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Kinetics and Mechanisms of Complexing of Nickel(II) Ion with 2-Methyl-8-hydroxyquinoline-5-sulphonic Acid

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Abstract

The kinetics of the formation of a bidentate mononuclear complex of nickel(II) with 2-methyl-8-hydroxyquinoline-5-sulphonic acid (2Me-HOx-$5SO_3H, H_2L$) were studied by the stopped-flow method, spectrophotometrically, in the pH range 3.0–6.0 over a temperature range, 20–35 ℃. The kinetics data obtained are discussed in terms of detailed reaction mechanisms and thermodynamic parameters. The reaction of nickel(II) with 2-Me-HOx-$5SO_3H$ coupled with a sluggish ring closure was due to the steric hindrance of coordinated 2-methyl-8-hydroxyquinoline-5-sulphonic acid. The reaction of nickel(II) with a 2-methyl-8-hydroxyquinoline anion (L) was sufficiently rapid ($k_L = 6.47 \times 10^6$ M^{-1} s^{-1}) and is explained in terms of an internal conjugated base (ICB) mechanism. The activation energy was also calculated.

Introduction

The kinetics of the formation of nickel(II) complexes with various ligands have been deeply investigated [1–3] and the Eigen mechanism [4], for the formation of labile complexes, is generally accepted. Accordingly to this mechanism, the rate-determining step, which takes place with a rate constant k_1, is the release of a water molecule from the inner coordination sphere of the metal and subsequent entrance of the ligand. This step is preceded by a pre-equilibrium which involves the formation of an outer-sphere ion pair between the metal ion and the ligand, with an equilibrium constant K_{OS} (equilibrium I).

$$M(H_2O)_6{}^{2+} + L \overset{K_{OS}}{\rightleftharpoons} M(H_2O)_6,L^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(H_2O)_5L^{2+} + H_2O \qquad (I)$$

Provided the first equilibrium is fast and displaced far to the left, the overall second-order observed rate constant is given by $k_t = K_{OS} \cdot k_1$ [5] which, in turn, can be predicted from the computed K_{OS} value [6] and the typical water exchange rate of the metal [5], k_{H_2O}, related to k_1 through a statistical factor S *i.e.*, $k_1 = S \cdot k_{H_2O}$. Previous investigation [7] of the complex reaction between Ni(II) and 8-hydroxyquinoline (HOx, H_2L) and 8-hydroxyquinoline-5-sulphonic acid ($HOx\text{-}5SO_3H, H_2L$) showed that the experimental value for the rate has been ascribed to the internal hydrogen-bonded monoanion structure of the ligands and by comparing the rate for these ligands it is found that the negative charge of the sulphonyl group in the ligands was not affected. In order to gain additional knowledge of this kinetics effect, using the stopped-flow technique at 25 ℃ and ionic strength 0.1 M ($NaClO_4$), we report here on the complexes formation equilibria, kinetic mechanisms and thermodynamic parameters of the nickel(II) complex with 2-Me-HOx-5-SO_3H (the ligand bears steric hindrance for coordination with metal and differs only in the basic strength) as well as an investigation into this effect on various anions.

Experimental

2-Methyl-8-hydroxyquinoline-5-sulphonic acid monohydrate was synthesized according to Sekido *et al.* [8]. The compound was crystallized and purified twice with water. A stock solution of the ligand was prepared from the weighed amount. Nickel nitrate, nickel chloride and nickel sulphate were recrystallized twice from water. Their stock solutions were standardized by titration with EDTA [9] and stored under purged nitrogen. Conductivity water was used to prepare the solutions and as a reaction medium. An acetic acid-sodium acetate buffer was used for a pH range 3.0–6.0. An ionic strength of 0.1 M in either $NaNO_3$, NaCl or Na_2SO_4 was found in kinetic runs. Spectrophotometric measurements were made with a Hitachi 124 model spectrophotometer. A pH meter was calibrated with three buffer solutions. Kinetic measurements were made by observing absorbance changes using a stopped-flow apparatus (Union Giken Co., RA-1300) equipped with a

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Komatsu electronics CTR-120, to control temperature (25 ± 0.1 ℃) by circulating water through the double-wall cell. The reaction trace was photographed on the storage screen of a oscilloscope (National model VP-383 A) using a polaroid camera or recorded with a National X-Y recorder, V.P-6421A.

Procedure

In all cases the concentration of total 2-methyl-8-hydroxyquinoline-5-sulphonic acid was 2×10^{-4} M ($=$mol dm^{-1}), while a nickel(II) concentration was varied between 5×10^{-2} and 5×10^{-3} M. A large excess of a nickel(II) over 2Me-HOx-5SO$_3$H was used to minimize the possible formation of a bis-complex and to increase the accuracy of the evaluation by providing pseudo-first-order conditions. To prevent any precipitation of nickel(II) hydroxide which starts around pH 6, the reaction was carried out at pH lower than 6.0. In all prepared solutions the acetate concentration was 5×10^{-2} M.

Calculation

The stoichiometric reaction for the association of NiL is given in reaction (II), where L represents a 2Me-HOx-5SO$_3$H ligand (the charge of species being omitted).

$$\mathrm{Ni} + \mathrm{L} \xrightarrow{k} \mathrm{NiL} \qquad \text{(II)}$$

The rate of the formation of NiL was studied under pseudo-first-order conditions and was consistent with the rate law given by eqn. (1), where k_{obs}, pseudo-first-order rate constant, is equal to $k[\mathrm{Ni}]$, [ ] concentration of species.

$$\mathrm{d}[\mathrm{Ni}]/\mathrm{d}t = k[\mathrm{Ni}][\mathrm{L}] = k_{\mathrm{obs}}[\mathrm{L}] \qquad (1)$$

One integrated first-order rate expression used for plotting the data is

$$\ln a/(a - x) = \ln A_\infty/(A_\infty - A_t) = k_{\mathrm{obs}}t \qquad (2)$$

where a is the initial concentration of the ligand and x is the instantaneous concentration of the complex, NiL at a given time t, respectively. The rate constant, k_{obs} is determined as the linear progression slopes of plots of $\ln A_\infty/(A_\infty - A_t)$ *vs.* time, where A_t is the absorbance at time t and A_∞ is the final absorbance reading after 10–12 h half-lives (Fig. 1).

Results and Discussion

The Formation Kinetics of Bidentate Mononuclear Complex of Nickel(II) with 2-Methyl-8-hydroxyquinoline-5-sulphonic Acid

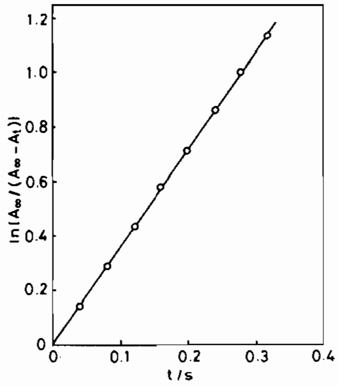


Fig. 1. Pseudo-first-order plot for the reaction between nickel(II) and 2-methyl-8-hydroxyquinoline-5-sulphonic acid. [2Me-HOx-5SO$_3$H]: 2.00×10^{-4} M, [Ni^{2+}]: 2.00×10^{-4} M, pH = 4.82, μ = 0.1 (NaNO$_3$).

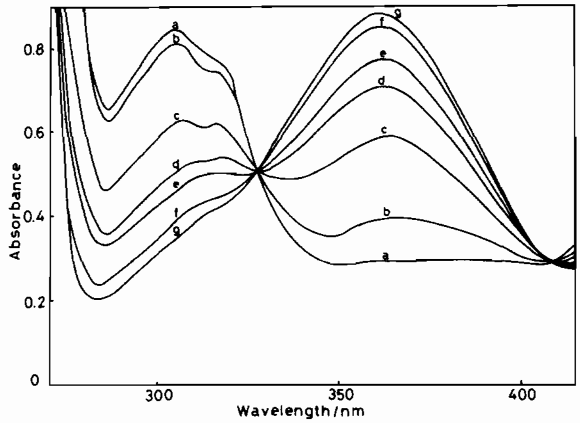


Fig. 2. Change of the absorption spectra with the formation of 1:1 nickel(II)–2-methyl-8-hydroxyquinoline-5-sulphonic acid complex. [Ni^{2+}]: 2.00×10^{-2} M, [2Me-HOx-5SO$_3$H]: 2.00×10^{-4} M, pH = 5.3, μ = 0.1 (NaNO$_3$). Upper labelling indicates standing time. (a) 0.02 s, (b) 0.05 s, (c) 0.10 s, (d) 0.15 s, (e) 0.20 s, (f) 0.30 s, (g) 0.40 s.

The visible spectrum of the aqueous nickel(II)–2Me-HOx-5SO$_3$H system is markedly dependent upon temperature and pH. The spectra of all the solutions used for analysis of the kinetics were recorded between 280 and 420 nm (Fig. 2). The concentration dependence is the same as that expected for the formation of 1:1 complex. In each system under study, the variation of the absorbance with the hydrogen ion concentration at a given concentration of metal ion and ligand, indicated that the main species was NiL under experimental conditions. Reactions were studied by stopped-flow spectrophotometry at 360 nm corresponding to a maximum in the absorption spectrum of the complex (Fig. 2). A plot of $k\,(1 + K_{\mathrm{a1}}/[\mathrm{H}])$ *vs.* $K_{\mathrm{a1}}/[\mathrm{H}]$ (refer to 'Appendix') is shown in Fig. 3. It should be noted that this plot revealed a hyperbolic shape. Thus, another reaction mechanism involving L species may be considered. Possible kinetic equation is expressed by

$$k'(1 + K_{\mathrm{a1}}/[\mathrm{H}] + K_{\mathrm{a1}}K_{\mathrm{a2}}/[\mathrm{H}]^2) = k_{\mathrm{H_2L}} + k_{\mathrm{HL}}K_{\mathrm{a1}}/[\mathrm{H}] + k_{\mathrm{L}}K_{\mathrm{a1}}K_{\mathrm{a2}}/[\mathrm{H}]^2 \qquad (3)$$

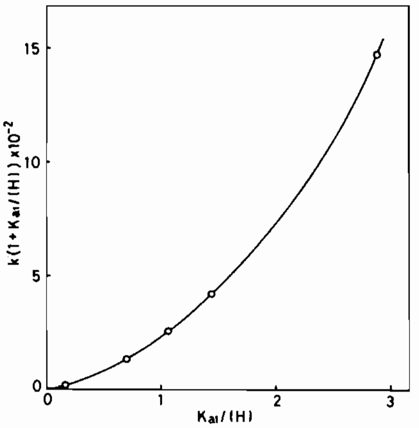


Fig. 3. Plot of $k(1 + K_{a1}/[H])$ vs. $K_{a1}/[H]$ for nickel(II)–2-methyl-8-hydroxyquinoline-5-sulphonic acid complex formation in nitrate medium at 25 °C.

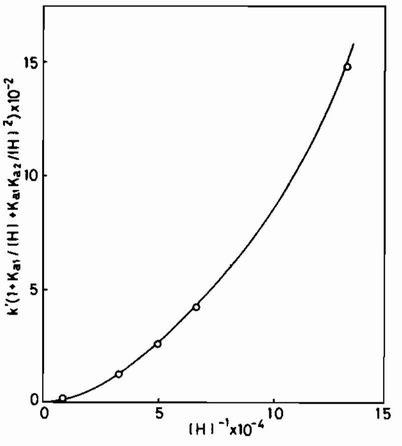


Fig. 4. Plot of $k'(1 + K_{a1}/[H] + K_{a1}K_{a2}/[H]^2)$ vs. $[H]^{-1}$ for nickel(II)–2-methyl-8-hydroxyquinoline-5-sulphonic acid complex formation in nitrate medium at 25 °C.

where k' is a conditional second-order rate constant. A plot of $k'(1 + K_{a1}/[H] + K_{a1}K_{a2}/[H]^2)$ vs. $1/[H]$ gives a hyperbolic shape (Fig. 4). Based on the least-square method, rate constants, k_{H_2L}, k_{HL} and k_L are calculated to be 0, 58.7 and 6.47×10^6 M^{-1} s^{-1} with respect to the NO_3^- anion medium, respectively (refer to Table I). It follows that the value of k_{H_2L} is small compared with the other rate constants (k_{HL} or k_L) in the pH range 4.2–5.2. If the reasonable assumption may be made that k_{H_2L} is zero, eqn. (4) was obtained.

$$k'(1 + K_{a1}/[H] + K_{a1}K_{a2}/[H]^2) = k_{HL}K_{a1}/[H] + k_LK_{a1}K_{a2}/[H]^2 \quad (4)$$

with $1 \gg K_{a1}K_{a2}/[H]^2$ and $K_{a1}/[H] \gg K_{a1}K_{a2}$, where $K_{a1}K_{a2} = 1.2 \times 10^{-4}$ for 2Me-HOx-5SO$_3$H; rearrangement of eqn. (4) leads to eqn. (5)

$$k'([H] + K_{a1}) = k_{HL}K_{a1} + k_LK_{a1}K_{a2}/[H] \quad (5)$$

TABLE I. Rate Constants for the Reaction of Nickel(II) Ion with 2-Methyl-8-hydroxyquinoline-5-sulphonic Acid

$$Ni + HL \xrightarrow{k_{HL}} NiL + H$$
$$Ni + L \xrightarrow{k_L} NiL$$

Anion medium	Temperature	k_{HL}	$k_L \times 10^6$
	(°C)	(M^{-1} s^{-1})	(M^{-1} s^{-1})
NO_3^- (μ = 0.1)	20	32.0	3.82
	25	58.7	6.47
	30	105	9.18
	35	191	13.8
Cl^- (μ = 0.1)	20	34.9	3.24
	25	51.6	5.38
	30	90.0	8.82
	35	152	14.4
SO_4^{2-} (μ = 0.1)	20	17.7	2.04
	25	29.4	3.20
	30	62.7	4.82
	35	117	8.56

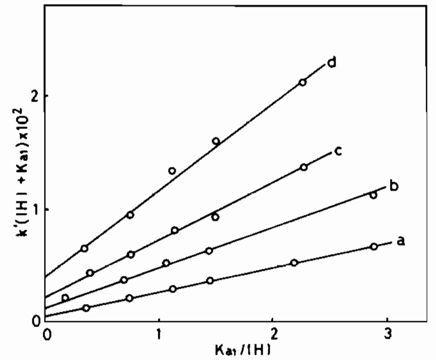
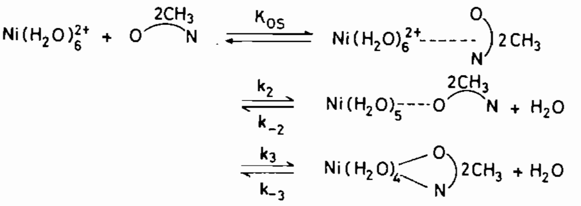


Fig. 5. Plot of $k'([H] + K_{a1})$ vs. $K_{a1}/[H]$ for nickel(II)–2-methyl-8-hydroxyquinoline-5-sulphonic acid complex formation in nitrate medium at various temperatures. (a) 20 °C, (b) 25 °C, (c) 30 °C, (d) 35 °C.

A plot of $k'([H] + K_{a1})$ vs. $K_{a1}/[H]$ gives straight lines, the gradient (k_LK_{a2}) and intercept ($k_{HL}K_{a1}$) of which yield values for k_L and k_{HL}, respectively. It was concluded that the value of the gradient and intercept observed with each anion, SO_4^{2-}, NO_3^- and Cl^- was enlarged with an increase in temperature. The typical result obtained in this work is shown in Fig. 5. It was found that the complex-formation rate constant in the nickel(II)–2Me-HOx-5SO$_3$H system with respect to the SO_4^{2-} anion medium is small as is well shown in the case of the nickel(II)–HOx-5SO$_3$H system [7]. The rate constant, k_{HL} of the former is small compared with that of the latter.

The abnormal low value of the rate constant, k_{HL} with nickel(II)–2Me-HOx-5SO$_3$H, can be explained in two ways, (a) a steric hindrance occurred by a methyl group on 2-position with a quinoline nucleus and (b) the closure of the chelate ring with simultaneous or subsequent expulsion of the proton of 2Me-HOx-5SO_3H. These effects were also explained in terms of an internal conjugated base (ICB) mechanism proposed by Basolo and Pearson [10, 11]. It is evaluated that k_L values may be of a 10^3 order enlargement for the complex formation compared with those of k_{HL}. The rate constant for a ring-closure step, k_L, should be greater than the product of the water exchange rate constant of the bidentate-bonded nickel(II) ion ($k_{HL} = K_{OS}k_2/k_{-2}k_3$), where the aquo nickel(II) ion, $Ni(H_2O)_6{}^{2+}$ and the entering ligand, $\overset{2CH_3}{O\frown N}$ are in rapid equilibrium with an outer sphere complex in which the entering group occupies a position in the second coordination sphere and the rate-determining step is the loss of a coordination water molecule.



(III)

Temperature Dependence

The rate constant for the reaction of the nickel(II)–2Me-HOx-5SO_3H system with respect to each anion medium was measured at 20, 25, 30 and 35 °C. Activation energy (E_a) calculated from a plot of ln k_{HL} *vs.* $1/T$ (refer to eqn. (6)) is presented in Table II. The enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and the free energy ($\Delta G^{\ddagger}$) of the formation of the activated complex, $(Ni + HL \xrightarrow{k_{HL}} NiL + H)$ were calculated from the eqns. (6 and 7).

$$\ln k_{HL} = \ln A - E_a/R \cdot 1/T \qquad (6)$$

and

$$\ln k_{HL}/T = \ln k/h + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/R \cdot 1/T \qquad (7)$$

TABLE II. Activation Parameters for the Reaction of Nickel(II) Ion with 2-Methyl-8-hydroxyquinoline-5-sulphonic Acid (HL form)

$$Ni + HL \xrightarrow{k_{HL}} NiL + H$$

	E_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
	kJ mol^{-1}	kJ mol^{-1}	JK^{-1} mol^{-1}	kJ mol^{-1}
NO_3^-	89.96	87.03	31.79	76.99
Cl^-	89.12	83.26	24.98	75.73
SO_4^{2-}	106.27	97.07	46.86	125.10

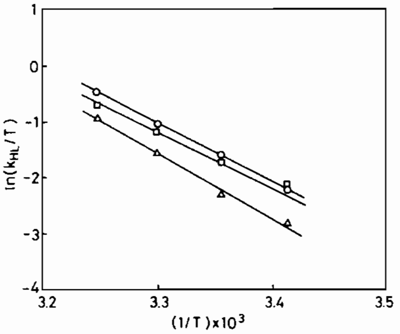


Fig. 6. Plots of ln(k_{HL}/T) *vs.* $1/T$ according to eqn. (7) for nickel(II)–2-methyl-8-hydroxyquinoline-5-sulphonic acid. (○) NO_3^-, (□) Cl^-, (△) SO_4^{2-}.

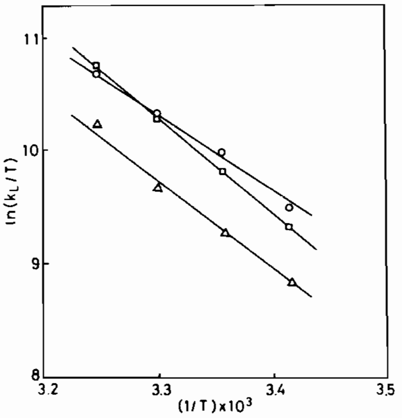


Fig. 7. Plots of ln(k_L/T) *vs.* $1/T$ for nickel(II)–2-methyl-8-hydroxyquinoline-5-sulphonic acid. (○) NO_3^-, (□) Cl^-, (△) SO_4^{2-}.

The activation energy (E_a) calculated for the nickel(II)–2Me-HOx-5SO_3H system with NO_3^- or Cl^- is 89.96 ± 0.84 kJ/mol and log A = 5.6 ± 0.2. Values of $\Delta H^{\ddagger}$ = 84.94 ± 1.67 kJ/mol and $\Delta S^{\ddagger}$ = 28.41 ± 0.42 e.u. were calculated in the usual manner by using the absolute reaction rate theory. The values of $\Delta G^{\ddagger}$ (kJ/mol) decrease from 125.1 ± 0.4 in an SO_4^{2-} anion to 75.57 ± 0.4 in an NO_3^- or Cl^- anion. The normal chelation mechanism for the nickel(II)–2Me-HOx-5SO_3H system appears to be entropic rather than enthalpic in nature (Table II and Fig. 6). Analogically estimated for the reaction of nickel(II) with the 2-methyl-8-hydroxyquinoline-5-sulphonic anion (L), $\Delta H^{\ddagger}$ = 63.43 ± 6.69 kJ/mol, $\Delta S^{\ddagger}$ = 43.52 ± 10.4 e.u. and $\Delta G^{\ddagger}$ = 52.3 ± 3.35 kJ/mol (Fig. 7). The activation energy of the homogeneous process (58 kJ/mol) provides good evidence that the process of S_N2 type can occur. For explanation of much lower $\Delta S^{\ddagger}$ values for the reaction of nickel(II) with a 2-methyl-8-hydroxyquinoline-5-sulphonic anion it has been suggested that the planar complex is not completely free of axial solvation, as shown by the results for complexes of tetra-amines [12]. Thus, the free energy of activation for the process contains a contribution for a ring strain and one for entropy loss [13]. These facts have suggested some π interaction between nickel(II) and the 2Me-HOx-5SO_3H ligand. Compensating electron donor effects between σ and back π bonding could be involved. The rate-determining step of the nickel(II)–2Me-HOx-5SO_3H reaction is the closure of the chelate ring, while that of nickel(II)–HOx-5SO_3H is the release of a coordination water molecule from the octahedral $Ni(H_2O)_5L^{2+}$ complex. This work on 2Me-HOx-5SO_3H presents some new information on the reactivity of the free base L.

Acknowledgement

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Appendix

Kinetics of the formation of a nickel(II)–2Me-HOx-5SO_3H complex may be written as follows:

$$H_2L \overset{K_{a1}}{\rightleftharpoons} HL + H \qquad K_{a1} = [H][HL]/[H_2L] \qquad (1S)$$

$$HL \overset{K_{a2}}{\rightleftharpoons} L + H \qquad K_{a2} = [L][H]/[HL] \qquad (2S)$$

$$Ni + H_2L \xrightarrow{k_{H_2L}} NiL + 2H \qquad (3S)$$

$$Ni + HL \xrightarrow{k_{HL}} NiL + H \qquad (4S)$$

$$Ni + L \xrightarrow{k_L} NiL \qquad (5S)$$

where $K_{a_1}(10^{-4.66})$ and $K_{a2}(10^{-9.27})$ denote first and second dissociation constants of 2Me-HOx-5SO_3H, respectively, and k_{H_2L}, k_{HL} and k_L are rate constants for the nickel(II)–2Me-HOx-5SO_3H complex (NiL): for reactions (3S)–(5S), rate law (6S) may be derived.

$$\begin{aligned} d[NiL]/dt &= k[Ni]([H_2L] + [HL] + [L]) \\ &= k_{H_2L}[Ni][H_2L] + k_{HL}[Ni][HL] \\ &\quad + k_L[Ni][L] \end{aligned} \qquad (6S)$$

where [ ] is the analytical concentration of each species. Under the experimental conditions, *i.e.* between pH 3.2 and 4.6, it is assumed that $[H_2L] + [HL] \gg [L]$. Thus, the rate expression can be written in the form of eqn. (7S).

$$\begin{aligned} &k([H][HL]/K_{a1} + [HL]) \\ &\quad = k_{H_2L}[H][HL]/K_{a1} + k_{HL}[HL] \end{aligned} \qquad (7S)$$

Equation (7S) can be simplified and rearranged to give:

$$k(1 + K_{a1}/[H]) = k_{H_2L} + k_{HL}K_{a1}/[H] \qquad (8S)$$

Plot of $k(1 + K_{a1}/[H])$ *vs.* $K_{a1}/[H]$ gives a straight line, the gradient and intercept of which yield values of k_{HL} and k_{H_2L}, respectively.