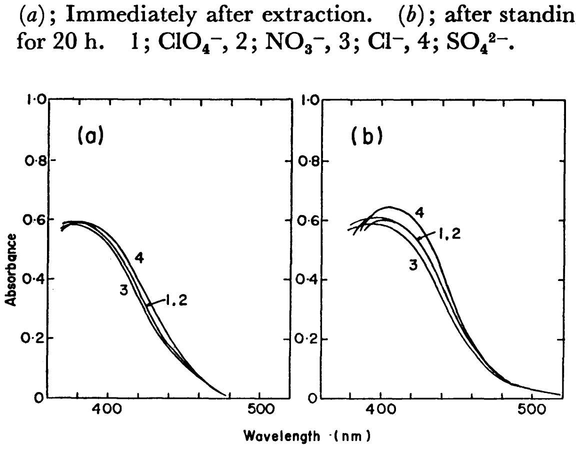


Fig. 5. Absorption spectra of the chloroform extracts from the aqueous solutions containing 1 M anion at pH 8.1.
(*a*); Immediately after extraction. (*b*); After standing for 20 h. 1; ClO_4^-, 2; NO_3^-, 3; Cl^-, 4; SO_4^{2-}.

absorption spectra after standing for 20 h for the extracts at pH 6.5 are located at longer wavelengths, in the order of $ClO_4^- < NO_3^- < Cl^- < SO_4^{2-}$ (Figs. 4a and 4b). This is the order for the rate of the oxidation to cobalt(III) 8-quinolinol complex, in other words, the order of the increase of species A, and the decrease of species B in the chloroform phase. On the other hand, for the extraction at pH 8.1, the absorption curves immediately after extraction are similar to those obtained 20 h after extraction, regardless of the kind of anion, and the oxidation seems to occur rapidly in all cases (Figs. 5a and 5b). These results indicate that species A is probably formed in the chloroform phase.

Table 2. Concentrations of cobalt and perchlorate in the chloroform extracts

pH[a]	[Co] × 10⁴ (M)[b]	[ClO₄⁻] × 10⁵ (M)[c]	[ClO₄⁻]/[Co]
3.85	1.00	5.13	0.513
4.20	1.05	5.20	0.495
4.40	1.08	5.73	0.513
5.10	1.12	5.68	0.508
5.30	1.13	4.67	0.413
5.40	1.13	4.33	0.383
6.05	1.14	3.88	0.340
7.70	1.15	0.533	0.046
8.50	1.13	0.465	0.041
	—	0.330	—

a) pH of the aqueous phase after extraction. b) Concentration of cobalt in the chloroform extracts. c) Concentration of perchlorate ion in the chloroform extracts.

Compositions of Species A and Species B. The perchlorate ion in species A and species B extracted into chloroform from the aqueous cobalt solution containing perchlorate ions was determined. The results are shown in Table 2. The chloroform phases extracted below pH 5.1 contain cobalt and perchlorate ions in the ratio of 2 to 1, but the concentration of perchlorate ions decreases gradually with increasing pH and becomes very low above pH 7.7, although the concentration of cobalt remains constant above pH 5.1. Therefore, the species extracted below pH 5.1, species B, might be an ion-pair complex, similar to that for zinc described in a previous report.[8] On the other hand, the species extracted above pH 7.7, species A, may be a complex containing no perchlorate ions. The prediction that the species extracted into chloroform to form the cobalt solution containing 1.0 M sulfate ion may be not species B but species A was confirmed by the follow. The aqueous solution containing 3.05×10^{-4} M cobalt and 1.0 M sulfate ions is extracted with 0.1 M 8-quinolinol chloroform solution at pH 3.7. The extracts in the chloroform phase can be back-extracted with 1.0 M hydrochloric acid, and then 0.1 M barium sulfate solution is added into the aqueous phase. No turbid material and no precipitate forms, so the extracts contain no sulfate ions.

On the basis of the above mentioned results, the compositions of species A and species B extracted from the cobalt solution containing perchlorate ions are represented by the formulae, $Co_n ql_m(Hql)_l$ and $Co_{2s}ql_t(Hql)_u(ClO_4)_s$ respectively; then the reactions of extraction for species A and species B will be represented by the following equations:

$$nCo^{2+} + (m+l)Hql_{(o)} \rightleftarrows Co_n ql_m(Hql)_{l(o)} + mH^+ \tag{1}$$

$$2sCo^{2+} + (t+u)Hql_{(o)} + sClO_4^- \rightleftarrows Co_{2s}ql_t(Hql)_u(ClO_4^-)_{s(o)} + tH^+ \tag{2}$$

where l, m, n, s, t, and u are integers. The equilibrium constants of Eqs. 1 and 2, that is, the exraction constants, K_{ex}^A and K_{ex}^B are represented as follows:

$$K_{ex}^A = \frac{[Co_n ql_m(Hql)_l]_o[H]^m}{[Co]^n[Hql]_o^{m+l}} \tag{3}$$

$$K_{ex}^B = \frac{[Co_{2s}ql_t(Hql)_u(ClO_4^-)_s]_o[H]^t}{[Co]^{2s}[Hql]^{t+u}[ClO_4^-]^s} \tag{4}$$

where the charge of the chemical species was abbreviated. The distribution ratios of species A and species B, D_A and D_B, are represented by Eqs. 5 and 6 respectively:

$$D_A = \frac{n[Co_n ql_m(Hql)_l]_o}{[Co]_T} \tag{5}$$

$$D_B = \frac{2s[Co_{2s}ql_t(Hql)_u(ClO_4^-)_s]_o}{[Co]_T} \tag{6}$$

Here $[Co]_T$ represents the analytical concentration of cobalt(II) in the aqueous phase. If the hydrolysis of cobalt ions and the complex formation of cobalt ions with other anions can be neglected in the aqueous phase, Eq. 7 is obtained:

$$\begin{aligned}[Co]_T &= [Co](1+\sum_{i,j}\beta_{i,j}[ql]^i[Hql]^j) \\ &\quad + [Co]\sum_{p,q}\beta_{p,q}[ql]^p[Hql]^q \\ &= [Co](1+N) \end{aligned} \tag{7}$$

Here, $\beta_{i,j}$ and $\beta_{p,q}$ represent the formation constants of the mononuclear cobalt 8-quinolinol complex and the binuclear complex respectively, and N represents the sum of the second and third terms in the parentheses on the right-hand side of Eq. 7. When Eqs. 3 and 4 are replaced by Eqs. 5, 6, and 7 and both sides of the equations are made logarithmic, Eqs. 8 and 9 can be deduced.

$$\begin{aligned}\log D_A &= (n-1)\log[Co]_T + m\text{pH} + (m+l)\log[Hql]_o \\ &\quad - n\log(1+N) + \log n + \log K_{ex}^A \end{aligned} \tag{8}$$

$$\begin{aligned}\log D_B &= (2s-1)\log[Co]_T + t\text{pH} + (t+u)\log[Hql]_o \\ &\quad - 2s\log(1+N) + s\log[ClO_4^-] \\ &\quad + \log 2s + \log K_{ex}^B \end{aligned} \tag{9}$$

Under the conditions that the terms except for $\log[Co]_T$ on the right-hand side of Eqs. 8 and 9 are constant, the plots of $\log D$ *vs.* $\log[Co]_T$ should give a straight line having the slope $n-1$ or $2s-1$. When $[Co]_T = [Co]_{int.}/(1+D)$, where $[Co]_{int.}$ is the initial concentration of cobalt, is placed Eqs. 8 and 9, the following Eqs. 10 and 11, which are into convenient for obtaining the values of m, l and t, u, can be deduced.

$$\begin{aligned}\log D_A + (n-1)\log(1+D_A) &= m\text{pH} + (m+l)\log[Hql]_o \\ &\quad + (n-1)\log[Co]_{int.} - n\log(1+N) + \log n + \log K_{ex}^A \end{aligned} \tag{10}$$

$$\log D_{\mathrm{B}} + (2s-1)\log(1+D_{\mathrm{B}}) = t\mathrm{pH} + (t+u)\log[\mathrm{Hql}]_o + s\log[\mathrm{ClO_4^-}] + (2s-1)\log[\mathrm{Co}]_{\mathrm{int.}} - 2s\log(1+N) + \log 2s + \log K^{\mathrm{B}}_{\mathrm{ex}} \qquad (11)$$

The following three conditions are selected in order to determine the compositions of the extracted species A and species B: 1) the condition under which only one of species A and species B is extracted 2) the hydrolysis and the complex formation with the other anions for the cobalt ion can be neglected; 3) N can be neglected in comparison with 1 in Eq. 7. For condition 1), the extraction in the presence of sulfate ions was selected as a condition in which only species A is extracted, and the extraction in the presence of perchlorate ions at a low pH was selected as a condition in which only species B is extracted. For condition 2), the hydrolysis of cobalt ions can be neglected at low pH and the use of a low concentration of the buffer($<1\times10^{-3}$ M acetate) allows us to neglect the effect of the complex formation. For condition 3), the extraction at a pH below 3.6 satisfies the the condition of 3), according to the calculation of the concentrations of cobalt 8-quinolinol complexes.

The plots of log D *vs.* log$[\mathrm{Co}]_T$ from Eqs. 8 and 9 are shown in Figs. 6a and 6b respectively. Both curves give straight lines with the slope of +1 in the vicinity of $[\mathrm{Co}]_{\mathrm{int.}}=10^{-4}-10^{-5}$ M. The plots in Fig. 6a, however, seem to deviate from a straight line. Perhaps the condition of 3) is less satisfied at the higher pH in the extraction, 3.8, than at 3.6. It is suggested that both species A and species B may be dimer complexes, because $n=2$ for species A and $s=1$ for species B. In the regions of high and low concentrations of cobalt, the slopes are close to zero, which suggests that a mononuclear complex is extracted. This suggestion was supported by Table 3, which gives the data for the absorption spectra of the chloroform extracts from the cobalt solutions of various concentrations corresponding to Fig. 6a. As the concentration of cobalt becomes higher, the absorption maximum shifts to longer wavelengths. For the concentration of $[\mathrm{Co}]_{\mathrm{int.}}=1.15\times10^{-3}$ M, the absorption maximum is located at 400 nm and the apparent molar absorptivity at 410 nm is 2000. It was confirmed that the shift to longer wavelengths can not be attributed to the oxidation to a cobalt(III) 8-quinolinol complex, because of the fact that the chloroform phase back-extracted with 1.0 M hydrochloric acid is clolorless. It is well-known that the absorption maximum of the chloroform solution of 1:2 cobalt 8-quinolinol complex is located at 395 nm and its molar absorptivity is 2200 at 410 nm, which agrees with the above results, so that the species extracted at 1×10^{-3} M of $[\mathrm{Co}]_{\mathrm{int.}}$ may be the normal 1:2 cobalt 8-quinolinol complex.

The relationships of log $D(1+D)$ and log$[\mathrm{Hql}]_o$, according to Eqs. 10 and 11, are plotted in Figs. 7a and 7b. Straight lines with the slope +6 are obtained for both species A and B, so that $m+l=6$ for species A, and $t+u=6$ for species B. The plot of log D *vs.* pH for species A, and the plot of log $D(1+D)$ *vs.* log$[\mathrm{ClO_4}]$ for

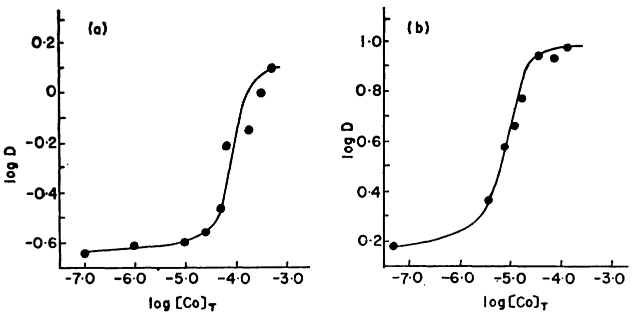


Fig. 6. Effect of the concentration of cobalt on extraction of species A and B.
(a); For species A, pH 3.80, Initial concentration; 8-quinolinol 0.1 M, $\mathrm{SO_4^{2-}}$ 0.1 M.
(b); For species B, pH 3.20, Initial concentration; 8-quinolinol 0.1 M, $\mathrm{ClO_4^-}$ 0.1 M.

Table 3. Effect of concentration of cobalt on absorption spectra of chloroform extracts

$[\mathrm{Co}]_{\mathrm{int.}}$[a] (M)	%E	$[\mathrm{Co}]_o$ (M)	Abs. (410 nm)	ε_{410}[b]	$\lambda_{\max}$[c] (nm)
3.45×10^{-4}	91.7	3.16×10^{-4}	0.840	2660	380
6.90×10^{-4}	94.2	6.50×10^{-4}	1.550	2380	390
1.15×10^{-3}	91.3	1.05×10^{-3}	2.10	2000	400

a) Initial concn. of cobalt in aqueous phase. b) Apparent molar absorptivity at 410 nm. c) Wavelength of absorption maximum.

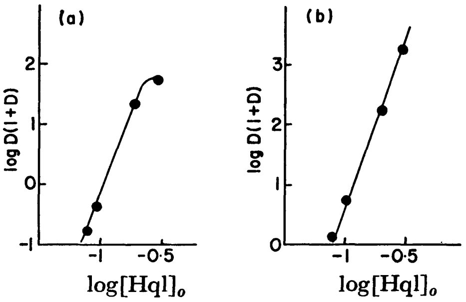
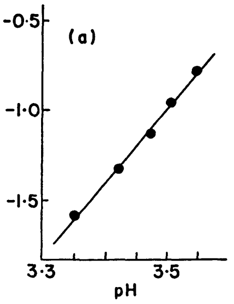


Fig. 7. Plot of log $D(1+D)$ *vs.* log[Hql].
(a); For species A, pH 3.50, Initial concentration; cobalt 1.02×10^{-4} M, $\mathrm{SO_4^{2-}}$ 0.1 M.
(b); For species B, pH 2.90, Initial concentration; cobalt 1.15×10^{-4} M, $\mathrm{ClO_4^-}$ 0.1 M.



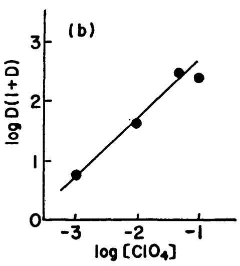


Fig. 8(a). Plot of log D *vs.* pH for species A. Initial concentration; cobalt 1.02×10^{-4} M, 8-quinolinol 0.1 M and $\mathrm{SO_4^{2-}}$ 0.1 M.

Fig. 8(b). Plot of log D *vs.* log $[\mathrm{ClO_4^-}]$ for the species B. Initial concentration; cobalt 1.15×10^{-4} M, 8-quinolinol 0.1 M. Ionic strength; 0.1($\mathrm{ClO_4^-}$ and $\mathrm{SO_4^{2-}}$).

species B are also shown in Figs. 8a and 8b, respectively. Straight lines were obtained with the slope +2 for the former and +1 for the latter. From these results it is concluded that $n=2$, $m=4$, and $l=2$ for species A and $s=1$, $t=3$, and $u=3$ for species B, so that the composition of species A and species B can be represented by $\mathrm{Co_2ql_4(Hql)_2}$ and $\mathrm{Co_2ql_3(Hql)_3ClO_4}$, respectively.

Equilibrium between Species A and Species B. The following equilibrium can be considered between species A, $\mathrm{Co_2ql_4(Hql)_2}$, and species B, $\mathrm{Co_2ql_3(Hql)_3ClO_4}$, in the chloroform phase.

$$\mathrm{B_{(o)}} \rightleftarrows \mathrm{A_{(o)}} + \mathrm{H^+} + \mathrm{ClO_4^-} \qquad (12)$$

$\mathrm{A_{(o)}}$ and $\mathrm{B_{(o)}}$ represent species A and species B in the chloroform phase. The equilibrium constant, K_{AB}, for Eq. 12 is shown in Eq. 13.

$$K_{\mathrm{AB}} = \frac{[\mathrm{A}]_o[\mathrm{H^+}][\mathrm{ClO_4^-}]}{[\mathrm{B}]_o} \qquad (13)$$

$[\mathrm{A}]_o$ and $[\mathrm{B}]_o$ represent the concentrations of species A and species B in the chloroform phase. As species A and species B are both assumed to be dimer complexes, their molar absorptivities at 410 nm, $\varepsilon^{\mathrm{A}}_{410}$, and $\varepsilon^{\mathrm{B}}_{410}$, can be estimated to be double the values of the apparent molar absorptivities of the species which are extracted at pH 4.0 and 7.0, respectively, in the presence of of 0.1 M perchlorate ions, that is, $\varepsilon^{\mathrm{A}}_{410}=8140$ and $\varepsilon^{\mathrm{B}}_{410}=4620$.

The analytical concentration of cobalt in the chloroform phase, $[\mathrm{Co}]_o$, is represented by Eq. 14 and the apparent molar absorptivity at a particular pH, ε_{410}, is represented by Eq. 15.

$$[\mathrm{A}]_o + [\mathrm{B}]_o = \frac{1}{2}[\mathrm{Co}]_o \qquad (14)$$

$$[\mathrm{A}]_o\varepsilon^{\mathrm{A}}_{410} + [\mathrm{B}]_o\varepsilon^{\mathrm{B}}_{410} = \varepsilon_{410}[\mathrm{Co}]_o \qquad (15)$$

When the values of $[\mathrm{A}]_o$ and $[\mathrm{B}]_o$ obtained from Eqs. 14 and 15 are placed in Eq. 13 and both sides of the equation are made logarithmic, Eq. 16 is obtained.

$$\log\frac{2\varepsilon_{410}-\varepsilon^{\mathrm{B}}_{410}}{\varepsilon^{\mathrm{A}}_{410}-2\varepsilon_{410}} = \mathrm{pH} + \mathrm{p[ClO_4^-]} + \log K_{\mathrm{AB}} \qquad (16)$$

The plots of $\log\{(2\varepsilon_{410}-\varepsilon^{\mathrm{B}}_{410})/(\varepsilon^{\mathrm{A}}_{410}-2\varepsilon_{410})\}$ against $\mathrm{p[ClO_4^-]}$ at pH=5.50 and against pH at $\mathrm{p[ClO_4^-]}=1$ are shown in Figs. 9a and 9b, respectively. A straight line with the slope +1 was obtained in each figure, which indicates that the equilibrium represented by Eq. 12 is valid. $\log K_{\mathrm{AB}}=-7.2$ was obtained as the average of −7.1 and −7.3, which were derived from the intercepts in Figs. 9a and 9b.

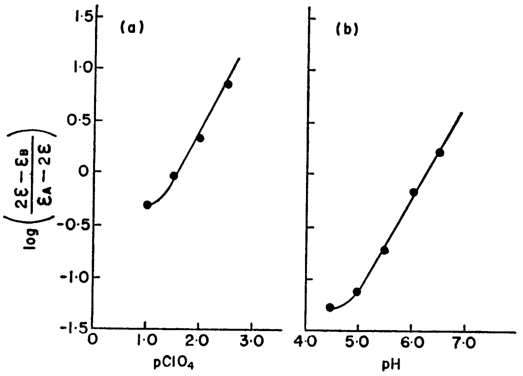


Fig. 9(a). Plot of $\log\{(2\varepsilon-\varepsilon_B)/(\varepsilon_A-2\varepsilon)\}$ *vs.* pH. Initial concentration; cobalt 1.02×10^{-4} M, 8-quinolinol 0.1 M, and $\mathrm{ClO_4^-}$ 0.1 M.

Fig. 9(b). Plot of $\log\{(2\varepsilon-\varepsilon_B)/(\varepsilon_A-2\varepsilon)\}$ *vs.* $\mathrm{p[ClO_4^-]}$ a pH 5.50. Initial concentration; cobalt 1.15×10^{-4} M, 8-quinolinol 0.1 M. Ionic strength; 0.1 ($\mathrm{ClO_4^-}$ and $\mathrm{NO_3^-}$).

The equilibrium constant, K_{AB} was also derived from the ratio of the extraction constants $K^{\mathrm{A}}_{\mathrm{ex}}$ to $K^{\mathrm{B}}_{\mathrm{ex}}$. The extraction constant of species A, $K^{\mathrm{A}}_{\mathrm{ex}}=10^{-4.61}$ was obtained by using the intercept of Fig. 7a and Eq. 10, and that of species B, $K^{\mathrm{B}}_{\mathrm{ex}}=10^{2.60}$ by Fig. 7b and Eq. 11. Therefore, $\log K_{\mathrm{AB}}=\log K^{\mathrm{A}}_{\mathrm{ex}}-\log K^{\mathrm{B}}_{\mathrm{ex}}=-4.61-2.60=-7.21$. This value is in good accord with the value obtained absorptiometrically, −7.2.

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