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Equilibrium and Structural Studies on the Species Formed in the Extraction of Divalent Transition Metal Ions with 8-Quinolinol

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The equilibria were studied in the extraction of divalent transition metal ions (M^{2+}: Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) with 8-quinolinol (Hq) from aqueous solutions containing various anions (X^-) into some organic solvents. The effects of $-\log[H^+]$ and total concentrations of 8-quinolinol and metal ions on the distribution were examined in detail. Three species, $M_2q_3(Hq)_3X$, $Mq_2(Hq)$, and $M_2q_4(Hq)_2$ are responsible for the extraction. The extraction of $M_2q_3(Hq)_3X$ is favorable when hydrophobic anions and polar solvents are used. On the other hand, the extraction constants of $Mq_2(Hq)$ are almost the same for each metal ion irrespective of anions and solvents. With increasing the metal ion concentration in the organic phase, $Mq_2(Hq)$ dimerizes to form $M_2q_4(Hq)_2$. The decrease in the distribution ratio by prolonged shaking under certain conditions is reasonably ascribed to the slow precipitation of $Mq_2 \cdot 2H_2O$ which has been made supersaturated by the rapid establishment of all the equilibria except the precipitation reaction. An X-ray crystallographic study for $Ni_2q_4(Hq)_2$ showed that two nickel atoms are surrounded by three bidentate ligands with facial and meridional configurations about their oxygen atoms and these two isomers form a binuclear structure jointed by two strong hydrogen bonds.

8-Quinolinol (Hq) is one of the most familiar extracting reagents, and its behavior in the extraction of various metal ions has been repeatedly studied.[1)] Among the divalent transition metal ions copper is simply extracted as Cuq_2. In contrast, the extraction equilibria of other metal ions, such as cobalt, nickel, zinc and cadmium, are rather complicated and conflicting results have been reported as shown in Table 1.[2-18)] As for nickel ion, Oki and Terada have found the presence of two extracted species $Ni_2q_3(Hq)_3X$ (X^-: anion) and $Ni_2q_4(Hq)_2$,[10,11)] whereas Bhatki et al. have stated the unique presence of $Niq_2(Hq)$.[12)] Moreover, Sekido et al. found that the species once extracted into chloroform gradually precipitate during the prolonged shaking.[19,20)] About the extracted species of the other metal ions there has also been similar confusion. Thus we made extensive equilibrium study to understand these findings altogether.

Among these proposed species, $Ni_2q_3(Hq)_3X$(X^-: I_3^- or ClO_4^-) has recently been identified by X-ray crystallographic studies.[21)] We determined the crystal structure of one of the neutral extracted species $Ni_2q_4(Hq)_2$.

Table 1. Earlier Studies on the Extraction of Divalent Transition Metal Ions with 8-Quinolinol

Extracted species	$\log K_{ex}$	C_{Hq} / mol dm^{-3}	C_M / mol dm^{-3}	Medium	Method[a)]	Ref.
$Coq_2(Hq)_2$	−2.16	10^{-2}—10^{-1}	—	0.1 $KClO_4$	SP, R	2
$Coq_2(Hq)_2$	−2.6	—	—	0.5	—	3
$Coq_2(Hq)$	−3.71[b)]	5×10^{-2}—2×10^{-1}	2×10^{-7}, 7×10^{-5}	0.1 $NaClO_4$	SP, R	4
$Coq_2(Hq)$	—	10^{-3}—10^{-2}	—	0.1 $NaClO_4$	R	5
$Co_2q_4(Hq)_2$	−4.61	0.1	1×10^{-4}	0.1 Na_2SO_4	SP, R	6
$Co_2q_3(Hq)_3ClO_4$	2.60			0.1 $NaClO_4$		
$Coq_2(Hq)$	−3.83[b)]	4×10^{-3}—6×10^{-2}	—	0.25 $NaClO_4$	R	7
$Co_2q_4(Hq)_2$[c)]	—	1×10^{-1}—3×10^{-1}	2×10^{-4}—10^{-3}	0.25 $NaClO_4$	AAS	8
Niq_2	−2.18	10^{-2}—10^{-1}	—	0.1 $KClO_4$	SP	2
$Niq_2(Hq)$	−0.56[b)]	10^{-2}—10^{-1}	9×10^{-7}, 8×10^{-5}	0.1 $NaClO_4$	SP, R	9
$Ni_2q_4(Hq)_2$	−0.82	10^{-2}—10^{-1}	1×10^{-4}	0.1 Na_2SO_4	SP	10
$Ni_2q_3(Hq)_3ClO_4$	7.58			0.1 $NaClO_4$		
$Ni_2q_3(Hq)_3X$	var	10^{-2}—10^{-1}	1×10^{-4}	0.1 NaX	SP	11
$Niq_2(Hq)$	−2.55[b)]	5×10^{-4}—10^{-2}	6×10^{-6}	0.25 $NaClO_4$	R	12
$Znq_2(Hq)_2$	−2.41	10^{-2}—10^{-1}	—	0.1 $KClO_4$	SP, R	2
var	—	10^{-2}—3×10^{-1}	5×10^{-7}	0.1 $NaClO_4$	R	13
$Znq_2(Hq)$	−4.1[b)]	10^{-2}—1.9	10^{-5}—10^{-4}	0.1 $NaClO_4$	R	14
$Znq_2(Hq)_2$	−2.66[b)]	10^{-2}—10^{-1}	6×10^{-5}	0.1 $NaClO_4$	R	15
$Zn_2q_3(Hq)_3ClO_4$	1.10	10^{-1}	2×10^{-4}	0.1 $NaClO_4$	SP, R	16
$Cdq_2(Hq)_2$	−5.29	10^{-2}—10^{-1}	—	0.1 $KClO_4$	SP, R	2
$Cdq_2(Hq)_2$	−6.1	5×10^{-2}—1	8×10^{-6}	0.1 $NaClO_4$	R	17
$Cdq_2(Hq)$	−6.5[b)]	3×10^{-2}—1	2×10^{-6}	1.0 $NaClO_4$	R	18

a) SP: spectrophotometry; R: radiometry; AAS: atomic absorption spectrometry. b) Converted from the constants in literature. c) Into toluene, whereas others into chloroform.

Experimental

Reagents and Equipments. Metal(II) solutions were prepared from the sulfates and standardized against a Na_2H_2 edta solution. Organic solvents were shaken successively three times with conc. sulfuric acid, 4 mol dm^{-3} potassium hydroxide solution and distilled water. Other reagents were used as received.

All experiments were carried out in a room at 25±2 °C. Absorption spectra and $-\log[H^+]$ were measured with a thermoelectric circulating bath at 25±0.5 °C. The ionic strength was maintained at 0.10 mol dm^{-3} except for sulfate medium at 0.30 mol dm^{-3}.

Hydrogen ion concentration was measured with a Radiometer pH METER 26. The solution containing 1.00×10^{-2} mol dm^{-3} perchloric acid and 9.00×10^{-2} mol dm^{-3} sodium perchlorate was used as a $-\log[H^+]$ standard. Visible absorption spectra were recorded on a Union spectrometer SM-401 and atomic absorption spectrometry was carried out with a Daini Seikosha SAS-727.

Procedure. The details of the measurement were the same as described previously.[22] A 4×10^{-5} to 4×10^{-3} mol dm^{-3} metal solution was shaken with an equal volume of an organic solvent containing 1.6×10^{-3} to 2.4×10^{-1} mol dm^{-3} 8-quinolinol. Shaking 15—30 min for nickel and 1—5 min for other metal ions at 250 strokes min^{-1} was found sufficient for equilibration. In the cases of nickel, zinc and cadmium the absorbance of the organic phase was decreased by prolonged shaking under certain conditions (see below).

After centrifugation, $-\log[H^+]$ and metal concentration were measured for the aqueous phases. The visible spectra of the organic phases were recorded with a quartz cell of 1 or 10 mm. Absorbances at 410 nm for cobalt complexes and at 400 nm for others were used for the determination of the extraction constants.

With less 8-quinolinol and at high $-\log[H^+]$ cobalt(II) is oxidized to form extractable Coq_3. In this study extraction was examined without any reducing reagents, and the data were discarded when absorption spectra indicated the formation of Coq_3.

Perchlorate ion in the organic phase was stripped into an aqueous phase buffered at $-\log[H^+]$ 7 and was determined by modifying the method in literature.[23]

Preparation of the Nickel 8-Quinolinolate Complex. The complex was prepared by two methods: One is the addition of less polar solvents to chloroform extracts of the nickel complex from sulfate solution.[10,24] The other is the reaction of Niq_2 with an excess of 8-quinolinol in refluxing benzene. These complexes were recrystallized from benzene to give greenish crystals suitable for X-ray structural determination.

The infrared spectra of these compounds were the same to each other and were also identical to those reported elsewhere.[25] Although it was assigned as $Niq_2(Hq)$,[24,25] the elemental analysis suggested the presence of water and benzene molecules. Found: C, 68.1; H, 4.1; N, 7.7%. Calcd for $Ni_2q_4(Hq)_2\cdot H_2O\cdot C_6H_6$: C, 66.7; H, 4.3; N, 7.8%.

X-Ray Analysis. Crystal data: $Ni_2q_4(Hq)_2\cdot H_2O\cdot C_6H_6$, $F.W.=1080.5$, triclinic, $P\bar{1}$, $a=13.900(6)$, $b=15.797(7)$, $c=13.353(6)$ Å, $\alpha=110.82(3)$, $\beta=94.84(3)$, $\gamma=78.73(3)°$, $V=2687(2)$ Å^3, $D_m=1.34$, $D_x=1.335$ g cm^{-3}, $Z=2$, $\mu(\text{Mo}\,K\alpha)=0.76$ mm^{-1}, $F(000)=1120$.

Approximately spherical crystal of 0.15 mm diameter was used. Three-dimensional intensity data were collected on a Rigaku AFC-5R diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). 6346 reflections of 9456 unique ones measured in the range of $\theta\leq25.0°$ were observed with $|F_o|>2\sigma(F_o)$. No correction was applied for absorption.

The structure was solved by conventional heavy atom method and refined by block-diagonal least-squares technique. H atoms were not located. Positional and thermal parameters, anisotropic for the non-H atoms except for benzene and isotropic for the benzene atoms, were refined to $R=0.091$, $R_w=0.125$, and $S=1.04$ for 6213 reflections.[26] Weights for observed reflections were estimated as $w=[\sigma^2(F_o)+0.00712|F_o|^2]^{-1}$. Very intense reflections (8) and unreliable ones with $w^{1/2}|\Delta F|\geq4.0$ (125) were rejected for the final refinement. Computations using the program of MULTAN84, PLUTO and XPACK86 SHIONOGI[27] were performed by a FACOM M-340R computer at Shionogi Research Laboratories.

Results and Discussion

Distribution data were collected under various conditions in each system. In many systems more than one species coexist in the organic phase, so the change in the distribution ratio with $-\log[H^+]$ is not straightforward. There are the conditions where only the ion-pair species is extracted in M^{2+}-ClO_4^--chloroform systems, whereas only the neutral species is extracted in M^{2+}-SO_4^{2-}-chloroform systems. The compositions of the species were determined by the slope methods with the data in these systems. The results are shown for nickel systems.

Species Extracted as an Ion-Pair. The concentration of perchlorate was determined to be half that of nickel in chloroform as reported earlier.[10] Taking into account the electroneutrality, the extraction equilibrium for a general ion-pair species, $Ni_2q_3(Hq)_m$-ClO_4, is expressed by

$$2Ni^{2+} + (3+m)(Hq)_o + ClO_4^- \rightleftharpoons (Ni_2q_3(Hq)_mClO_4)_o + 3H^+ \quad :K_{ex,1}, \tag{1}$$

where the subscript o refers to the organic phase. When D' is defined by $[Ni_2q_3(Hq)_mClO_4]_o/[Ni]^2$, we have the following relations:

$$\log D' - (3+m)\log[Hq]_o = -3\log[H^+] + \log K_{ex,1} + \log[ClO_4] \tag{2}$$

$$[Hq]_0 = K_DC_{Hq}/(1/K_1[H^+] + 1 + K_2[H^+] + K_D), \tag{3}$$

where K_D is the partition constant of 8-quinolinol and K_1 and K_2 are the stepwise protonation constants of 8-quinolinolate.[28] The best linearity of the plot was obtained for $m=3$ as shown in Fig. 1, when various values were applied to m. Thus the extraction of the ion-pair species is expressed by[10]

$$2Ni^{2+} + 6(Hq)_o + ClO_4^- \rightleftharpoons (Ni_2q_3(Hq)_3ClO_4)_o + 3H^+. \tag{4}$$

Neutral Extracted Species. Extraction equilibrium

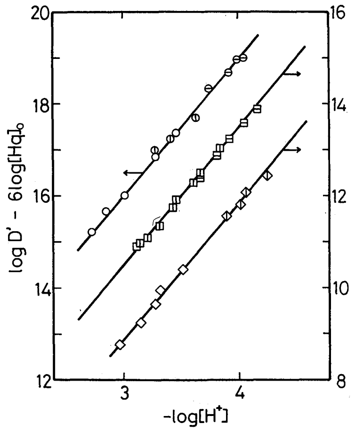


Fig. 1. Determination of the composition of the ion-pair extracted species according to Eq. 2. Ionic strength of 0.1 mol dm^{-3} NaClO$_4$. Solvent: chloroform. Metal ion: (◫, ⊟) Co^{2+}; (○, ⦶, ⊖) Ni^{2+}; (◇, ⟐) Zn^{2+}. Total concentration of 8-quinolinol in the organic phase, C_{Hq}/mol dm^{-3}: (◫, ◇) 0.12; (⊟, ⟐) 0.06; (○) 0.012; (⦶) 0.006; (⊖) 0.003. Solid lines: straight lines with a slope of three.

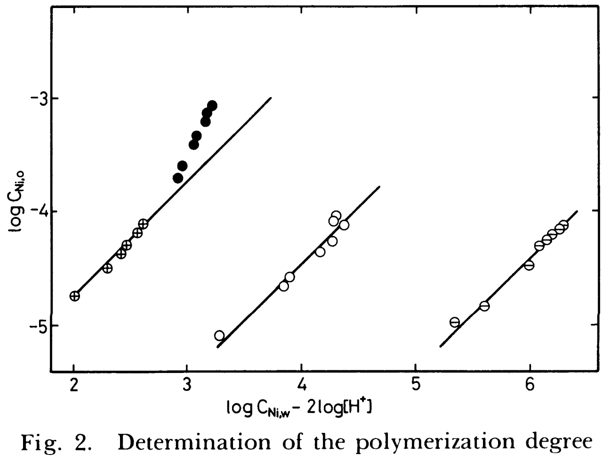


Fig. 2. Determination of the polymerization degree of neutral nickel(II) 8-quinolinolate according to Eq. 6. Ionic strength of 0.3 mol dm^{-3} Na$_2$SO$_4$. Solvent: chloroform. C_{Hq}/mol dm^{-3}: (⊕, ●) 0.05; (○) 0.013; (⊖) 0.0031. Solid lines: straight lines with a slope of unity.

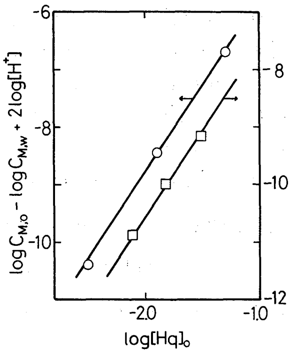


Fig. 3. Determination of the number of 8-quinolinol molecules involved in the neutral monomeric metal(II) 8-quinolinolate. Solvent: chloroform. Metal ion: (○) Ni^{2+}; (□) Co^{2+}. Solid lines: straight lines with a slope of three.

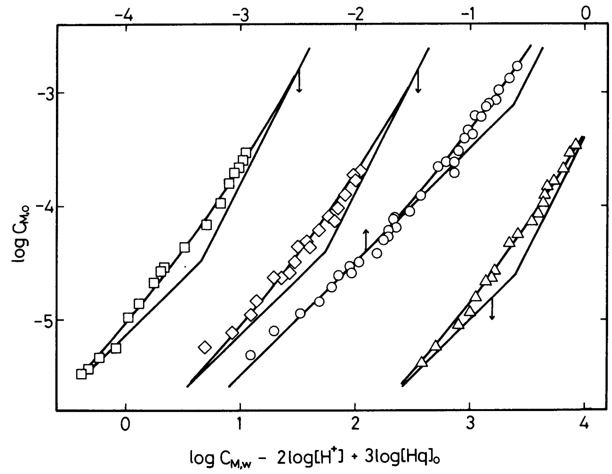


Fig. 4. Determination of the polymerization degree of neutral metal(II) 8-quinolinolate according to Eq. 8. Ionic strength of 0.3 mol dm^{-3} Na$_2$SO$_4$. Solvent: chloroform. Metal ion: (□) Co^{2+}; (○) Ni^{2+}; (◇) Zn^{2+}; (△) Cd^{2+}. Solid curves are the normalized curves, log $V(1+V)$ vs. log V. Solid lines are the asymptotes of the normalized curves.

of a neutral j-meric complex of the composition $\mathrm{Ni}_j\mathrm{q}_{2j}(\mathrm{Hq})_m$ is represented by[22,29)]

$$j\,\mathrm{Ni}^{2+} + (2j+m)(\mathrm{Hq})_o \rightleftharpoons (\mathrm{Ni}_j\mathrm{q}_{2j}(\mathrm{Hq})_m)_o + 2j\mathrm{H}^+ \quad : K_{\mathrm{ex,n}}. \tag{5}$$

The total concentration of nickel(II) in the organic phase, $C_{\mathrm{Ni,o}}$ is given by

$$\begin{aligned} C_{\mathrm{Ni,o}} &= j[\mathrm{Ni}_j\mathrm{q}_{2j}(\mathrm{Hq})_m]_o \\ &= jK_{\mathrm{ex,n}}[\mathrm{Ni}]^j[\mathrm{Hq}]_o^{(2j+m)}[\mathrm{H}]^{-2j}, \end{aligned}$$

which is rewritten as a logarithmic form:

$$\begin{aligned} \log C_{\mathrm{Ni,o}} &= j(\log C_{\mathrm{Ni,w}} - 2\log[\mathrm{H}^+]) \\ &\quad + (2j+m)\log[\mathrm{Hq}]_o + \log jK_{\mathrm{ex,n}} \end{aligned} \tag{6}$$

If the j-meric species is responsible for the extraction, the plot of $\log C_{\mathrm{Ni,o}}$ vs. ($\log C_{\mathrm{Ni,w}} - 2\log[\mathrm{H}^+]$) would yield a straight line of slope j.

The results are shown in Fig. 2. Only monomeric species is extracted when the total concentration of nickel in the organic phase is less than 10^{-4} mol dm^{-3}, whereas at higher region some polymerized species also participate (closed circles in Fig. 2).

The number of neutral 8-quinolinol molecules in the monomeric extracted species was determined from the slope of the plot of ($\log C_{\mathrm{Ni,o}} - \log C_{\mathrm{Ni,w}} + 2\log[\mathrm{H}^+]$) vs. $\log[\mathrm{Hq}]_o$. The actual plot falls on the straight line with a slope of 3, so m is equal to unity (Fig. 3). Thus the extraction equilibrium for the monomeric species is expressed by

$$\mathrm{Ni}^{2+} + 3(\mathrm{Hq})_o \rightleftharpoons (\mathrm{Niq_2(Hq)})_o + 2\mathrm{H}^+ \quad : K_{\mathrm{ex,2}}. \tag{7}$$

When the total concentration of nickel is increased, higher total concentration of 8-quinolinol is required to avoid the precipitation of $\mathrm{Niq_2 \cdot H_2O}$ (see below).

Then nickel is extracted at lower $-\log[H^+]$ region, where $[Hq]_o$ in Eq. 6 is no longer constant to give an systematic error in such plot shown in Fig. 2. Taking account of the composition of the solid complex prepared under the same conditions, m is assumed to be equal to j. Then Eq. 6 becomes as follows:

$$\log C_{Ni,o} = j(\log C_{Ni,w} - 2\log[H^+] + 3\log[Hq]_o) + \log jK_{ex,n}. \qquad (8)$$

The plot according to Eq. 8 is given in Fig. 4. At higher $\log C_{Ni,o}$ the slope of the plot tends to approach to two, which suggests the extraction of $Ni_2q_4(Hq)_2$.

$$2Ni^{2+} + 6(Hq)_o \rightleftharpoons (Ni_2q_4(Hq)_2)_o + 4H^+ : K_{ex,3} \qquad (9)$$

Fitting the obtained curves with the normalized curve, $X=\log V$, $Y=\log V(1+V)$,[30] two extraction constants were obtained.

Against the previous works,[2-18] both monomeric and dimeric species prove to be responsible for the extraction. Narrow range of the total concentration of metal ion studied and unreasonable assumption of the degree of polymerization may have led to incorrect conclusion. All the reported extraction constants are too high because it was assumed that only one species was extracted instead of two (Table 1).

These two species are related by the following equation:

$$2(Niq_2(Hq))_o \rightleftharpoons (Ni_2q_4(Hq)_2)_o \quad : K_{dim} = K_{ex,3}/(K_{ex,2})^2, \qquad (10)$$

where K_{dim} is the dimerization constant. The constant is around 10^4 $mol^{-1}\,dm^3$ for all the metal ions except nickel. The reason for the smaller constant of nickel complexes is not clear.

Effects of Anions, Solvents and Central Metal Ions. When the total concentration of a metal ion is less than 10^{-4} $mol\,dm^{-3}$, only $M_2q_3(Hq)_3X$ and $Mq_2(Hq)$ are responsible for the extraction and the formation of $M_2q_4(Hq)_2$ is negligible. Using the absorbance vs. $-\log[H^+]$ data under these conditions (Fig. 5(a)—(i)), $K_{ex,1}$ and $K_{ex,2}$ in each system were refined to give a minimum error square sum about absorbance, $U=\sum(A_{obsd}-A_{calcd})^2$ (Table 2). The effects of anions on the distribution were examined in nickel-chloroform systems, whereas those of organic solvents in cobalt-perchlorate systems. As there formed a precipitate in hexane, carbon tetrachloride and toluene, comprehensive data were obtained in benzene, chlorobenzene and chloroform.

The extraction constant for the neutral species, $K_{ex,2}$ is almost the same for each metal ion irrespective of anions and organic solvents. Although the constants from the sulfate solution are slightly smaller than those from others, the difference is reasonably ascribed to a side reaction of metal ions with 0.1 $mol\,dm^{-3}$ sulfate ion. The solvent effect on the extraction constants appears in the change of the distribution constants of the reagent and the chelate, but these influences sometimes cancel out to each other to make the effect small.[31,32] It holds also in this system.

When hydrophobic anions and polar solvents are used, the extraction is actually enhanced because of the contribution of the ion-pair species (Fig. 6). This is why polar solvents have been favorably used in the extraction with 8-quinolinol in relation to the precipitation of $Mq_2\cdot H_2O$ (see below).

As to metal ion, all the three constants follow the well-known order, Co<Ni>Zn>Cd. Use of perchlorate medium is advantageous for the separation of cadmium ion.

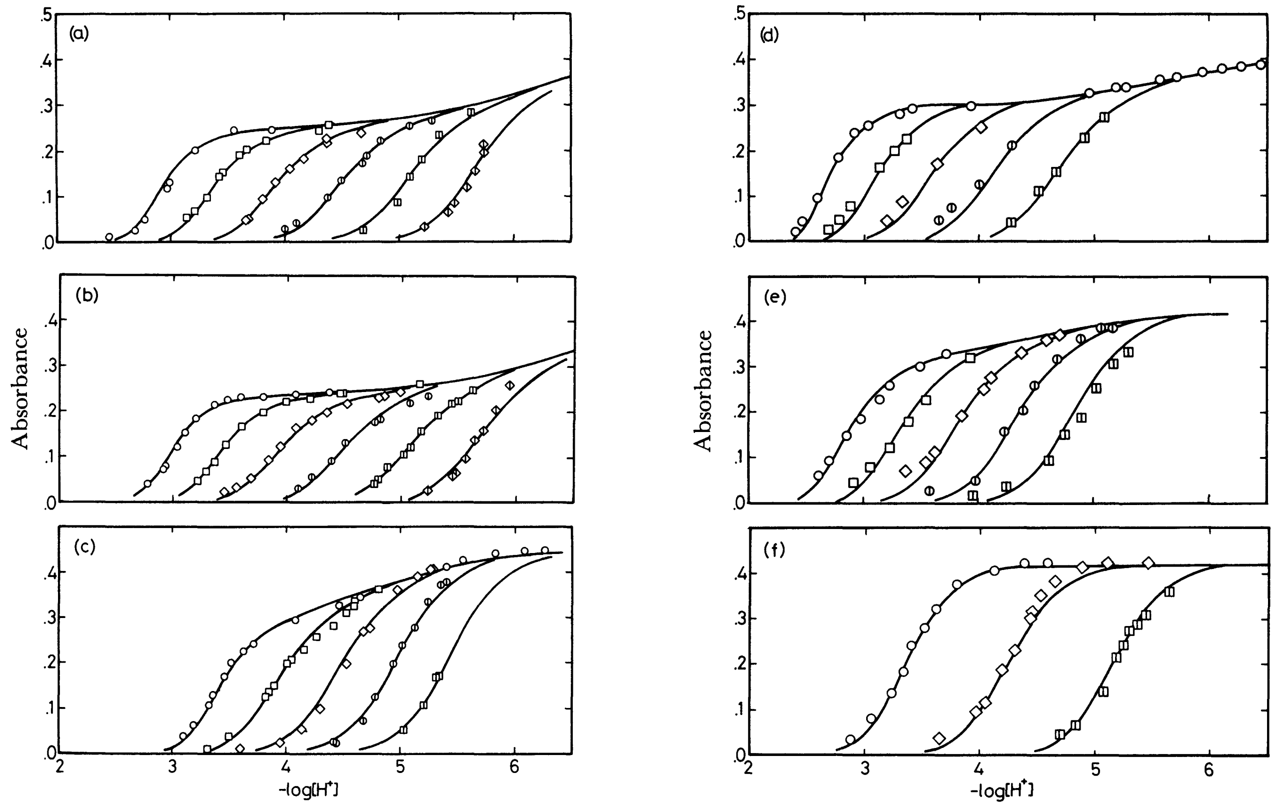
Slow Reaction-Precipitation of $Mq_2\cdot 2H_2O$. When nickel, zinc or cadmium is extracted with smaller concentration of 8-quinolinol at higher $-\log[H^+]$, decrease in absorbance of the organic phase is observed during the prolonged shaking. It has been ascribed to the precipitation of $Mq_2\cdot 2H_2O$ by chemical analyses and infrared spectra of the precipitates,[19,20] but has not been given a sound explanation.

Figure 7 shows absorbance in Zn^{2+}-ClO_4^--chloroform system after prolonged shaking at $C_{Zn}=10^{-4}$ and $C_{Hq}=0.06$ $mol\,dm^{-3}$. If only the three extraction equi-

Table 2. Extraction and Dimerization Constants of Metal 8-Quinolinolate Complexes

Metal	Anion	Solvent	$\log K_{ex,1}$	$\log K_{ex,2}$	$\log K_{ex,3}$	$\log K_{dim}$
Co^{2+}	ClO_4^-	Chloroform	2.39	−4.43	N.d.[a]	
	ClO_4^-	Chlorobenzene	2.37	−4.57	N.d.	
	ClO_4^-	Benzene	0.47	−4.54	N.d.	
	SO_4^{2-}	Chloroform	N.f.[b]	−5.13	−6.09	4.17
Ni^{2+}	ClO_4^-	Chloroform	8.00	−2.24	N.d.	
	I^-	Chloroform	8.12	−2.12	N.d.	
	NO_3^-	Chloroform	5.97	−2.35	N.d.	
	Br^-	Chloroform	5.96	−2.34	N.d.	
	Cl^-	Chloroform	4.92	−2.22	N.d.	
	SO_4^{2-}	Chloroform	N.f.	−2.48	−2.19	2.77
Zn^{2+}	ClO_4^-	Chloroform	1.01	−4.99	N.d.	
	SO_4^{2-}	Chloroform	N.f.	−6.18	−8.26	4.10
Cd^{2+}	ClO_4^-	Chloroform	−3.22	−7.17	N.d.	
	SO_4^{2-}	Chloroform	N.f.	−8.09	−11.68	4.50

a) Not determined. b) Not found.



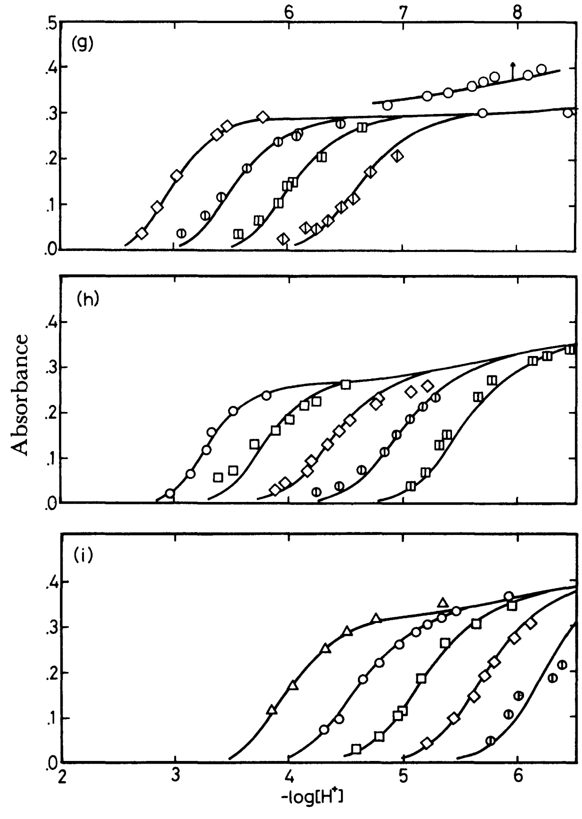


Fig. 5. Plot of absorbance vs. $-\log[H^+]$. $C_M=1\times10^{-4}$ mol dm^{-3}. Systems, C_{Hq}/mol dm^{-3}: (a) Co^{2+}–ClO_4^-–chloroform, 0.12, 0.06, 0.03, 0.015, 0.0075, 0.0038; (b) Co^{2+}–ClO_4^-–chlorobenzene; (c) Co^{2+}–ClO_4^-–benzene; (d) Ni^{2+}–NO_3^-–chloroform, 0.05, 0.025, 0.013, 0.0062, 0.0031; (e) Ni^{2+}–Cl^-–chloroform; (f) Ni^{2+}–SO_4^{2-}–chloroform, 0.05, 0.013, 0.0031; (g) Ni^{2+}–ClO_4^-–chloroform, 0.013, 0.0061, 0.0032, 0.0016; (h) Zn^{2+}–ClO_4^-–chloroform, 0.12, 0.06, 0.03, 0.015, 0.0075; (i) Cd^{2+}–ClO_4^-–chloroform, 0.24, 0.12, 0.06, 0.03, 0.015.

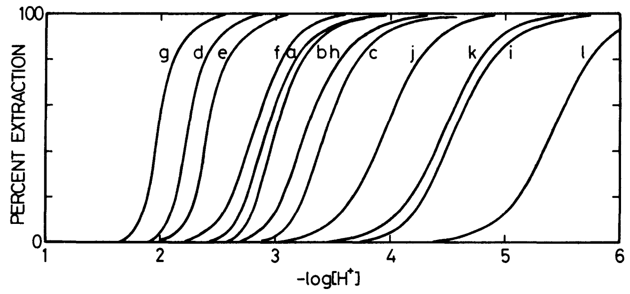


Fig. 6. Effects of anions, solvents and central metal ions on the extraction with 8-quinolinol at $C_M=10^{-4}$ and $C_{Hq}=0.12$ mol dm^{-3}. System: (a)—(i) same with Fig. 5; (j) Co^{2+}–SO_4^{2-}–chloroform; (k) Zn^{2+}–SO_4^{2-}–chloroform; (l) Cd^{2+}–SO_4^{2-}–chloroform.

libria identified above were considered, the absorbance should be as the solid line. At $-\log[H^+]$ below 4.7 the absorbance simply increased with time and the final one agreed with that given by this line. At higher $-\log[H^+]$, however, it once reached a maximum value and then slowly decreased to that shown by a circle. Table 3 tells that under these conditions the product $[Zn^{2+}][q^-]^2$ exceeds the solubility product of $Znq_2\cdot H_2O$.[33] Thus when the extraction is performed with usual procedure, all the equilibria except the precipi-

Table 3. Calculated Logarithmic Values of $[Zn^{2+}][q^-]^2$ by Assuming no Precipitation of $Znq_2{\cdot}2H_2O$[a)]

$-\log[H^+]$	$C_{Hq}/mol\ dm^{-3}$			
	0.12	0.06	0.03	0.015
3	−24.64	−25.37	−25.97	−26.53
4	−24.05	−23.81	−23.87	−24.41
5	−23.60	−23.30	−23.01	−22.81
6	−23.23	−22.93	−22.63	−22.33
7	−23.05	−22.74	−22.44	−22.14

a) $C_{Zn}=1\times10^{-4}\ mol\ dm^{-3}$. The solubility product of zinc 8-quinolinolate is $10^{-23.34}$.[33)]

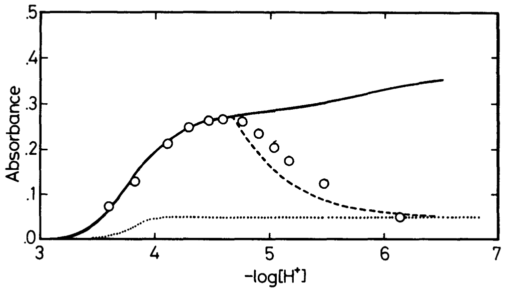


Fig. 7. Plot of absorbance vs. $-\log[H^+]$ in Zn^{2+}–ClO_4^-–chloroform system after prolonged shaking. $C_{Zn}=1\times10^{-4}\ mol\ dm^{-3}$. $C_{Hq}=0.06\ mol\ dm^{-3}$. Solvent: chloroform. Solid line: calculated curve by considering all the equilibria except precipitation of $Mq_2{\cdot}H_2O$. Broken and dotted lines: calculated curves by considering all the equilibria including the precipitation in ClO_4^- and SO_4^{2-} systems, respectively.

tation reaction are attained rapidly and Znq_2 becomes supersaturated in aqueous phase. Then $Znq_2{\cdot}2H_2O$ starts precipitating slowly with shifting other equilibria until the precipitation equilibrium holds.

When the precipitation equilibrium of $Znq_2{\cdot}2H_2O$ as well as extraction equilibria is included in the consideration, the calculated value given by a broken line well explains the experimental points. More pronounced decrease in Zn^{2+}-SO_4^{2-}-chloroform system shown by a dotted line is explained by the absence of species extracted as an ion-pair.

Crystal Structure of $Ni_2q_4(Hq)_2{\cdot}H_2O{\cdot}C_6H_6$. The atomic coordinates and isotropic thermal parameters are listed in Table 4, and the atomic-numbering system is presented in Fig. 8. The atoms of water and benzene are represented by O(600) and C(701)—C(706), respectively.

Two crystallographically independent nickel atoms are surrounded by three bidentate ligands with facial and meridional configurations about their oxygen atoms. These two octahedra are joined by the two strong hydrogen bonds, O(11)···O(411) [2.44(1) Å] and O(111)···O(311) [2.41(1) Å], to form the binuclear unit as shown in Fig. 8. The direction of the hydrogen bonds on the oxygen atoms is reasonable: 125 for Ni(1)-O(11)-O(411), 121 for Ni(1)-O(111)-O(311), 128 for Ni(2)-O(311)-O(111) and 124° for Ni(2)-O(411)-O(11). The two equivalent units related by a center of symmetry are linked by the hydrogen bonds between the respective O(211) atoms and the water molecules, 2.93(1) and 2.81(1) Å. Only O(511) does not form any

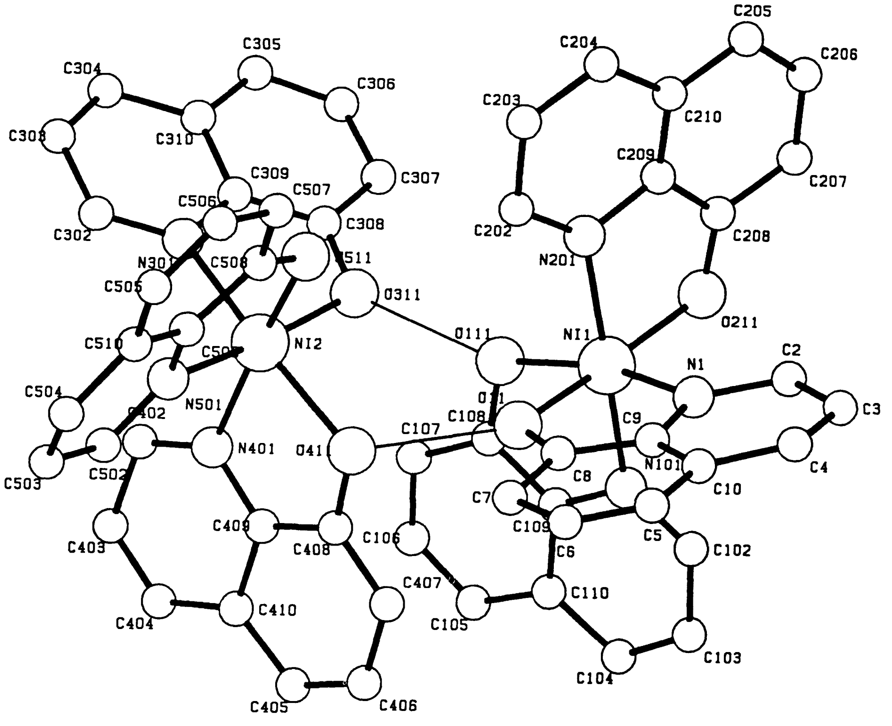


Fig. 8. Perspective drawing of binuclear structure of $Ni_2q_4(Hq)_2$.

Table 4. Fractional Coordinates (×10⁴) and Isotropic Temperature Factors (B_{eq}/Å²×10) with e.s.d. Values in Parentheses for $Ni_2q_4(Hq)_2 \cdot H_2O \cdot C_6H_6$

Atom	*x*	*y*	*z*	B_{eq} or B [a)]	Atom	*x*	*y*	*z*	B_{eq} or B [a)]
Ni(1)	1007(1)	6966(1)	7042(1)	31(1)	C(304)	6286(5)	4472(6)	9343(6)	46(2)
N(1)	−187(4)	8019(4)	7530(4)	39(2)	C(305)	4982(6)	3656(5)	8198(6)	45(2)
C(2)	−1131(5)	7962(6)	7397(7)	53(3)	C(306)	4159(6)	3709(5)	7601(6)	45(2)
C(3)	−1880(6)	8746(7)	7786(8)	66(4)	C(307)	3681(5)	4526(5)	7446(5)	41(2)
C(4)	−1619(6)	9574(6)	8300(8)	64(3)	C(308)	4085(4)	5315(4)	7907(5)	31(2)
C(5)	−313(7)	10511(6)	8985(8)	67(3)	C(309)	4971(4)	5288(4)	8537(5)	29(2)
C(6)	641(9)	10543(6)	9082(8)	78(4)	C(310)	5426(5)	4452(5)	8697(5)	39(2)
C(7)	1410(7)	9726(5)	8683(6)	53(3)	O(311)	3693(3)	6131(3)	7812(3)	37(1)
C(8)	1108(5)	8889(4)	8180(5)	37(2)	N(401)	5247(4)	7019(4)	7281(4)	36(2)
C(9)	68(5)	8859(5)	8064(5)	41(2)	C(402)	6134(6)	6543(6)	7019(7)	52(3)
C(10)	−616(6)	9679(6)	8463(6)	55(3)	C(403)	6626(6)	6525(6)	6102(7)	58(3)
O(11)	1715(3)	8094(3)	7780(4)	38(1)	C(404)	6155(7)	7006(6)	5506(7)	59(3)
N(101)	1072(4)	7060(4)	5540(4)	36(2)	C(405)	4684(7)	8032(6)	5171(7)	61(3)
C(102)	413(6)	7498(6)	5045(6)	50(3)	C(406)	3755(8)	8503(6)	5466(7)	63(3)
C(103)	574(7)	7582(7)	4053(7)	63(3)	C(407)	3309(6)	8505(5)	6383(6)	50(3)
C(104)	1466(7)	7172(6)	3582(6)	57(3)	C(408)	3847(5)	8017(4)	6998(5)	36(2)
C(105)	3157(6)	6262(7)	3675(6)	60(3)	C(409)	4764(5)	7522(4)	6685(5)	37(2)
C(106)	3783(5)	5822(7)	4218(6)	59(3)	C(410)	5210(6)	7533(5)	5749(6)	47(2)
C(107)	3559(5)	5764(5)	5188(6)	48(2)	O(411)	3492(3)	8013(3)	7908(4)	38(1)
C(108)	2650(4)	6159(4)	5615(5)	33(2)	N(501)	5130(4)	8243(4)	9609(5)	43(2)
C(109)	1960(4)	6642(4)	5061(5)	32(2)	C(502)	5867(7)	8575(6)	9375(8)	62(3)
C(110)	2199(5)	6686(5)	4085(5)	43(2)	C(503)	6209(8)	9342(7)	10111(8)	68(4)
O(111)	2352(3)	6147(3)	6547(3)	34(1)	C(504)	5821(8)	9715(6)	11093(9)	70(4)
N(201)	1009(4)	6701(4)	8443(4)	36(2)	C(505)	4625(7)	9730(6)	12408(7)	63(3)
C(202)	1507(6)	7034(5)	9366(6)	46(2)	C(506))	3854(8)	9342(8)	12575(7)	72(3)
C(203)	1252(6)	6924(6)	10305(6)	52(3)	C(507)	3516(6)	8576(5)	11759(6)	52(3)
C(204)	494(7)	6477(6)	10291(7)	54(3)	C(508)	3937(5)	8227(5)	10752(5)	40(2)
C(205)	−779(7)	5601(7)	9227(7)	61(3)	C(509)	4726(5)	8623(4)	10585(5)	39(2)
C(206)	−1199(6)	5233(6)	8202(8)	60(3)	C(510)	5039(6)	9379(5)	11390(7)	56(3)
C(207)	−897(6)	5339(6)	7310(7)	52(3)	O(511)	3635(3)	7544(3)	9954(4)	42(2)
C(208)	−152(5)	5823(5)	7368(5)	39(2)	O(600)	1236(4)	4234(4)	5120(5)	64(2)
C(209)	293(5)	6211(5)	8402(5)	37(2)	C(701)	8043(10)	7349(10)	3712(12)	104(4)
C(210)	−6(6)	6087(5)	9310(6)	48(3)	C(702)	7388(12)	8157(11)	4014(13)	115(4)
O(211)	163(3)	5974(3)	6553(3)	42(2)	C(703)	7078(12)	8552(11)	3248(13)	112(4)
Ni(2)	4457(1)	7177(1)	8626(1)	31(1)	C(704)	7405(10)	8161(10)	2316(12)	103(4)
N(301)	5342(4)	6088(4)	8971(4)	38(2)	C(705)	7965(12)	7353(12)	1972(13)	117(4)
C(302)	6157(5)	6080(6)	9589(6)	45(2)	C(706)	8341(12)	6935(11)	2632(13)	113(4)
C(303)	6629(5)	5267(6)	9761(6)	49(3)					

a) Equivalent isotropic temperature factors for Ni(1)—O(600) were estimated as $B_{eq}=4/3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$. For C(701)—C(706), isotropic ones, *B*, were used.

hydrogen bond.

The interatomic distances between Ni and O are 2.095(6), 2.064(5), 2.030(5), 2.063(5), 2.110(6), and 2.034(6) Å for O(11)—O(511). Oxygen atoms participating in the strong hydrogen bonds lie more distant from a nickel atom than those completely deprotonated. The Ni-N distances range from 2.057(7) to 2.098(7) Å, their average value being 2.074 Å. The bond lengths and angles in the ligand part are all comparable for the six ligands and reasonable compared with those of metal complexes with 8-quinolinol already reported.

The benzene molecules lie more than 3.35 Å apart from the metal complex and water molecules, the atoms of which undergo large thermal motion (B=10.3—11.7 Å²). The average bond lengths and angles are 1.34 Å [1.26(3)—1.42(2) Å] and 120° [117(2)—125(2)°], respectively.

The structure of the conjugate acid complex, $Ni_2q_3(Hq)_3X$ ($X=I_3^-$ or ClO_4^-), is different in that there are three hydrogen bonds and only facial configuration about their oxygen atoms. But there is essential similarity that hydrogen atoms of free 8-quinolinol are located deep in the large hydrophobic structure.

The dimeric species can have the same structure also in the organic solvents.

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