Bull. Chem. Soc. Jpn., **71**, 603—608 (1998)

Catalytic Effect of *N*,*N*-Dimethyl-4-(2-pyridylazo)aniline on the Extraction Rate of Ni(II) with 1-(2-Pyridylazo)-2-naphthol: Ligand-Substitution Mechanism at the Liquid–Liquid Interface

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(Received August 1, 1997)

The catalytic effect of *N*,*N*-dimethyl-4-(2-pyridylazo)aniline (PADA) on the extraction rate of Ni(II) with 1-(2-pyridylazo)-2-naphthol (Hpan) in toluene was investigated by the high-speed stirring method. The extracted species was only $Ni(pan)_2$ under the highly stirred system. The extraction rate of $Ni(pan)_2$ was proportional to both concentrations of $Ni(pada)^{2+}$ adsorbed at the liquid–liquid interface and Hpan in the toluene phase, suggesting that the rate-determining step was the reaction between $Ni(pada)^{2+}$ and Hpan at the interface, followed by a successive fast ligand-substitution reaction with another Hpan. The rate constant for the rate-determining step was estimated as $90 \pm 6\ M^{-1}\ s^{-1}$. That the value was rather smaller than the ordinary formation rate constants of Ni(II) complexes was explained by the ring-closure mechanism in the coordination of Hpan.

The kinetic studies on solvent extraction of metal ions are worthwhile not only for the purposes of identifying the rate-determining step, but also for clarifying the role of the liquid–liquid interface in the solvent extraction mechanism. The high-speed stirring method is outstandingly advantageous for the kinetic measurements, because it allows the simultaneous measurements of the extraction rate and the concentrations of interfacially adsorbed substances.[1,2] By using this method, the kinetic synergistic effect of 1,10-phenanthroline (phen) on the extraction rate of Ni(II) with dithizone (Hdz) has been recently studied.[2] It was found that the rate-determining step in the synergistic extraction of $Ni(dz)_2(phen)$ was the formation process of the intermediate adduct complex $Ni(dz)(phen)^+$ at the interface. This study has demonstrated that $Ni(dz)(phen)^+$, thermodynamically unfavorable in bulk aqueous phase, was formed specifically at the interface and could play an important role in the synergistic extraction mechanism.

1-(2-Pyridylazo)-2-naphthol (Hpan) reacts with a wide variety of metal ions to form colored complexes, so that it has been used as a colorimetric extractant for the determination of trace amounts of metal ions.[3] Hpan is especially useful for the spectrophotometric determination of Ni(II), because the extracted $Ni(pan)_2$ is fairly stable in an inert organic solvent, with an absorption maximum wavelength far from that of Hpan, e.g., 464 nm for Hpan and 573 nm for $Ni(pan)_2$ in toluene (Fig. 1). However, its extraction rate at room temperature is so slow that the system should be heated for the quantitative analysis. *N*,*N*-Dimethyl-4-(2-pyridylazo)aniline (PADA) is a bidentate and neutral ligand which reacts rapidly with Ni(II) to form $Ni(pada)^{2+}$ in the aqueous phase.[4] We found out in the present study that the extraction rate of Ni(II) with Hpan was significantly accelerated by the addition of PADA without any adduct complexes extracted into the toluene phase. Notably, this result is completely different from the previous synergistic extraction systems, where adduct complexes including neutral ligands are extracted into the organic phase. In this work, we will examine the acceleration effect of PADA in detail and propose an interfacial ligand-substitution mechanism.

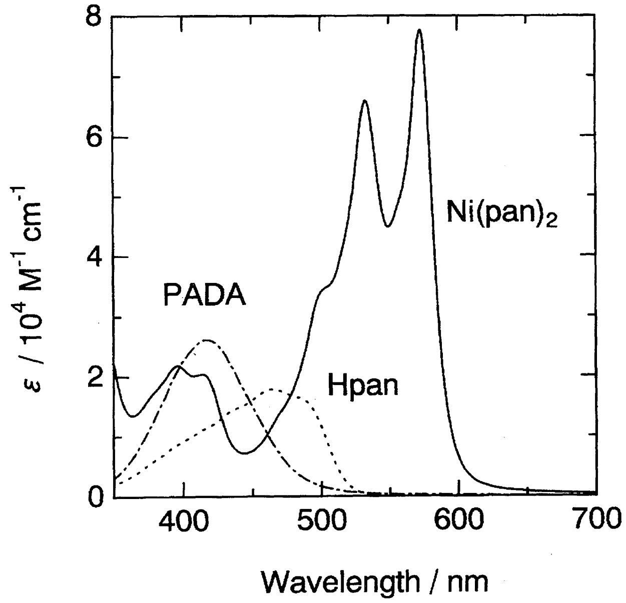

Fig. 1. Absorption spectra of Hpan, PADA, and $Ni(pan)_2$ in toluene.

Experimental

Reagents. 1-(2-Pyridylazo)-2-naphthol (Dojindo Laboratories) and *N*,*N*-dimethyl-4-(2-pyridylazo)aniline (Sigma Chemical) were used as purchased. Toluene (G.R., Nacalai Tesque) was distilled after the treatment with concentrated sulfuric acid. The stock solution of Ni(II) was prepared by dissolving pure Ni metal (Nilaco) in a small amount of $HClO_4$, and the concentration of Ni(II) was standardized by EDTA titration. The pH of the aqueous phase was controlled from 4.7 to 7.2 by the buffer solutions prepared with $(0.5—2.5)\times10^{-3}$ M (1 M = 1 mol dm^{-3}) 2-morpholinoethanesulfonic acid (MES) and sodium hydroxide. The ionic strength of the aqueous phase was maintained at 0.10 by adding $NaClO_4$. All aqueous solutions were prepared with water distilled and deionized by a Milli-Q system (Millipore, Milli-Q SP. TOC.).

Apparatus. The extraction rate of Ni(II) with Hpan in the presence or absence of PADA was measured by the high-speed stirring apparatus. Two immiscible phases were vigorously agitated at 5000 rpm (high-speed stirring), giving a large interfacial area, while at the low-stirring speed of 200 rpm they were properly separated in a glass stir cell. The bulk toluene phase was continuously separated from the agitated mixture by a Teflon® phase separator and circulated through a flow cell with 10 mm optical path length at a flow rate of 15—16 $cm^3 min^{-1}$. Absorption spectra of the organic phase were measured in the range of 380—670 nm using a photodiode-array UV-vis detector interfaced with a NEC PC-9801 computer. During the extraction, the absorbances in the flow cell at two wavelengths, usually the absorption maximum wavelengths of a ligand and its complex, were monitored and recorded. All the measurements were carried out at 298.2±0.1 K.

Interfacial Adsorption Equilibrium of $Ni(pada)^{2+}$. Fifty cm^3 of aqueous buffer solution and the same volume of PADA toluene solution in the range of $10^{-6}—10^{-4}$ M were agitated at 5000 rpm in the glass stir cell. Under the measurement of the absorbance of the toluene phase at the absorption maximum wavelength of PADA (418 nm, Fig. 1), a small amount (0.5 cm^3) of 0.10 M Ni(II) solution was added to the mixture. The absorbance was rapidly decreased, because of the fast complexation of Ni(II) with PADA in the aqueous phase and at the interface. When the stirring speed was lowered to 200 rpm, the two phase separation was accomplished and the interfacial area was abruptly decreased. At the same time, the absorbance of the organic phase was increased and its absorption spectrum was not different from that observed at 5000 rpm, i.e., both were the same as the absorption spectrum of PADA in toluene. This means that Ni(II)–PADA complex adsorbed at the interface during the high-speed stirring was dissociated due to the abrupt decrease of the interfacial area, and PADA was re-distributed between the organic phase and the aqueous phase. From the decrement and the increment in the absorbance change, the concentrations of Ni(II)–PADA complexes both in the aqueous phase and at the interface were estimated.

Kinetic Measurements. After the adsorption measurements described above, Hpan in toluene was injected into the agitated mixture including Ni(II), PADA, and Ni(II)–PADA complexes, to start the extraction. The increase in the absorbance of $Ni(pan)_2$ at the absorption maximum wavelength (573 nm, Fig. 1) was recorded as a function of time to measure the extraction rate. The stirring speed was maintained at 5000 rpm in all kinetic measurements.

Distribution Equilibria. The distribution constants of Hpan and PADA were determined as $10^{4.5}$ and $10^{3.0}$, respectively, by an ordinary batch method at 298±1 K. The absorption spectra in the toluene phase were measured by a UV-vis spectrophotometer (JASCO V-550).

Results and Discussion

Extraction of Ni(II) with Hpan. As shown in Fig. 2, the extraction rate of Ni(II) with Hpan in the absence of PADA was very slow even under the rather high concentration of Ni(II) $(1.0\times10^{-3}$ M). The extraction rate showed no dependence on pH of the aqueous phase in the range of 4.7—6.0 examined in the present study. Neither Hpan nor $Ni(pan)_2$ was adsorbable at the interface, as found from the absence of stirring effect on the absorbances of Hpan and $Ni(pan)_2$ in the toluene phase. Therefore, the contribution of interfacial reaction in this extraction process was neglected. The formation reaction of $Ni(pan)^+$ in the aqueous phase was thought to be the rate-determining step[5] and the observed slow extraction rate was explained as a consequence of the extremely low aqueous Hpan concentration because of the large distribution constant of Hpan, $10^{4.5}$. The extraction rate of $Ni(pan)_2$ governed by the aqueous phase reaction should be represented by $(k_a/K_D)[Ni^{2+}][Hpan]_o$, where k_a and K_D refer to the formation rate constant of $Ni(pan)^+$ in the aqueous solution and the distribution constant of Hpan, respectively. The subscript o refers to the concentration in the bulk organic phase. The extraction rate of 2×10^{-10} M s^{-1} under the conditions shown in Fig. 2 was in good agreement with 1.4×10^{-10} M s^{-1} calculated by using $K_D=10^{4.5}$ and $k_a=95$ M^{-1} s^{-1} determined by a stopped-flow method.[5] Therefore, the formation reaction of $Ni(pan)^+$ in the aqueous solution was concluded to be the rate-determining step in this system.

Complexation of Ni(II) with PADA. When PADA was used instead of Hpan, Ni(II) was not extracted into the toluene phase at all, though the rapid formation of Ni(II)–PADA complex in the aqueous phase was found from purple coloration. Like Hpan and $Ni(pan)_2$, PADA was not adsorbed at the interface, because the absorbance of the toluene phase at

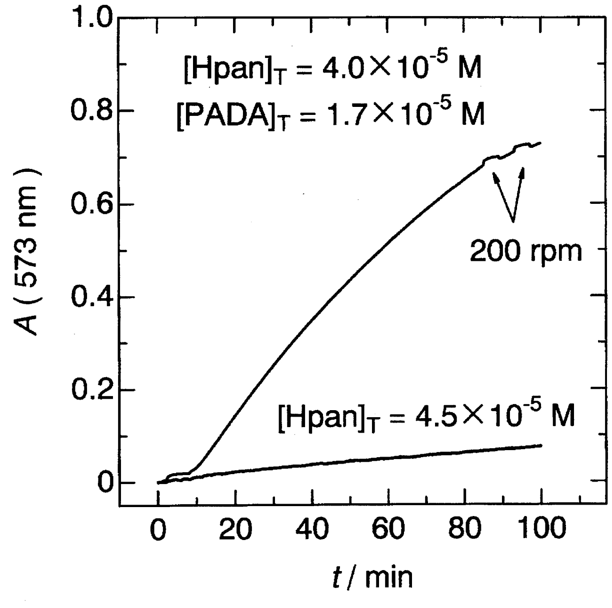

Fig. 2. The catalytic effect of PADA on the extraction rate of Ni^{2+} with Hpan. $[Ni^{2+}]_T=1.0\times10^{-3}$ M, pH 5.4—5.6. The subscript T refers to the total concentration.

418 nm was not affected by the high-speed stirring (Fig. 3). The injection of Ni(II) solution rapidly decreased the absorbance of the organic phase. When the stirring speed was lowered to 200 rpm, the absorbance was partially restored as a consequence of the dissociation of Ni(II)–PADA complex adsorbed at the interface. As shown in Fig. 3, the increment in the absorbance recovery, ΔA, was slightly less than the decrement at the injection of Ni(II) solution, suggesting the existence of Ni(II)–PADA complex in the aqueous phase after the cease of the high-speed stirring, which was confirmed by the spectra of the aqueous phase. When the interfacially adsorbed complex was dissociated, PADA was distributed between the organic phase and the aqueous phase. Therefore, ΔA must be corrected in order to obtain the concentration of Ni(II)–PADA complex at the interface under the high-speed stirring condition. The corrected absorbance change, $\Delta A'$, can be described as

$$\Delta A' = \frac{A_\mathrm{T}}{A_\mathrm{o}}\Delta A, \tag{1}$$

where A_T and A_o are the absorbances of the organic phase before the injection of Ni(II) and at the low-stirring speed of 200 rpm, respectively (Fig. 3). $\Delta A'$ showed a second-order dependence on the concentration of PADA in the toluene phase, indicating the formation of $\mathrm{Ni(pada)^{2+}}$ and $\mathrm{Ni(pada)_2{}^{2+}}$ at the interface (Fig. 4). Thus, $\Delta A'$ can be represented by

$$\begin{aligned}\Delta A' &= \varepsilon\left([\mathrm{Ni(pada)}^{2+}]_\mathrm{i}\frac{A_\mathrm{i}}{V_\mathrm{o}} + 2[\mathrm{Ni(pada)_2}^{2+}]_\mathrm{i}\frac{A_\mathrm{i}}{V_\mathrm{o}}\right) \\ &= \varepsilon\left(\beta_1'[\mathrm{Ni}^{2+}][\mathrm{PADA}]_\mathrm{o} + 2\beta_2'[\mathrm{Ni}^{2+}][\mathrm{PADA}]_\mathrm{o}^2\right),\end{aligned} \tag{2}$$

where ε is the molar absorptivity of PADA in toluene, the subscript i refers to the concentration at the interface, A_i is the total interfacial area, V_o (0.050 dm^3) the volume of the organic phase, and β_1' and β_2' are the conditional interfacial formation constants of $\mathrm{Ni(pada)^{2+}}$ and $\mathrm{Ni(pada)_2{}^{2+}}$, respectively, defined by

$$\begin{aligned}\beta_1' &= \frac{[\mathrm{Ni(pada)}^{2+}]_\mathrm{i}}{[\mathrm{Ni}^{2+}][\mathrm{PADA}]_\mathrm{o}}\frac{A_\mathrm{i}}{V_\mathrm{o}}, \\ \beta_2' &= \frac{[\mathrm{Ni(pada)_2}^{2+}]_\mathrm{i}}{[\mathrm{Ni}^{2+}][\mathrm{PADA}]_\mathrm{o}^2}\frac{A_\mathrm{i}}{V_\mathrm{o}}.\end{aligned} \tag{3}$$

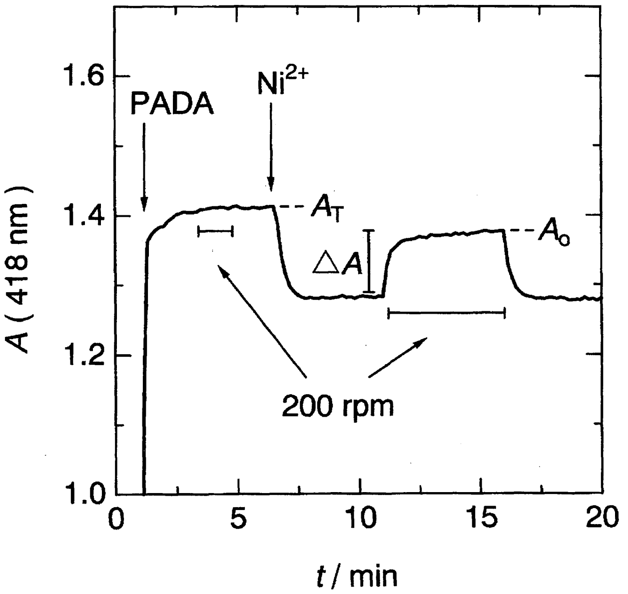

Fig. 3. Effect of stirring on the absorbance of PADA showing the complexation of $\mathrm{Ni^{2+}}$ with PADA in the aqueous phase and at the interface. $[\mathrm{Ni^{2+}}]_\mathrm{T} = 1.0\times10^{-3}$ M, $[\mathrm{PADA}]_\mathrm{T} = 5.2\times10^{-5}$ M, pH 5.5.

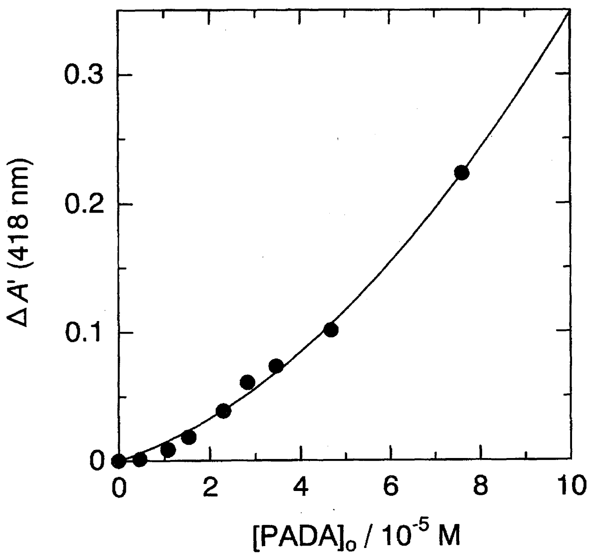

Fig. 4. Second-order dependence of $\Delta A'$ on the PADA concentration. $[\mathrm{Ni^{2+}}]_\mathrm{T}=1.0\times10^{-3}$ M, pH 5.5—5.8.

The values of β_1' and β_2' were determined as 53 ± 6 M^{-1} and $(3.0\pm0.5)\times10^2$ M^{-2} from the best fitting of Eq. 2 to the experimental results, as shown in Fig. 4. Small $A_\mathrm{T}-A_\mathrm{o}$ values, corresponding to the formation of Ni(II)–PADA complexes in the aqueous phase, depended proportionally on the PADA concentration in the toluene phase. The stability constant, β_1, of $\mathrm{Ni(pada)^{2+}}$ in the aqueous phase was estimated as $(3.2\pm0.2)\times10^4$ M^{-1}, which was close to the literature value, 1.29×10^4 M^{-1}.[6] In addition, the interfacial adsorption parameter of $\mathrm{Ni(pada)^{2+}}$, defined by $K'A_\mathrm{i}=[\mathrm{Ni(pada)^{2+}}]_\mathrm{i}A_\mathrm{i}/[\mathrm{Ni(pada)^{2+}}]$, was determined as $(8\pm1)\times10^{-2}$ dm^3.

Extraction of Ni(II) with Hpan and PADA. In the presence of PADA, the extraction rate of $\mathrm{Ni(pan)_2}$ was significantly accelerated, as shown in Fig. 2. The accelerating effect was independent of pH of the aqueous phase in the observed pH range of 5.7—6.5. The absorbance of the toluene phase at a given wavelength λ can be written as

$$A_\lambda = \varepsilon_{\mathrm{Hpan},\lambda}[\mathrm{Hpan}]_\mathrm{o} + \varepsilon_{\mathrm{PADA},\lambda}[\mathrm{PADA}]_\mathrm{o} + \varepsilon_{\mathrm{Ni(pan)_2},\lambda}[\mathrm{Ni(pan)_2}]_\mathrm{o} \tag{4}$$

where $\varepsilon_{\mathrm{Hpan},\lambda}$, $\varepsilon_{\mathrm{PADA},\lambda}$, and $\varepsilon_{\mathrm{Ni(pan)_2},\lambda}$ are the molar absorptivities of Hpan, PADA, and $\mathrm{Ni(pan)_2}$ in toluene, respectively. From the absorbances at the three different wavelengths, λ_1, λ_2, and λ_3, the concentrations of the three components in the bulk toluene phase, C_Hpan, C_PADA, and $C_{\mathrm{Ni(pan)_2}}$, can be calculated by the determinant:

$$\begin{pmatrix} C_{\mathrm{Hpan}} \\ C_{\mathrm{PADA}} \\ C_{\mathrm{Ni(pan)_2}} \end{pmatrix} = \begin{pmatrix} \varepsilon_{\mathrm{Hpan},\lambda_1} & \varepsilon_{\mathrm{PADA},\lambda_1} & \varepsilon_{\mathrm{Ni(pan)_2},\lambda_1} \\ \varepsilon_{\mathrm{Hpan},\lambda_2} & \varepsilon_{\mathrm{PADA},\lambda_2} & \varepsilon_{\mathrm{Ni(pan)_2},\lambda_2} \\ \varepsilon_{\mathrm{Hpan},\lambda_3} & \varepsilon_{\mathrm{PADA},\lambda_3} & \varepsilon_{\mathrm{Ni(pan)_2},\lambda_3} \end{pmatrix}^{-1} \begin{pmatrix} A_{\lambda_1} \\ A_{\lambda_2} \\ A_{\lambda_3} \end{pmatrix}. \tag{5}$$

A typical example of the concentration profiles of Hpan, PADA, and $\mathrm{Ni(pan)_2}$ in the toluene phase is shown in Fig. 5, which was calculated by using the observed absorbances at λ_1=464 nm, λ_2=418 nm, and λ_3=573 nm, the absorption maximum wavelengths of Hpan, PADA, and $\mathrm{Ni(pan)_2}$, respectively. It should be noticed that the PADA concentration is not seriously changed even after the injection of Hpan solution. This means that PADA is not consumed during the extraction and works like a catalyst on the extraction of $\mathrm{Ni(pan)_2}$. The increase and the decrease of the PADA concentration caused by the low-speed and high-speed stirrings in the later stage of the extraction in Fig. 5 correspond to the dissociation and the formation of $\mathrm{Ni(pada)^{2+}}$ and $\mathrm{Ni(pada)_2{}^{2+}}$ at the interface. The extraction rate of $\mathrm{Ni(pan)_2}$ defined by $\mathrm{d[Ni(pan)_2]_o}/\mathrm{d}t$ was obtained by differentiating the concentration profile of $\mathrm{Ni(pan)_2}$ with respect to time. As shown in Fig. 6, the extraction rate proportionally depended on the Hpan concentration in the organic phase, which was decreasing during the extraction. Therefore, the extraction rate can be represented by

$$\mathrm{d[Ni(pan)_2]_o}/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Hpan}]_{\mathrm{o}}. \tag{6}$$

The apparent extraction rate constant, k_{obs}, depended linearly on the concentration of PADA in the toluene phase, and was proportional to that of Ni(II) in the aqueous phase,

$$k_{\mathrm{obs}} = k[\mathrm{Ni^{2+}}] + k'[\mathrm{Ni^{2+}}][\mathrm{PADA}]_{\mathrm{o}}, \tag{7}$$

where k is the extraction rate constant of Ni(II) with Hpan alone and k' the catalytic constant of PADA on the extraction rate, which were determined as (9±6)×10^{-3} $\mathrm{M^{-1}\,s^{-1}}$, and (4.7±0.3)×10^{3} $\mathrm{M^{-2}\,s^{-1}}$, respectively. The second term in the right-hand side of Eq. 7 can be related to the formation of $\mathrm{Ni(pada)^{2+}}$ at the interface, represented in Eq. 3, as

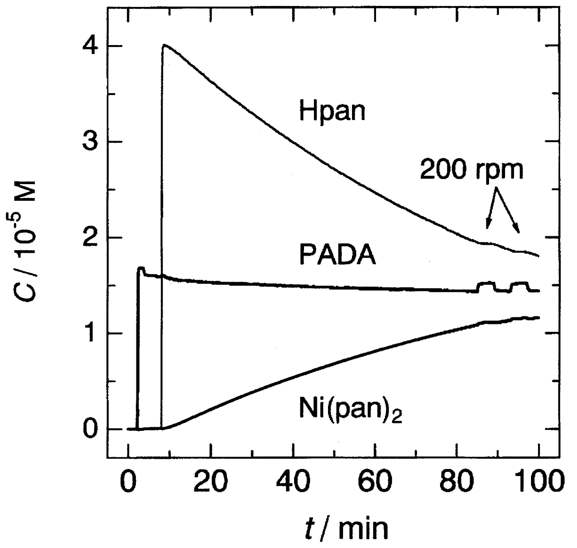

Fig. 5. A typical example of the concentration profiles of Hpan, PADA, and $\mathrm{Ni(pan)_2}$ in the toluene phase during the extraction. $[\mathrm{Ni^{2+}}]_{\mathrm{T}}$=1.0×$10^{-3}$ M, $[\mathrm{Hpan}]_{\mathrm{T}}$=4.0×$10^{-5}$ M, $[\mathrm{PADA}]_{\mathrm{T}}$=1.7×$10^{-5}$ M, pH 5.6.

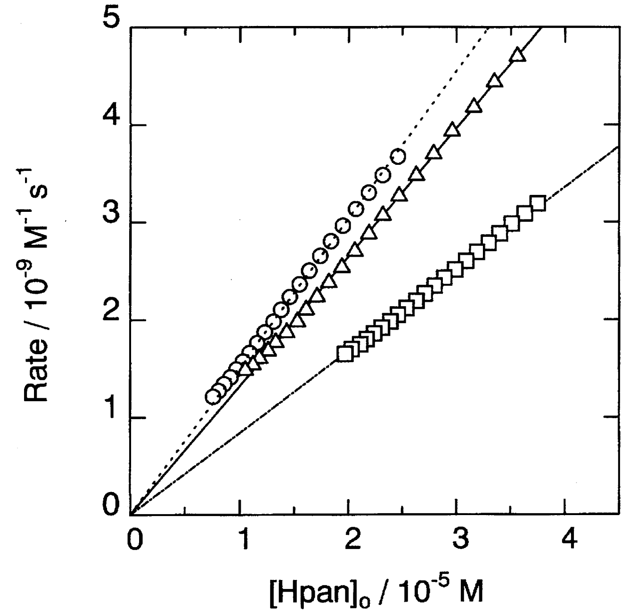

Fig. 6. First-order dependence of the extraction rate of $\mathrm{Ni(pan)_2}$ on the Hpan concentration in the organic phase. $[\mathrm{Ni^{2+}}]_{\mathrm{T}}$=1.0×$10^{-3}$ M, $[\mathrm{PADA}]_{\mathrm{T}}$=1.7×$10^{-5}$ M (square); 2.5×10^{-5} M (triangle); 3.1×10^{-5} M (circle), pH 5.6—5.8.

$$k'[\mathrm{Ni^{2+}}][\mathrm{PADA}]_{\mathrm{o}} = k'[\mathrm{Ni(pada)^{2+}}]_{\mathrm{i}}A_{\mathrm{i}}/(V_{\mathrm{o}}\beta_1'). \tag{8}$$

Thus, the apparent extraction rate constant can be described as

$$k_{\mathrm{obs}} = k_{\mathrm{a}}K_{\mathrm{D}}^{-1}[\mathrm{Ni^{2+}}] + k_{\mathrm{i}}[\mathrm{Ni(pada)^{2+}}]_{\mathrm{i}}A_{\mathrm{i}}/V_{\mathrm{o}}, \tag{9}$$

where $k_{\mathrm{a}}=kK_{\mathrm{D}}$ is the rate constant of the formation of $\mathrm{Ni(pan)^{+}}$ in the aqueous phase,

$$\mathrm{Ni^{2+}} + \mathrm{Hpan} \xrightarrow{k_{\mathrm{a}}} \mathrm{Ni(pan)^{+}} + \mathrm{H^{+}} \tag{10}$$

and $k_{\mathrm{i}}=k'/\beta_1'$ is the rate constant of the reaction between $\mathrm{Ni(pada)^{2+}}$ and Hpan at the interface,

$$\mathrm{Ni(pada)_i^{2+}} + \mathrm{Hpan_o} \xrightarrow{k_{\mathrm{i}}} \mathrm{Ni(pan)(pada)_i^{+}} + \mathrm{H^{+}} \tag{11}$$

Equations 10 and 11 are the rate-determining processes of the extraction of $\mathrm{Ni(pan)_2}$ in the absence and presence of PADA, respectively. Figure 7 shows the linear dependence of k_{obs} on the concentration of $\mathrm{Ni(pada)^{2+}}$ adsorbed at the interface which was calculated by using β_1' in Eq. 3. Thus, the influence of $\mathrm{Ni(pada)_2{}^{2+}}$ on the extraction rate is corrected in the plot of Fig. 7. According to Eq. 9, k_{a}=(3±2)×10^{2} $\mathrm{M^{-1}\,s^{-1}}$ and k_{i}=90±6 $\mathrm{M^{-1}\,s^{-1}}$ were obtained from the intercept and the slope of Fig. 7, respectively. These values are of almost same order as the k_{a} value available in the literature, 95 $\mathrm{M^{-1}\,s^{-1}}$.[5] In the higher PADA concentration where k_{obs} deviated from the linear plot, it was found that, when the stirring speed was lowered to 200 rpm, $\mathrm{Ni(pan)(pada)^{+}}$ could be extracted with perchlorate ion. The possibility of the reaction

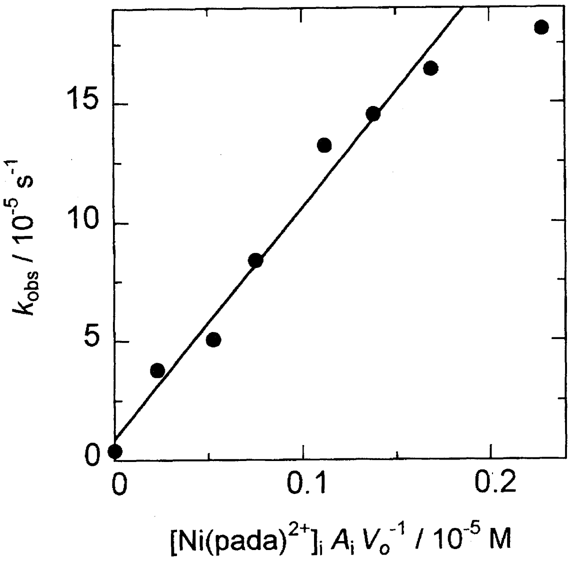

Fig. 7. First-order dependence of the apparent extraction rate constant on the interfacial concentration of $Ni(pada)^{2+}$. $[Ni^{2+}]_T = 1.0\times10^{-3}$ M, $[Hpan]_T = (4.0—4.5)\times10^{-5}$ M, $[PADA]_T=(0—5.2)\times10^{-5}$ M, pH 5.5—5.8.

between $Ni(pan)(pada)ClO_4$ and Hpan in toluene phase was negligible, because $Ni(pan)(pada)^+$ was highly adsorbable at the interface and was not detected in the organic phase during the high-speed stirring.

Extraction Mechanism. The proposed extraction mechanism is shown schematically in Fig. 8. First, PADA reacts rapidly with Ni(II) in the aqueous phase, producing $Ni(pada)^{2+}$, which distributes between the aqueous phase and the interface, attaining adsorption equilibrium. Hpan then added into the toluene phase reacts with $Ni(pada)^{2+}$ to form $Ni(pan)(pada)^+$ at the interface. This interfacial reaction becomes the rate-determining process. $Ni(pada)_2{}^{2+}$ can also be formed at the interface in the higher concentration of PADA. The reaction between Hpan and $Ni(pan)(pada)^+$ at the interface gives $Ni(pan)_2$ and PADA in the toluene phase, so that PADA works as a catalyst on the formation of $Ni(pan)_2$. The estimated values for k_a and k_i are fairly close to each other. This is reasonably explained by considering that both of them are the rate constants for the coordination of Hpan, though occurring at different circumstances. The extraction rate was independent of pH of the aqueous phase in the range of 5.7—6.5, but slightly increased with pH in the range of 6.5—7.2, while the adsorptivity of $Ni(pada)^{2+}$ was not affected by pH. This result suggested that the reaction between $Ni(pada)^{2+}$ and dissociated pan^- was also contributing to the extraction rate in the higher pH range.

$Ni(pada)^{2+}$, $Ni(pada)_2{}^{2+}$, and $Ni(pan)(pada)^+$ were adsorbable at the interface, but Hpan, PADA, and $Ni(pan)_2$ were not at all. These results correspond to the general tendency that the ions with larger hydrophobic groups have higher interfacial adsorptivity.

Reactivities of Hpan and PADA. The extraction process studied in this work can be divided into three steps: the formation and the adsorption of $Ni(pada)^{2+}$, the interfacial reaction between $Ni(pada)^{2+}$ and Hpan, and the interfacial ligand substitution producing $Ni(pan)_2$.

The formation of $Ni(pada)^{2+}$ in the aqueous phase was relatively fast, with the rate constant of 1.2×10^3 M^{-1} s^{-1}.[4)] The rate-determining step in this reaction is considered to be the loss of water molecules from the inner solvation shell of Ni(II).

In the interfacial reaction, water molecules coordinating to Ni(II) of $Ni(pada)^{2+}$ must be replaced by Hpan. The rate constant obtained here, $k_i=90\pm6$ M^{-1} s^{-1}, is about 100 times smaller than that for the water loss from hydrated Ni^{2+} ion, 3×10^4 s^{-1}.[7)] Therefore, the slow rate of this reaction seems to reflect the ring-closure mechanism assumed previously in the coordination of Hpan.[4,8)] The ring-closure mechanism in the reaction between Ni(II) and Hpan was simulated by molecular mechanics calculation, as shown in Fig. 9. The software used was the $Cerius^2$ Minimizer (MSI). The energy required for the reaction was estimated as 8.54 kJ mol^{-1}, which was higher than −5.61 kJ mol^{-1} for the reaction between Ni(II) and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol, H(5-Br-padap).[9)] The formation rate constant of $Ni(5\text{-}Br\text{-}padap)^+$ was determined as 5.3×10^2 M^{-1} s^{-1} in the aqueous phase, which is larger than that for $Ni(pan)^+$. The positive energy difference for the ring closure of Hpan will result in a slower reaction rate, i.e., a larger activation energy than that for H(5-Br-padap). Both Hpan and H(5-Br-padap) are tridentate ligands having coordinating atoms of N, N, O, and they have an intramolecular hydrogen bond (–N···HO–) between an azo N atom and the OH group before forming a final complex.[10)] Therefore, the energy for the ring-closure should depend on the strength of the hydrogen bond. Indeed, the pK_a value of the OH of Hpan ($pK_a=12.3$)[11)] is larger than that of the OH of H(5-Br-padap) ($pK_a=11.30$).[12)] Thus, in Hpan a larger energy should be required to break the intramolecular hydrogen bond. This situation will be the cause of the slower formation rate of Hpan complex.

In the final step of the extraction, PADA in $Ni(pan)(pada)^+$

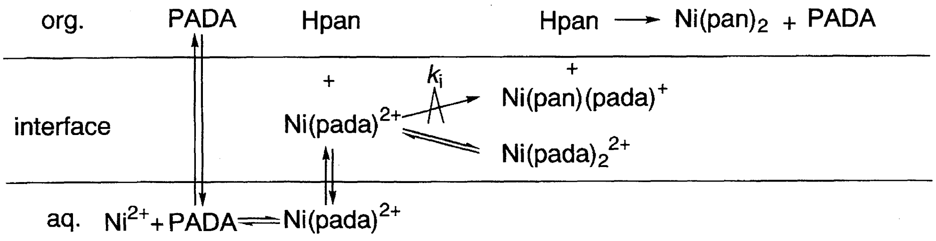

Fig. 8. Proposed ligand-substitution mechanism for the extraction of Ni^{2+} with Hpan and PADA under high-speed stirring.

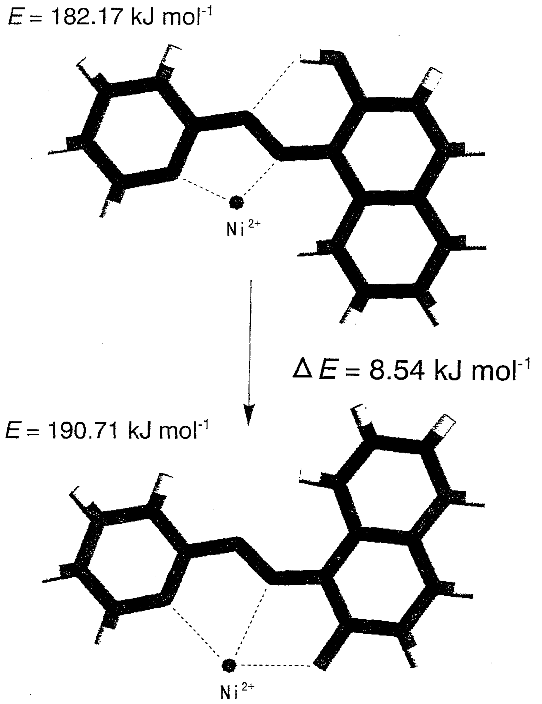

Fig. 9. Molecular mechanics calculation of the complexation of Ni^{2+} with Hpan in water.

will be substituted with another Hpan, which satisfies the coordination number of Ni(II) of six. The lability of Ni(pan)(pada)$^+$ may be ascribable to the less stable coordination number of five.

In conclusion, the extraction rate of Ni(II) with Hpan was accelerated due to the formation of Ni(pada)$^{2+}$ at the toluene–water interface. The formation of the intermediate complex, Ni(pan)(pada)$^+$, was followed by the ligand-substitution reaction, which made PADA act as a catalyst in the extraction rate. This kind of catalysis in the solvent extraction rate was analyzed for the first time in the present work. Extension of this study is in progress, using a neutral tridentate ligand as an auxiliary ligand in the Ni(II)/Hpan system.

The authors thank Mr. N. Gotoh of KGT Inc. for estimating the energy required for the ring-closure of Ni(pan)$^+$ by a molecular mechanics calculation. This work was supported by a Grant-in-Aid for General Scientific Research No. 07404042 from the Ministry of Education, Science, Sports and Culture.

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