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Effect of Protolytic Behavior of Ligands on Formation Rates of Mono-complexes of Nickel(II) Ion with 2,2′-Bipyridine and 1,10-Phenanthroline in Aqueous Solution

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The mono-complex formation of nickel(II) ion with 2,2′-bipyridine(bpy) and 1,10-phenanthroline (phen) was studied in aqueous solution by means of a stopped-flow method. The apparent complex formation rates of the Ni(II)–bpy and Ni(II)–phen complexes depended on the pH of the solution. The rate constants of the mono-complex formation with the ligand in the free base form, k_f, and that with the monoprotonated ligand, k_{fh}, were evaluated from the rate-[H$^+$] profiles in the region of high hydrogen ion concentration where the pseudo-equilibrium of acid dissociation of the ligands was attained during the complex formation. The rate constants determined for the Ni(II)–phen were $k_f=(2.6\pm0.3)\times10^3$ mol^{-1} dm^3 s^{-1} and $k_{fh}=2.4\pm0.3$ mol^{-1} dm^3 s^{-1}, which are practically the same as those reported elsewhere. On the other hand, the rate constants for the Ni(II)–bpy were $k_f=(5.3\pm1.2)\times10^3$ mol^{-1} dm^3 s^{-1} and $k_{fh}=5.0\pm2.6$ mol^{-1} dm^3 s^{-1}, which are quite different from the values reported by other researchers. The validity of the present data was discussed in terms of slow proton-transfer reactions of the ligands.

Nickel(II) ion is one of the ions suitable for kinetic studies on complex formation because it has the slowest rate among metal ions which form labile octahedral complexes. In addition, the behavior of this nickel(II) ion is representative. Therefore, the complex formation reactions of nickel(II) ion have been investigated in detail by many workers.[1–17)]

Cassatte *et al.*[18)] studied the complex formation of nickel(II) ion with a number of ligands involving 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). They reported that both the monoprotonated form and the free base form of the ligands take part in the complex formation and that the rate constant with the former is much smaller than that with the latter because of the shielding effect on the reaction site by a proton. The rate constants with the ligand in the two forms were evaluated separately from the rate-[H$^+$] profiles which were obtained by kinetic measurements of apparent rates at various pH, assuming that the pseudo-equilibrium between the two forms of the ligand is attained throughout the complex formation.[18–22)]

On the other hand, we have recently found that ligands such as bpy and phen undergo an unexpectedly slow reaction with respect to the proton-transfer process.[23,24)] This fact suggests that in the complex formation with bpy and phen there is a region of hydrogen ion concentration where the pseudo-equilibrium of acid dissociation of the ligands is no longer maintained and hence the proton-transfer process of the ligands is a rate-determining step. The rate constants evaluated from the kinetic data in such a hydrogen ion concentration range should be erroneous.

Therefore, this study was undertaken in order to confirm that the rate-determining step interchanges depending on hydrogen ion concentration for the mono-complex formation of nickel(II) ion with bpy and phen. The rate constants of the complex formation were determined in the region of hydrogen ion concentration where the pseudo-equilibrium of acid dissociation holds during the reaction.

Theoretical

With a ligand of weak acids such as bpy and phen, the mono-complex formation of nickel(II) ion in aqueous solution is thought to proceed through both reaction paths, 1 and 2:[18)]

$$\mathrm{Ni^{2+} + L \xrightarrow{(rate\ f)} NiL^{2+}}, \tag{1}$$

$$\mathrm{Ni^{2+} + HL^+ \xrightarrow{(rate\ fh)} NiL^{2+} + H^+}, \tag{2}$$

where L and HL$^+$ represent the free base form and the monoprotonated form of the ligand, respectively, and (rate f) and (rate fh) denote the rates of the Reactions 1 and 2, respectively. Assuming that the diprotonated species of the ligand, H_2L^{2+}, is negligible and that the equilibrium between HL$^+$ and L,

$$\mathrm{HL^+ \overset{K_2}{\rightleftharpoons} L + H^+}, \tag{3}$$

holds in the whole course of the complex formation, the acid dissociation constant, K_2, can be introduced into a rate expression. Since the backward reactions of Eqs. 1 and 2 can be ignored in the early stage of the reaction, the formation rate of the mono-complex is expressed by

$$\begin{aligned}\mathrm{d[NiL^{2+}]/d}t &= (k_f[\mathrm{L}]+k_{fh}[\mathrm{HL^+}])[\mathrm{Ni^{2+}}]\\ &= \{(k_f+k_{fh}[\mathrm{H^+}]/K_2)/(1+[\mathrm{H^+}]/K_2)\}[\mathrm{Ni^{2+}}][\mathrm{L'}],\end{aligned} \tag{4}$$

where k_f and k_{fh} denote the rate constants of the Reactions 1 and 2, respectively, and [L′] designates the analytical concentration of the ligand. Consequently, the apparent second order rate constant, k_{obsd}, can be correlated with k_f and k_{fh} by

$$k_{obsd}(1+[\mathrm{H^+}]/K_2) = k_f + k_{fh}[\mathrm{H^+}]/K_2. \tag{5}$$

As long as the equilibrium of Eq. 3 holds during the complex formation, the k_f and k_{fh} values can be evaluated from the k_{obsd} values at various hydrogen ion concentrations according to Eq. 5.

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However, Eq. 5 is not applicable when the deprotonation rate of HL^+, (rate dp), or the protonation rate of L, (rate p), in Reaction 3 is slower than the (rate f) or the (rate fh), that is, when the pseudo-equilibrium between HL^+ and L does not hold in progress of Reactions 1 and 2. Namely, the requirement for the applicability of Eq. 5 is

$$(\text{rate dp}) > (\text{rate f}) \text{ and } (\text{rate p}) > (\text{rate fh}). \tag{6}$$

These four rates for the mono-complex formation in acidic solution are given by

$$(\text{rate f}) = k_f[Ni^{2+}][L], \tag{7}$$

$$(\text{rate fh}) = k_{fh}[Ni^{2+}][HL^+], \tag{8}$$

$$(\text{rate dp}) = k_{dp}[HL^+], \tag{9}$$

and

$$(\text{rate p}) = k_p[H^+][L], \tag{10}$$

where k_{dp} and k_p are the rate constants of the forward and the backward reaction of Eq. 3, respectively. The contribution of hydroxide ion is negligibly small in acidic solution.[23,24] The (rate fh), (rate dp), and (rate p) decrease and the (rate f) increases with lowering hydrogen ion concentration. Therefore, the pseudo-equilibrium of the ligand holds in adequately high hydrogen ion concentration, but it might fail at lower hydrogen ion concentration.

Experimental

Materials and Sample Solutions. Nickel(II) perchlorate was synthesized with nickel(II) carbonate and perchloric acid in the usual way. 2,2′-Bipyridine was purchased from Wako Pure Chemical Ind. and 1,10-phenanthroline monohydrate from Nakarai Chemicals; these ligands were used without further purification. All other chemicals were of guaranteed reagent grade and used without further purification, unless otherwise noted.

The stock solution of nickel(II) ion was prepared by dissolving nickel(II) perchlorate in deionized-distilled water. The concentration was determined by a chelate titration with edta. The stock solution of bpy or phen was prepared by dissolving a weighed amount of it in water. These stock solutions were diluted appropriately for kinetic measurements. The ionic strength of the solution was adjusted to 0.20 mol dm^{-3} with sodium perchlorate except for the case of evaluating the effect of ionic strength on the formation rate constant of the Ni(II)–bpy complex.

Kinetic Measurements. The rates of the complex formation were measured by means of a Union RA-1300 stopped-flow spectrophotometer at 25.0 °C. In order to determine the formation rate of a mono-complex, the concentration of nickel(II) ion to be mixed in the stopped-flow apparatus was one hundred or more times that of the ligand. The pH values of both the nickel(II) ion and ligand solutions to be mixed were adjusted to be the same within the 0.05 pH unit with perchloric acid. The change in absorbance of the mixture was followed at the wavelength at which the absorbance change accompanied by the complex formation was most marked. The optimum wavelength varied slightly depending on the pH of the solution in the vicinity of 314 nm for bpy and 277 nm for phen, respectively.

Both of the nickel(II) ion and ligand solutions were thermally equilibrated at 25.0 °C in separate reservoirs of the stopped-flow apparatus. Equal volumes of them were mixed instantaneously by a pressure-drive device. The change in absorbance of the mixture at the optimum wavelength was stored in a high speed memory unit and displayed on an X-Y recorder as a function of time. The pseudo-first order rate constant was determined from the first order plot of the concentration of mono-complex, $[NiL^{2+}]$, against time. The apparent rate constant of the second order, k_{obsd}, was obtained by dividing the pseudo-first order rate constant by the concentration of nickel(II) ion existing in large excess.

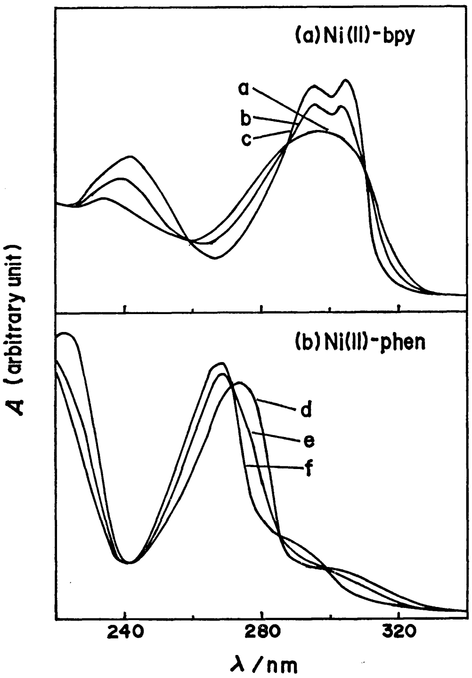

Fig. 1. Rapid scanning spectra of mono-complex of nickel(II) ion with bpy or phen at 25.0 °C. The pHs are 3.99 for the Ni(II)–bpy complex and 1.90 for the Ni(II)–phen complex. Times after mixing: a, 0—10 ms; b, 1.9—2.0 s; c, 7.9—8.0 s; d, 0—10 ms; e, 4.9—5.0 s; f, 10—20 s.

Results and Discussion

Figure 1 shows a typical example of the spectral change of the mixed solution of nickel(II) ion and bpy or phen, measured by a rapid scanning technique during the complex formation. The spectra of c and f in Fig. 1 were identical with those of the mixed solutions at equilibrium which contain nickel(II) ions in large excess to the respective ligands. This indicates that only the mono-complex formation of nickel(II) ion with bpy or phen can be followed spectrophotometrically under the experimental conditions.

The apparent second order rate constant for the Ni(II)–bpy complex formation tended to decrease slightly with the increasing ionic strength from 0.1 to 1.0 mol dm^{-3}. The k_{obsd} values for the Ni(II)–bpy and the Ni(II)–phen complex formations were almost independent of the concentration of nickel(II) ion, as can be seen in Figs. 2 and 3. In contrast to the insensitiveness to the ionic strength and the concentration of nickel(II) ion, the k_{obsd} values varied significantly depending on the pH of the solutions and increased markedly with increasing pH.

Figures 4 and 5 show the plots of $k_{obsd}(1+[H^+]/K_2)$

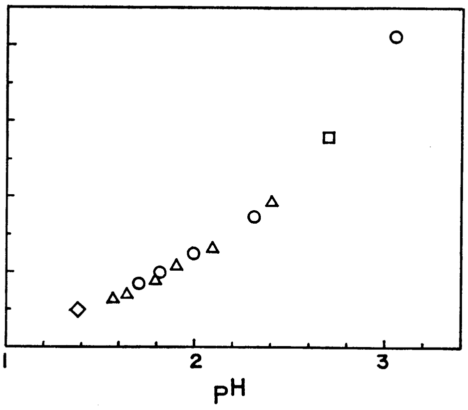

Fig. 2. pH dependence of k_{obsd} values for the Ni(II)–bpy complex. $[Ni^{2+}]$: □, 5.28×10^{-3}; ○, 9.26×10^{-3}; ◇, 1.06×10^{-2}; △, 2.11×10^{-2} mol dm^{-3}; [bpy]: 5.00×10^{-5} mol dm^{-3}. Temperature: 25.0 °C.

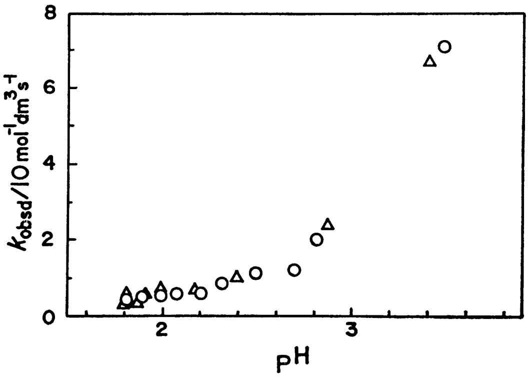

Fig. 3. pH dependence of k_{obsd} values for the Ni(II)–phen complex. $[Ni^{2+}]$: ○, 5.28×10^{-3}; △, 2.40×10^{-2} mol dm^{-3}; [phen]: 2.50×10^{-5} mol dm^{-3}. Temperature: 25.0 °C.

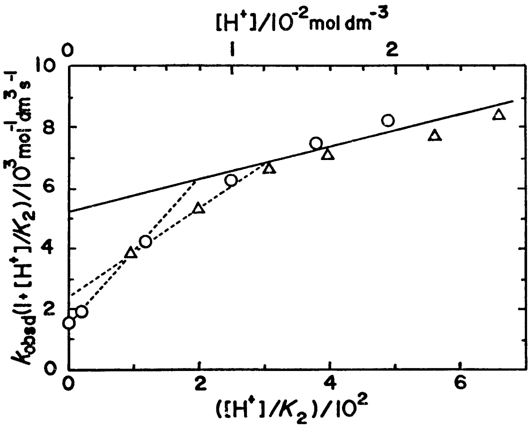

Fig. 4. Plots of k_{obsd} $(1+[H^+]/K_2)$ against $[H^+]/K_2$ for the Ni(II)–bpy complex. Data were taken from Fig. 2. Cross points of solid and broken lines indicate critical points (see text). $[Ni^{2+}]$: ○, 9.26×10^{-3}; △, 2.11×10^{-2} mol dm^{-3}; [bpy]: 5.00×10^{-5} mol dm^{-3}.

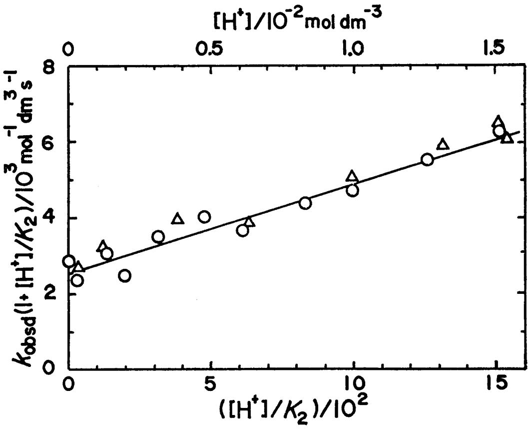

Fig. 5. Plot of k_{obsd} $(1+[H^+]/K_2)$ against $[H^+]/K_2$ for the Ni(II)–phen complex. Data were taken from Fig. 3.
$[Ni^{2+}]$: ○, 5.28×10^{-3}; △, 2.40×10^{-2} mol dm^{-3}; [phen]: 2.50×10^{-5} mol dm^{-3}.

against $[H^+]/K_2$. For the Ni(II)–bpy system, the plot seems to consist of two straight lines: one in the region of high hydrogen ion concentration, the other in that of low concentration. The boundary of the two regions somewhat changes depending on the concentration of nickel(II) ion. On the other hand, the plot for the Ni(II)–phen system consists approximately of one straight line under the present experimental conditions.

As mentioned in Theoretical, it was assumed in this study that the ligands exist as the monoprotonated form and/or as the free base form. However, if bpy and phen exist partly as a diprotonated species in the range of high hydrogen ion concentration, the rates of the complex formation shall be reduced because of the unreactivity of H_2L^{2+}. Based on the pK_1 values of H_2L^{2+}, 1.5 for bpy and 1.9 for phen, reported by Condike and Martell,[25)] the amount of H_2L^{2+} cannot be ignored in the acidic region. Other workers, however, reported the pK_1 values of -0.2—-0.5 for bpy[26—30)] and -0.9—-1.7 for phen.[30—33)] Hence, we also determined the pK_1 value of bpy by a spectrophotometric method under the present experimental conditions and obtained the value of -0.35. This pK_1 value, different from that of Condike and Martell, indicates that the H_2L^{2+} species of bpy is negligible in the pH region of this study (pH 1.5—5.0). The H_2L^{2+} of phen can be also neglected, because of its pK_1 values of -0.9—-1.7 given in the literature.

Consequently, it is concluded that the pseudo-equilibrium of the proton transfer on bpy holds in the region represented by the straight line in the higher hydrogen ion concentration in Fig. 4. The pseudo-equilibrium may fail in hydrogen ion concentrations lower than the cross point of the two straight lines. On the other hand, the pseudo-equilibrium of proton transfer on phen is established in the whole region of hydrogen ion concentration in Fig. 5. Table 1 lists the k_f and k_{fh} values obtained from the intercept and the slope of the linear plot in the high hydrogen ion concentration in Fig. 4 and from those in Fig. 5 by the least-squares method, together with the literature values.

In order to add support to the validity of k_f and k_{fh} determined in the present study, the establishment of the pseudo-equilibria of acid dissociation of the

Table 1. Rate constants of nickel(II) mono complex formation at 25.0 °C

k_f / $mol^{-1} dm^3 s^{-1}$	k_{fh} / $mol^{-1} dm^3 s^{-1}$	Ref.
	Ni(II)-bpy	
$(5.3 \pm 1.2) \times 10^3$ [a]	5.0 ± 2.6[a]	This work
1.6×10^3		9
1.61×10^3		11
1.6×10^3		16
2.6×10^3	25	18
	Ni(II)-phen	
$(2.6 \pm 0.3) \times 10^3$ [a]	2.4 ± 0.3[a]	This work
2.95×10^3		11
3.2×10^3		16
3.5×10^3	5.0	18
4.2×10^3	3.0	19

a) These values are shown together with the 0.95 confidence intervals.

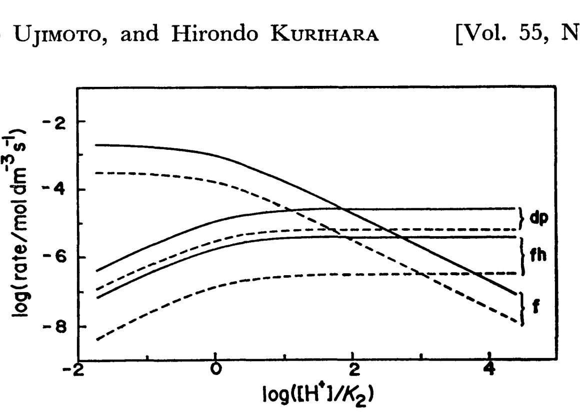

Fig. 6. Relationship between initial rates and $[H^+]/K_2$ at 25.0 °C.
Curve f, (rate f); curve fh, (rate fh); curve dp, (rate dp). Solid lines: for the Ni(II)-bpy complex, $[Ni^{2+}] = 9.26 \times 10^{-3}$, $[bpy] = 5.00 \times 10^{-5}$ mol dm^{-3}; broken lines: for the Ni(II)-phen complex, $[Ni^{2+}] = 5.28 \times 10^{-3}$, $[phen] = 2.50 \times 10^{-5}$ mol dm^{-3}.

ligands were confirmed as follows. The rates of the processes 1 to 3 at $t=0$ were calculated as functions of hydrogen ion concentration according to Eqs. 7 to 10 by use of the k_f and k_{fh} values in this study, the k_{dp} values of bpy and phen in the previous papers,[23,24] and the initial concentrations of the species participating in the reaction. An example of the results is shown in Fig. 6. The (rate p)$_0$ is identical with the (rate dp)$_0$ at $t=0$. Then the (rate p)$_0$ is greater than the (rate fh)$_0$ over the whole range of hydrogen ion concentration investigated. Accordingly, the inequality 6 is satisfied at $t=0$, in the high hydrogen ion concentration where the (rate dp)$_0$ is larger than the (rate f)$_0$. At $t>0$, the (rate p) and (rate dp) values will no longer be identical with each other, owing to the difference in the magnitude between the (rate f)$_0$ and (rate fh)$_0$. The (rate p) and (rate dp) values, however, do not presumably vary so much that the inequality 6 will also fail in the high hydrogen ion concentration. Consequently, the requirement 6 may be satisfied in the hydrogen ion concentrations higher than that at the cross point of the (rate f) and (rate dp) curves. For the Ni(II)-bpy system, the hydrogen ion concentrations at the cross points, $[H^+]_{cp}$, were calculated to be 4.0×10^{-3} mol dm^{-3} at $[Ni^{2+}] = 9.26 \times 10^{-3}$ mol dm^{-3} and 9.2×10^{-3} mol dm^{-3} at $[Ni^{2+}] = 2.11 \times 10^{-2}$ mol dm^{-3}. These values agree approximately with 8.2×10^{-3} mol dm^{-3} at $[Ni^{2+}] = 9.26 \times 10^{-3}$ mol dm^{-3} and 1.2×10^{-2} mol dm^{-3} at $[Ni^{2+}] = 2.11 \times 10^{-2}$ mol dm^{-3}, which were obtained from the critical points deviating from the straight line in the high hydrogen ion concentration in Fig. 4. For the Ni(II)-phen system, the $[H^+]_{cp}$ values were calculated to be 5.4×10^{-4} mol dm^{-3} at $[Ni^{2+}] = 5.28 \times 10^{-3}$ mol dm^{-3} and 2.4×10^{-3} mol dm^{-3} at $[Ni^{2+}] = 2.40 \times 10^{-2}$ mol dm^{-3}. However, no critical point was observed in Fig. 5. Since the $[H^+]_{cp}$ values calculated for the Ni(II)-phen system are small relative to the hydrogen ion concentration investigated, it is likely that the inequality 6 holds in all the hydrogen ion concentration region in Fig. 5. When the pseudo-equilibrium of acid dissociation of ligands is attained, Eqs. 7 and 9 give the following expression with respect to $[H^+]_{cp}$:

$$[H^+]_{cp} = k_f K_2 [Ni^{2+}]/k_{dp}, \qquad (11)$$

because the (rate f) is equal to the (rate dp) at the hydrogen ion concentration of $[H^+]_{cp}$. The $[H^+]_{cp}$ value obtained from the plot in Fig. 4 for the Ni(II)-bpy system increased with the increasing nickel(II) ion concentration, in agreement with the prediction of Eq. 11. The appearance of two regions in Fig. 4 can thus be interpreted in terms of the pseudo-equilibrium of acid dissociation of the ligand.

As can be seen in Table 1, the rate constants for the Ni(II)-phen complex obtained in this study agree well with the literature values.[11,16,18,19] In contrast, the k_f and k_{fh} values for the Ni(II)-bpy complex are considerably different from those reported by other workers.[9,11,16,18] This discrepancy is probably attributable to the fact that all the previous data were obtained under the conditions where the pseudo-equilibrium of acid dissociation of bpy failed during the mono-complex formation. Accordingly, it is concluded that the careful examination for the rate-determining step is necessary to evaluate the rate constant of the complex formation especially with ligands showing slow protolytic properties.

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