The Kinetics of Complexation of Nickel(II) and Cobalt(II) Mandelates in Aqueous Solution

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The rate constants for the formation and dissociation of nickel(II) and cobalt(II) complexes with mandelate have been determined by the pressure-jump relaxation study. The forward and reverse rate constants for the mandelate complex formation reactions were obtained to be $k_f=3.60\times10^4$ $M^{-1}s^{-1}$ and $k_r=1.73\times10^2$ s^{-1} for the nickel(II), and $k_f=1.75\times10^5$ $M^{-1}s^{-1}$ and 2.33×10^3 s^{-1} for the cobalt(II) in aqueous solution of zero ionic strength ($\mu\rightarrow0$) at 25℃. The results were interpreted by the use of the multistep complex formation mechanism. The rate constants evaluated for each individual steps in the multistep mechanism draw a conclusion that the rate of the reaction would be controlled by the chelate ring closure step in concert with the solvent exchange step in the nickel(II) complexation, while solely by the chelate ring closure step for the cobalt(II) complex.

Introduction

The rates and mechanisms of the complexation reaction of the labile metal ions have received considerable attention.[1-16] The broad outline of the mechanism of these reactions is described by well known the Eigen's multistep mechanism.[2] In this mechanism, the step of the release of a solvent molecule from the inner coordination sphere of the metal ion is generally considered as the rate determining step. However, in the kinetic studies on the complex formation reactions of nickel(II) and cobalt(II) ions with β-alanine and β-aminobutylic acid, Kustin *et al.*[3,4] have found that the reaction is sterically controlled.

Kinetic data[6-10] of the complexation reactions of nickel(II) and cobalt(II) ions with various kinds of dicarboxylates have shown that the rate determining step for the substitution reactions of cobalt(II) ion is the chelate ring closure step, while is the solvent exchange for those of nickel(II) ion. This is since that the rate of water exchange of cobalt(II) ion is much faster than that of nickel(II) ion. It has been reported that the rate constants (k_w)[11,12] of the water exchange process of cobalt(II) and nickel(II) ions are 2.6×10^6 sec^{-1} and 2.7×10^4 sec^{-1}, respectively. In the cases of the metal(II) complexes of bidentate monocarboxylate ligands which have a hydroxy[13-16] or amine[3-5] functional group at α or β positions, it is likely that the chelate ring closure process affect the rate of the reaction to considerable extent even for the nickel(II) ion. In this report, we present the results of a pressure-jump kinetic study on the complexation reactions of nickel(II) and cobalt(II) ions with the mandelate ligand which has a phenyl substituent at α position of the glycolate.

Experimental

All of the chemicals used were of a reagent grade and have been used without further purification. Stock solutions of the nickel(II) and cobalt(II) complexes were prepared by mixing stoichiometric amounts of respective metal sulphates with the mandelic acid in doubly distilled water. The sulphate ion was precipitated out as insoluble barium sulphate by titrating the solution with a standard solution of barium hydroxide. The solid barium sulphate was removed by filteration. The concentration of the metal ion in the stock solution was standardized by EDTA titration. The working solutions were prepared by diluting the stock solution to desired concentrations. The pH's of the solution were in the range 5.2-5.4, in which most of the ligand dissociates to the anionic form.

The pressure-jump apparatus which is similar to that previously described[17] in detail has been used to measure the relaxation times of the complexation reactions. The rise time of the apparatus was measured to be shorter than 67 μsec in a 0.2 M nickel sulphate solution. The relaxation time for each system was measured at 18, 25, and 35℃ for five different concentrations. A relaxation time characterized by a single relaxation step was observed for the solutions studied. A iteration method assuming an initial value of the equilibrium constants was used to calcualte simultaneously the rate constants and equilibrium constant from the relaxation times.

Results and Discussion

The relaxation processes observed are interpretated in terms of the complex formation equilibrium. The complex formation equilibrium of the metal(II) ions with the mandelate ligand would be expressed as

$$M^{2+}+L^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} ML^+ \tag{1}$$

where M^{2+} is the metal ion, L^- is the ligand anion, ML^+ is the complex. The relaxation time (τ) of the process is related to the forward and reverse rate constants (k_f and k_r) Eq. (2),

$$\frac{1}{\tau}=k_f f_\pm^2(\bar{C}_{M^{2+}}+\bar{C}_{L^-})+k_r \tag{2}$$

where $\bar{C}$ is the equilibrium concentrations of the species and $f_\pm$ is the mean activity coefficient of the free ions. The activity coefficients of the ions were estimated from the Davies equation[18] which is given by Eq. (3);

$$\log f_i=-0.5\,Z_i^2\left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}}-0.2\ \mu\right) \tag{3}$$

Table 1. Relaxation Data for Nickel(II) and Cobalt(II) Complexes with Mandelate at $\mu \rightarrow 0$

Temperature (℃)	$C_o \times 10^3$ (M)	$\overline{C}_{ML^+} \times 10^3$ (M)	$(\overline{C}_{M^{2+}} = \overline{C}_{L^-}) \times 10^3$ (M)	$\mu \times 10^3$	$f_\pm$	$1/\tau \times 10^{-2}$ (s^{-1})
			Nickel(II)			
18	10.10	4.95	5.15	12.88	0.80	2.26
	6.01	2.41	3.60	8.99	0.82	1.89
	4.01	1.34	2.68	6.69	0.84	1.72
	2.95	0.83	2.12	5.29	0.86	1.57
	2.01	0.45	1.56	3.89	0.88	1.49
25	10.10	5.14	4.96	12.40	0.80	4.02
	6.01	2.53	3.48	8.70	0.83	3.40
	4.01	1.41	2.60	6.50	0.85	3.08
	2.95	0.89	2.06	5.16	0.86	2.85
	2.01	0.49	1.52	3.81	0.88	2.55
35	10.10	5.35	4.75	11.88	0.80	6.88
	6.01	2.66	3.35	8.38	0.83	5.93
	4.01	1.50	2.51	6.28	0.85	5.27
	2.95	0.95	2.00	5.00	0.86	4.80
	2.01	0.52	1.49	3.72	0.88	4.33
			Cobalt(II)			
18	10.10	2.93	7.17	17.93	0.77	27.47
	8.01	2.03	5.98	14.94	0.78	26.18
	6.01	1.28	4.73	11.83	0.80	24.94
	4.01	0.65	3.37	8.41	0.83	23.53
	2.01	0.19	1.82	4.55	0.87	21.32
25	10.10	3.82	6.72	16.80	0.77	37.31
	8.01	2.38	5.63	14.08	0.79	35.59
	6.01	1.51	4.50	11.24	0.81	33.56
	4.01	0.78	3.23	8.07	0.83	31.15
	2.01	0.24	1.77	4.44	0.87	27.93
35	10.10	4.18	5.92	14.81	0.78	52.91
	8.01	3.00	5.02	12.54	0.80	49.51
	6.01	1.96	4.05	10.13	0.81	46.08
	4.01	1.05	2.96	7.41	0.84	42.02
	2.01	0.33	1.68	4.19	0.87	36.90

where Z_i is the charge of the ith ion and μ is the ionic strength of the solution.

The plot of $1/\tau$ against $f_\pm^2(\overline{C}_{M^{2+}} + \overline{C}_{L^-})$ by the Eq. (2) should give a linear line of which the slope and the intercept are k_f and k_r, respectively. However, we should know the thermodynamic formation canstant($K_{eq} = k_f/k_r$) of the complex in order to calculate the mean activity coefficient and equilibrium concentrations of the ions. Since the accurate values of the thermodynamic formation constants of nickel(II) and cobalt(II) mandelate complexes in aqueous solution were not available, we have calculated the formation constant, forward rate constant, and reverse rate constant simultaneously from the relaxation times observed by the following iteration method.

As the first approximation, an initial value of K_{eq} which is estimated from the literature value[19,20] obtained at higher ionic strength is used to calculate the activity coefficients and the equilibrium concentrations of the species. Then, the values of k_f and k_r are obtained from the plot of $1/\tau$ against $f_\pm^2(\overline{C}_{M^{2+}} + \overline{L}^-)$ by the Eq. (2). A new value of $K_{eq}(= k_f/k_r)$ should be close to and initial value of K_{eq} approximated. The above procedure is repeated until the standard deviation of the value is minimized. The final values of the equilibrium concentrations and the mean activity coefficients alone with the reciprocals of relaxation times are given in Table 1. The best fit plots of the final values for the nickel(II)-mandelate system at various temperature are shown in Figure 1.

The rate and thermodynamic formation constants obtained from the above procedure are summarized in Table 2. The activation parameters have been obtained from the Arrhenius plot of the rate constant against the reciprocal of temperature and general kinetic equations. They are given in Table 3.

The multistep mechanism[3,4] for the metal complex formation reaction with a monobasic chelating ligand such as the mandelate would be described as

$$M^{2+}_{(aq)} + L^-_{(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} W_2MW_1L^+ \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} W_2M\text{-}L^+ \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} M{=}L^+ \quad (4)$$

(I) (II) (III)

where W_1 and W_2 are the metal ion-coordinated water mole-

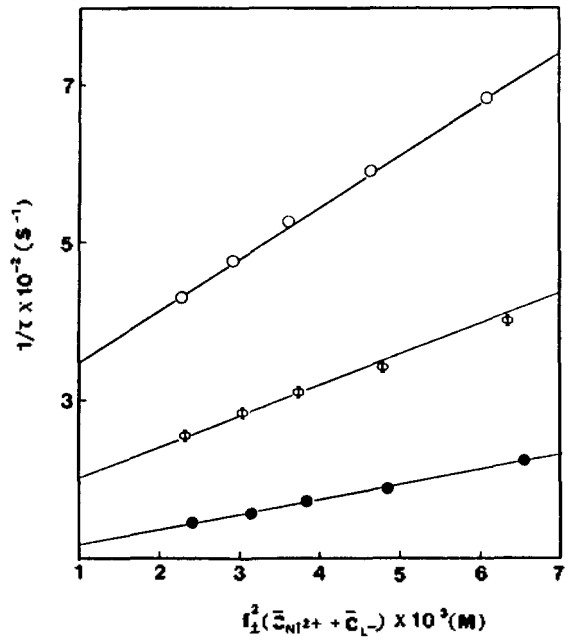

Figure 1. $1/\tau$ *vs* $f_{\pm}^2+(\bar{C}_{M^{2+}}+\bar{C}_{L^-})$ polt for nickel(II)-mandelate reaction system at 18℃ (●), 25℃ (Φ), 35℃ (○).

Table 2. Rate Constants and Stability Constants of Nickel(II) and Cobalt(II) Complexes with Mandelate at $\mu\rightarrow 0$

Metal	Temperature (℃)	$k_f\times10^{-4}$ ($M^{-1}s^{-1}$)	$k_r\times10^{-2}$ (s^{-1})	$K_w\times10^{-2}$ (M^{-1})
Nickel(II)	18	1.88± 0.10	1.01± 0.05	1.87± 0.14
	25	3.60± 0.09	1.73± 0.04	2.09± 0.07
	35	6.68± 0.13	2.82± 0.06	2.36± 0.06
Cobalt(II)	18	10.6± 1.1	18.5± 0.1	0.57± 0.13
	25	17.5± 1.5	23.3± 0.1	0.75± 0.07
	35	33.6± 5.6	28.2± 0.3	1.19± 0.03

cules. The step(I) is the diffusion controlled ion pair complex formation. The step(II) involves the loss of a water molecule from the inner hydration sphere of the metal ion and the formation of the monosubstituted metal complex. The step (III) is the formation of the fully chelated complex. The equilibrium constants for the step(I), (II), and (III) are represented by $K_0=k_{12}/k_{21}$, $K_2=k_{23}/k_{32}$, and $K_3=k_{34}/k_{43}$, respectively.

With the assumptions that the step(I) is very rapid with respect to other steps and the species $W_2M\text{-}L^+$ is in a steady state, the overall forward and reverse rate constants of Eq. (1) are related to the rate constants of individual steps of Eq. (4) as:

$$k_f=K_0k_{23}\left(\frac{k_{34}}{k_{32}+k_{34}}\right) \text{ and } k_r=k_{32}\left(\frac{k_{43}}{k_{32}+k_{34}}\right) \quad (5)$$

If the rate determining step is the loss of a water molecule from the inner hydration sphere and ring clsure step is much faster, *i.e.*, $k_{34}>k_{32}$, then Eq. (5) are reduced to $k_f=K_0k_{23}$ and $k_r=k_{32}/K_3$, respectively. k_{23} would be estimated when K_0 is known. The ion pair formation constant K_0 when $\mu\rightarrow0$ would be estimated theoretically by the Fuoss equation,[21]

Table 3. Kinetic Data for Nickel(II) and Cobalt(II) Complex Formation Reactions with Mandelate at 25℃ and $\mu\rightarrow0$

	Nickel(II)	Cobalt(II)
k_f, $M^{-1}s^{-1}$	$(3.60\pm0.09)\times10^4$	$(1.75\pm0.15)\times10^5$
k_r, s^{-1}	$(1.73\pm0.04)\times10^2$	$(2.33\pm0.01)\times10^3$
E_f^*, kjoule mol^{-1}	55.2± 5.6	50.7± 6.2
ΔH_f^*, kjoule mol^{-1}	52.7± 5.6	48.2± 6.2
ΔS_f^*, joule $K^{-1}mol^{-1}$	18.6± 1.9	17.3± 1.9
ΔG_f^*, kjoule mol^{-1}	47.2± 7.9	43.1± 8.4

$$K_0=\frac{4\pi Na^3}{3000}\,e^{-U(a)/kT} \quad (6)$$

where N is Avogadro's number, a is the distance of the closest approach of two ions, and $U(a)$ is a Coulomb energy term. Substituting 5Å for nickel(II) and 8Å for cobalt(II) ion pairs for a of Eq. (6), which are generally assumed in the literature,[22,23] the values of K_0 for the nickel(II) and cobalt(II) mandelates in the solution have been estimated to be 5.4 M^{-1} and 7.7 M^{-1}, respectively. With these values of K_0, it could be estimated that the values of k_{23} are 6.7×10^3 s^{-1} and 2.3×10^4 s^{-1} for the mandelate complexes of nickel(II) and cobalt(II) ions at 25℃, respectively.

As expected, the value of k_{23} for the cobalt(II) mandelate is about two order smaller than the water exchange rate constant k_w of the cobalt(II) ion which has been reported as 2.6×10^6 s^{-1}.[12] This would mean that the assumption $k_{34}>k_{32}$ does not sustain and the rate determing step for the reaction is also the step(III) in the α-hydroxy carboxylate ligand system, as proved already for the cobalt(II) complexation reactions with dicarboxylate ligands.[9,10]

However, the value of k_{23} for the nickel(II) mandelate is a little less than the water exchange rate constant k_w of the nickel(II) ion. The water exchange rate constant k_w of the nickel (II) ion has been determined from the ^{17}O-NMR study to be 2.7×10^4 s^{-1}.[11] The k_w is actually about four time larger than the k_{23}. This implies that the overall rate is controlled mainly by the step(III) but in some extent by the step(II). Therefore, it is suggested that the chelate ring closure step would control the rate of the reaction in concert with the solvent exchange step in the nickel(II) complexation with the α- hydroxy carboxylate ligand. This is interesting fact, as considering that the water exchange process mainly controls the reaction rate in the case of dicarboxylate complexation of nickel(II) ion.[6,8,10]

The activation parameters of Table 3 are very close values between the nickel(II) and cobalt(II) mandelate systems in contrast to that the activation energy of the nickel(II) cinchomeronate system is 17 kjoule mol^{-1} larger than that of cobalt (II) cinchomeronate.[10] This would mean that the reaction mechanisms of the nickel(II) and the cobalt(II) mandelate complexation reactions are similar each other, *i.e.*, the chelate ring closure process is the slowest for both systems.

To confirm the mechanism discussed above, we estimated the equilibrium and kinetic parameters of each individual step of the mandelate complexation reactions of nickel(II) and cobalt(II) ions. If the value of k_{32} is known, k_{34} and k_{43} can be calculated from Eq. (5). Hoffmann[24] has derived the following experimental relationship between log k_{32} and pK_a

Table 4. Rate and Equilibrium Constants of Each Individual Step of the Multistep Complex Formation of Nickel(II) and Cobalt(II) with Mandelate at 25℃ and $\mu \rightarrow 0$

	Nickel(II)	Cobalt(II)
pK_a	3.41	3.41
K_{eq}, M^{-1}	2.1×10^2	7.5×10^1
K_0, M^{-1}	5.4	7.7
K_2	1.9	0.9
K_3	2.0×10^1	10.4
k_w, s^{-1}	2.7×10^4	2.6×10^6
k_{32}, s^{-1}	1.4×10^4	2.8×10^6
k_{34}, s^{-1}	4.4×10^3	2.5×10^4
k_{43}, s^{-1}	2.2×10^2	2.4×10^3

of the ligand;

$$\log k_{32} = -0.22\ pK_a + C \qquad (7)$$

where C is a constant. C has been evaluated from the acetate system as 4.88 and 7.28 for the nickel(II) and the cobalt(II) systems, respectively. k_{32} could be estimated from Eq. (7). The solvent exchange rate constant of the corresponding cation k_w was assumed as k_{23}.

The rate and equilibrium data of each individual step of the complexation reactions of nickel(II) and cobalt(II) mandelates are given in Table 4. Again we find that k_{34} is about one sixth smaller than k_w in the nickel(II) mandelate system while k_{34} is about two order smaller than k_w in the cobalt(II) mandelate system. This also supports that the rate determining step of the mandelate complexations in aqueous solution is the chelate ring closure step for both nickel(II) and cobalt(II) ions. Similar results have been reported for the glycolate[14,15] and lactate[13,15] complexations of nickel(II) ion. Even though the water exchange rate of the metal ion is relatively much slower for nickel(II) ion than for cobalt(II) ion, the rate of the nickel(II) complexation reaction in this α-hydroxycarboxylate ligand system is controlled mainly by the chelate ring closure step, contrary to that in the dicarboxylate ligand system.[6,8,10]

Now, since $k_{32} > k_{34}$. Eq. (5) are reduced to $k_f = K_0K_2k_{34}$ and $k_r = k_{43}$. This means that the rate of the decomplexation reaction is solely influenced by the rate of the chelate ring rupture. It it noted from Table 4, making a comparision between the nickel(II) and cobalt(II) systems, that the slower is the rate (k_{43}) of the chelate ring rupture, the higher is the thermodynamic stability (K_{eq}) of the complex. The rate of chelate ring closure is faster for the cobalt(II) ion than for the nickel (II) ion. The size of the metal ion may affect in opposite way to the rates of the chelate ring closure and rupture. Since the size of nickel(II) ion is smaller than cobalt(II) ion, the nickel(II) ion would form stronger bond with α-hydroxy group of the mandelate ligand than the cobalt(II) ion. Thus the rate of bond breaking between the metal ion and α-hydroxy group would be slower in the nickel(II) complexation reaction. However, the rate of the chelate ring closure of cobalt(II) ion which is larger in size could be faster as seen.

In conclusion, the rate of complex formation reaction of Ni(II) ion with α-hydroxycarboxylate ligands in aqueous solution is controlled mainly by the chelate ring closure step. However, the water exchange process would affect some extent to the rate of the overall reaction. In the case of Co(II) ion, the rate of the reaction is determined solely by the chelate ring closure step.

Acknowledgement. Finacial support from the Korea Science and Engineering Foundation is gratefully acknowledged.

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