Extraction Equilibria of Nickel(II) with Several Heterocyclic Substituted-Hydrazones

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The extraction of nickel(II) with seven N,N,N-tridentate heterocyclic hydrazones, a neutral form of which is abbreviated as HL, using chloroform or benzene as an extraction solvent has been studied, the extraction equilibria being analyzed on the basis of the data for the proton dissociation of $H_3L^+$, the formation of $Ni(HL)^{2+}$ and $Ni(HL)^{3+}$ complexes and the proton dissociation of $Ni(HL)^{2+}$ complexes in aqueous solution. Nickel(II) is extracted as $NiL_2$, although it forms such complexing ions as $Ni(HL)^{2+}$ or $Ni(HL)^{3+}$ in the aqueous phase. The distribution constants of HL and $NiL_2$ (the abbreviations of which are $K_d$ and $K_{dm}$, respectively) have been determined under the same condition as in aqueous solution. The logarithmic plots of $K_{dm}$ VS. $K_d$ displayed two straight lines with slopes of 1.9; one is for hydrazones bearing one pyridyl or one quinolyl ring in the aldehyde moiety and the other for hydrazones bearing another pyridyl ring introduced to the aldehyde moiety. This is attributed to an intramolecular hydrogen bond between the imino hydrogen and the nitrogen of pyridine of the latter hydrazones.

Keywords Nickel(II) complex, heterocyclic substituted-hydrazone, extraction equilibrium, spectrophotometry

$N,N,N$-tridentate heterocyclic hydrazones have been widely used as chromogenic reagents in the spectrophotometric determination, mainly combined with an extraction technique, of transition metal ions. The extraction equilibria involving in the determination have been studied in detail for some anions, but not so much for metal ions(II). For the extraction of transition metal ions(II) with some hydrazones, the composition of extractable species has been examined by continuous variation and equilibrium concentration methods. These hydrazones bear a dissociable hydrogen bonded to the imino nitrogen that does not participate in coordination. Dissociation of this hydrogen occurs in more acidic solution by complex formation with metals. In a previous paper we preliminarily determined the extraction constants for some Ni$^{2+}$-hydrazone systems by using benzene or chloroform as a solvent and by plotting the logarithmic distribution ratio of nickel(II), $log D_{Ni}$, against pH. The experimental data also demonstrated that for the 2-pyridylmethanone 2-pyridylhydrazone (PAPH) system there is a considerably wide range in which $log D_{Ni}$ is independent of the logarithmic ligand concentration, $log[H_L]$ (HL denotes a neutral form of hydrazones), in the organic phase, showing only the Ni$^{2+}$ species being formed in the aqueous phase. Such a flat range, however, was not observed for the di-2-pyridylmethanone 2-quinolylhydrazone (DPQH) system, indicating the existence of complicated extraction equilibria involving Ni$^{2+}$, Ni$^{3+}$ and/or Ni$^{4+}$ species in the aqueous phase. The analysis of such complicated extraction equilibria is practically impossible by the equilibrium concentration method, and requires information concerning the complex formation equilibria in the aqueous phase. A similar situation arose in the analysis of the 2-quinolylmethanone 2-pyridylhydrazone (QAPH) and 2-pyridylmethanone 2-(5-nitro)pyridylhydrazone (PA5NPH) systems. It is worthwhile to establish the formation and extraction equilibria of the complex species involved in the extractive spectrophotometric determination of Ni$^{2+}$ with these ligands. The formation equilibria were investigated spectrophotometrically for all of the ionic species. The equilibrium constants for the formation of the NiL$^2$ complex, which is insoluble in water, were obtained by extrapolation of the values determined in aqueous dioxane to null dioxane. The extraction equilibria of nickel(II) with the hydrazones were analyzed so as to obtain the distribution constant ($K_{dm}$) of the NiL$^2$ complex on the basis of the equilibrium data obtained in aqueous solution. The extraction constant ($K_a$) was then evaluated based on the value of $K_{dm}$ and equilibrium data for the aqueous solution. The relationship between $K_a$ and $K_{dm}$ were also discussed for the Ni$^{2+}$-hydrazone systems.

Experimental

Reagents

Hydrazones. The seven hydrazones studied in this work were PAPH, 2-pyridylmethanone 2-quinolylhydrazone (PAQH), QAPH, PA5NPH, di-2-pyridylmethanone 2-
pyridylhydrazone (DPPH), DPQH and di-2-pyridylmethanone 2-(5-nitro)pyridylhydrazone (DP5NPH), all of which were prepared as described earlier.  

Nickel(II) solution. A nickel(II) stock solution (1 × 10^{-2} M) was prepared by dissolving nickel(II) sulfate in water containing a small amount of sulfuric acid and standardized against a 1 × 10^{-3} M EDTA solution using murexide as an indicator.

Buffers. When necessary, acetic acid, 2-(N-morpholino)ethanesulfonic acid, 3-(N-morpholino)propanesulfonic acid, N-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid, 3-cyclohexylaminopropanesulfonic acid (Dotite Good's buffer) and sodium tetraborate were used combined with sulfuric acid or potassium hydroxide.

**General methods**

The ionic strength was held constant at 0.1 with potassium sulfate. Hitachi U-3400 and Shimadzu UV-160 spectrophotometers were used for measuring the absorbance in quartz cells with a thermostated 1.0-cm path length (±0.1°C) or variable path lengths (5.0 and 10.0 cm; 25.0±0.2°C). A Toa Dempresa HM-30S pH meter standardized against buffer solutions (pH 1.68, 4.01, 6.86 and 9.18) was used for pH adjustments. The pH readings (hydrogen ion activity term) were used for data analysis without conversion to the concentration term. Extraction was carried out in a thermostated chamber (25±0.1°C) with a TAITEC personal-10 incubator.

**Procedure for the extraction of nickel(II)-hydrazone complex**

A 12-ml portion of an aqueous solution, buffered to the required pH and adjusted to an ionic strength of 0.1 with potassium sulfate, was placed in a stopped-glass tube and equilibrated with an equivalent volume of benzene or chloroform containing a known quantity of hydrazine for 6–15 h. The shaking speed was 190 strokes/min. After separation of the two phases, the absorbance of the organic phase was measured at the maximum wavelength of the NiL₂ complex.

**Analysis of the plots of absorbance vs. pH**

For a set of experimental data, the absorbance of each solution is expressed by the equation \( A_{obs} = \Sigma \alpha_i [C_i] \) (\([C_i]\) denotes the equilibrium concentration of each species), the value being calculated by using given values of the equilibrium constants and molar absorptivities (\( \alpha \)). The values of the unknown constants were refined to give the minimum error squares sum, \( U_{min} = \Sigma (A_{obs,i} - A_{cal,i})^2 \), using a non-linear regression with the aid of a computer.  

The square of the standard deviation (\( \sigma^2 \)) for each logarithmic equilibrium constant (log \( K_{eq} \)) was defined as the difference between the maximum logarithmic value within the tolerance, \( U_{min} + U_{min}/(l-m) \) and the value of log \( K_{eq} \) at the minimum, \( U_{min} \), where \( l \) is the number of data points and \( m \) is the number of unknown constants. The number of data points was 25–35 in each data set.

**Results and Discussion**

The equilibrium scheme for the extraction of nickel(II) with a hydrazone is illustrated in Fig. 1. The reported methods for the extractive spectrophotometric determination of nickel(II) are based on the formation of the uncharged bis complex, NiL₂. As pointed out in a previous paper, a protonated complex, Ni(HL)₂²⁺, is also formed in the aqueous phase. Such complicated

![Fig. 1 Scheme for the extraction of nickel(II) complex with hydrazones.](image)

### Table 1 Equilibrium constants for nickel(II) complexes of hydrazones in aqueous solution at 25°C

<table>
<thead>
<tr>
<th>Constant</th>
<th>PAPH</th>
<th>PAQH</th>
<th>QAPH</th>
<th>PA5NPH</th>
<th>DPPH</th>
<th>DPQH</th>
<th>DP5NPH</th>
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<tr>
<td>pKₐ¹</td>
<td>3.53±0.01</td>
<td>3.09±0.01</td>
<td>3.27±0.01</td>
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<td>5.48±0.01</td>
<td>5.76±0.01</td>
<td>3.96±0.01</td>
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<tr>
<td>pKₐ₃</td>
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<td>14.1±0.02</td>
<td>14.1±0.02</td>
<td>11.26±0.01</td>
<td>15.4±0.06</td>
<td>14.2±0.02</td>
<td>11.30±0.01</td>
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<td>-1.85±0.02</td>
<td>1.87±0.02</td>
<td>0.41±0.02</td>
<td>-0.77±0.02</td>
<td>2.53±0.02</td>
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<td>log βₐ¹</td>
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<td>7.36</td>
<td>7.05</td>
<td>6.76</td>
<td>9.23</td>
<td>7.95</td>
<td>7.26</td>
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<tr>
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<td>3.77±0.03</td>
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<td>15.4</td>
<td>14.1</td>
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<td>17.8</td>
<td>16.0</td>
<td>14.8</td>
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<tr>
<td>pKₐ₁</td>
<td>7.75±0.01</td>
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<td>6.34±0.02</td>
<td>4.14±0.02</td>
<td>7.06±0.01</td>
<td>5.15±0.02</td>
<td>3.44±0.03</td>
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<tr>
<td>pKₐ₂</td>
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<td>7.85±0.02</td>
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<td>4.70±0.03</td>
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<td>log βₐ³</td>
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<td>28.1</td>
<td>26.8</td>
<td>32.9</td>
<td>32.3</td>
<td>29.2</td>
</tr>
</tbody>
</table>

a. \( \beta_1 = K_{a1}/K_{a2} \).  
b. \( \beta_2 = K_{a2}/(K_{a1}K_{a2}) \).  
c. \( \beta_3 = \beta_1K_{a2}/K_{a3} \).
extraction systems cannot be expressed by simple extraction equilibria; a careful preliminary investigation of the equilibria between nickel(II) ion and hydrazone in an aqueous solution is therefore required. The equilibrium constants first determined in aqueous solution are listed in Table 1. The extraction equilibria were then analyzed on the basis of these data.

Formation and protolytic equilibria for nickel(II) complexes in aqueous solution

The two acid dissociation constants (K_{a1} and K_{a2}) shown in Fig. 1 were determined in the same manner as described previously. The acid dissociation constant (K_{a3}) for the dissociation of imino proton of a ligand was also previously determined for calculating \( \beta_1 ' \) (cf. Table 1). Below pH 1 in an aqueous solution, a hydrazone ligand almost exists in the form of \( H_3L^2^+ \) and does little form complexes with nickel(II) ion. With increasing pH, it forms mono and bis complexes, Ni(HL)^2^+ and Ni(HL)^2^2^+. In solution from weakly acidic to weakly basic region, the predominant bis complex, Ni(HL)^2^2^+, successively deprotonates to form Ni(HL)L^+ and NiL^2_ complexes with increasing pH. The following equilibria are therefore given:

\[
\begin{align*}
\text{Ni}^{2^+} + H_3L^2^+ & \rightleftharpoons K_{a1} \text{Ni(HL)^2^+} + 2H^+, \\
\text{Ni}^{2^+} + 2H_3L^2^+ & \rightleftharpoons K_{a2} \text{Ni(HL)^2^2^+} + 4H^+, \\
\text{Ni(HL)^2^2^+} + & \text{K_{a3} Ni(HL)L^+} + H^+ \\
\text{Ni(HL)L^+} & \rightleftharpoons K_{a3} \text{NiL^2} + H^+. 
\end{align*}
\]

In the presence of more than about 200-fold molar excess of nickel(II) ion, hydrazone ligands form only a negligible concentration of 1:2 complex (<5%) with nickel(II) ion in a weakly acid solution. The absorbance \( A \) of the solution at the wavelength of maximum absorption for \( H_3L^2^+ \) is given by

\[
A = \epsilon_{a1}[\text{Ni(HL)^2^+}] + \epsilon_{a2}[\text{Ni(HL)^2^2^+}] + \epsilon_{a3}[\text{Ni(HL)L^+}] + \epsilon_{a4}[\text{NiL^2}].
\]

where \( \epsilon_{a1}, \epsilon_{a2} \) and \( \epsilon_{a3} \) refer to the molar absorbptivities of the species Ni(HL)^2^+ and NiL^2_ (n=1 - 3), respectively. The values of \( K_{a1} \) and \( \epsilon_{a1} \) were refined by using the known values of \( K_{a1}, K_{a2}, K_{a3}, K_{a4}, \epsilon_1, \epsilon_2 \) and \( \epsilon_3 \). Under the conditions in which \( C_L \approx C_M \) at the wavelength of maximum absorption for NiL^2_ by assuming successive acid dissociation of Ni(HL)^2^+. The equilibrium constants determined are listed in Table 1. All of the constants were determined in an aqueous solution, except for \( K_{a1} \) and \( K_{a2} \). Because of the low solubility of HL and ML^2_ species in water, \( K_{a1} \) and \( K_{a2} \), except for nickel(II)-PAPH and -DPPH systems, were obtained by extrapolation of the values in 10 - 40% aqueous dioxane to null dioxane.

Distribution equilibria of hydrazones

Almost all of the hydrazones examined are quantitatively distributed into the organic phase in the weakly acidic to the strongly alkaline region of the aqueous phase, and are partially or fully distributed into the aqueous phase with their protonations in a more acidic region. The distribution constants of hydrazones, \( K_d(=[HL]_o/[HL]) \), were determined in a similar manner as described elsewhere, except for DP5NPH. Because of the very low distribution of DP5NPH into the aqueous phase, even in a strongly acidic medium, it was impossible to determine the \( K_d \) value for this reagent at an ionic strength of 0.1. Of the hydrazones examined in this work, DP5NPH is the most sensitive to Ni^2^+ in the extractive spectrophotometric determination of this ion and, thus, it would be interesting to analyze the extraction equilibrium of nickel(II) with DP5NPH, in which the \( K_d \) value is necessarily required. The ligand was extracted into hexane from a solution of pH 12 - 13. The \( K_d \) value for this solvent was firstly determined by an analysis of the extraction equilibrium involving deprotonation of HL at the above mentioned pH, and then the \( K_d \) value for benzene was evaluated from the value for hexane, as described below. The stoichiometric relationship is

\[
C_L = [HL]_o + [HL] + [L^-].
\]

and the absorbance \( A_{cal} \) of the solution at the absorption maximum of HL is calculated by

\[
A_{cal} = \frac{\epsilon_{HL}[HL]_o}{1 + 1/K_d(1 + K_{a3}/[H^+]')}.
\]
where subscript (o) refers to the species in the organic phase. The values of $K_d$ of DP5NPH in hexane (=1.52) and $\delta_{HL,o}$ were refined by using the known value of $K_{a3}$. According to regular solution theory\textsuperscript{11} the distribution system can be expressed as follows by using the distribution constant ($K_d$) of a hydrazone (HL) into a given organic solvent, the solubility parameters, $\delta$ (cal$^{1/2}$ cm$^{-3/2}$), and the molar volumes ($V$),

$$ \log K_d = \frac{V_{org}}{V_{aq}} \frac{1}{\delta_{aq} - \delta_{org}} + \frac{V_{HL}}{2.303RT} (\delta_{aq} - \delta_{org} - 2\delta_{HL}), $$

(9)

where subscripts org and aq designate an organic solvent and water, respectively; \( R \) and \( T \) are the gas constant (cal K$^{-1}$ mol$^{-1}$) and temperature (K), respectively. To evaluate the value of $K_d$ of DP5NPH in benzene, the distribution constants of DPPH were preliminarily determined for various organic solvents, the logarithmic values being 1.19 for hexane, 1.20 for heptane, 2.78 for carbon tetrachloride, 3.15 for benzene, 3.51 for 1,2-dichloroethane, 3.94 for dichloromethane, and 4.35 for chloroform. The left hand side of Eq. (9) were plotted against $\delta_{org}$ in which the literature values\textsuperscript{11} were used for $V_{org}$, $V_{aq}$, $\delta_{org}$ and $\delta_{aq}$. The values of $V_{HL}$ (=235) and $\delta_{HL}$ (=11.3) of DPPH were evaluated from the slope and intercept of the plot. For DP5NPH, the value of $V_{HL}$ was obtained to be 251 based on the additivity rule of molar volume, where the value of the molar volume of the nitro group is 15.5;\textsuperscript{12,13} then, the value of $\delta_{HL}$ was calculated from Eq. (9) using the value of $K_d$ of DP5NPH in hexane. The value of $K_d$ of DP5NPH in benzene was evaluated by substituting the obtained values for $V_{HL}$ and $\delta_{HL}$ of Eq. (9).

### Distribution equilibria of nickel(II)-hydrazone complexes

In the Ni$^{II}$-hydrazone systems, the extractive species is merely an uncharged bis complex, NiL$_2$, as shown in Fig. 1. The charged species present in the aqueous phase are Ni$^{2+}$, Ni(HL)$^{2+}$, Ni(HL)$_2^{2+}$ and Ni(HL)L$^+$. The values of $D_{Ni}$, were calculated from the change in the absorbance of the organic phase at the absorption maximum of NiL$^+$,\textsuperscript{7} Plots of $\log D_{Ni}$ vs. the pH of the aqueous phase are shown in Fig. 2, indicating all of the slopes to be 2. This implies that the concentration of Ni(HL)L$^+$ was small in the aqueous phase so that it could be ignored in the analyses. In a region where $D_{Ni}$ is independent of the concentrations of PAPH, PAQH, QAPH and DPQH in benzene and of PAPH and PAQH in chloroform\textsuperscript{7}, the extraction constant ($K_{ex}$) is simply given by

$$ \text{Ni}(HL)L^+ \Leftrightarrow \text{NiL}_2 + 2H^+, $$

(10)

$$ K_{ex} = \frac{[\text{NiL}_2][H^+]^2}{[\text{Ni}(HL)L^+]}. $$

(11)

On the other hand, in other regions where $D_{Ni}$ is dependent of the ligand concentrations in the organic phase, the following additional extraction equilibria are considered:

$$ \text{Ni}(HL)^2+ + (HL)_o \Leftrightarrow (\text{NiL}_2)_o + 2H^+ $$

(12)

$$ \text{Ni}^{2+} + 2(\text{HL})_o \Leftrightarrow (\text{NiL}_2)_o + 2H^+. $$

(13)

The total concentrations of the ligand and nickel(II) are given, respectively, by

$$ C_L = [\text{HL}] + \sum [H_a L^{2n-m}] + [\text{Ni(HL)}^{2+}] $n
$$

$$ + \gamma_{NiHL}[\text{Ni}(HL)_2^{2+}] $$

(14)

and

$$ C_{Ni} = [\text{Ni}^{2+}] + [\text{Ni(HT)}^{2+}] $$

$$ + \gamma_{NiHL}[\text{Ni}(HL)_2^{2+}] + [\text{NiL}_2]. $$

(15)
where $y_{Ni(HL)_2} = (1 + K_{ac1}/[H^+] + K_{ac2}/[H^+])$. The distribution constant ($K_{dm}$) of NiL$_2$ is given by

$$K_{dm} = \frac{\text{[NiL}_2]\text{[H}^+]\text{[H}_2\text{O}]}{\text{[NiL}_2]}.$$  \hfill (16)

Each equilibrium concentration for the extraction system can be calculated by using the values of $K_d$, $K_{dm}$ and the equilibrium constants in an aqueous solution, i.e., $K_{a1}$, $K_{a2}$, $K_{a3}$, $K_{a4}$, $K_{a5}$, $K_{a6}$ (cf. Table 1). The absorbance at the absorption maximum of NiL$_2$ in the organic phase is given by

$$A_{cal} = \varepsilon_{NiL_2}\text{[NiL}_2],$ \hfill (17)

where $\varepsilon_{NiL_2}$ is the molar absorptivity of the NiL$_2$ complex in the organic phase. The values of $\varepsilon_{NiL_2}$ and $K_{dm}$ were refined by using the known values of $K_d$ and the above equilibrium constants in an aqueous solution. The calculated absorbances ($A_{cal}$) are plotted in Fig. 3 (solid lines) as a function of the pH of the aqueous phase, showing good agreement with the experimental absorbances. The value of $K_{ex}(Ni(HL)_2)$ is calculated from Eq. (18),

$$K_{ex}(Ni(HL)_2) = K_{dm}K_{ac1}K_{ac2}. \hfill (18)$$

The extraction constant ($K_{ex}(Ni)$) for reaction (13) is given by

$$K_{ex}(Ni) = \frac{[\text{NiL}_2][H^+]^2}{\text{[Ni}^2\text{+}[HL]_2]}.$$ \hfill (19)

which can be transformed as

$$K_{ex}(Ni) = K_{dm}K_d^{-2}\beta_2K_{ac1}K_{ac2}. \hfill (20)$$

The values of $K_{dm}$ and $K_{ex}$ obtained are summarized in Table 2. The values of $K_{ex}(Ni(HL)_2^{2+})$ are in good agreement with those obtained from a plot of log $D_{Ni}$ vs. pH.

For $K_d$ and $K_{dm}$, the order of the values is PAPH < PAQH < QAPH, PAPH < DPPH and PAQH < DPQH. That is to say, the introduction of a quinolyl ring to a hydrazone molecule instead of a pyridyl ring and the introduction of another pyridyl ring to the aldehyde moiety of PAPH and PAQH increase the distributions of HL and NiL$_2$ into the organic phase. Since some charged complexes are also formed in the aqueous phase, depending on the experimental conditions used, a mutual comparison of the apparent extractability of the NiL$_2$

Fig. 3 Molar absorptivity vs. pH plots for Ni$^{II}$-hydrazone complexes in chloroform. (a) PAPH (O), (b) PAQH (□). (c) QAPH (△), (d) DPPH (●), (e) DPQH (▲), (f) DPSNPH (■). Selected maximum wavelengths ($\lambda_{max}$) are referred to Table 3.

Table 2 Distribution and extraction equilibrium constants for nickel(II) complexes of hydrazones in chloroform and/or benzene

<table>
<thead>
<tr>
<th>Ligand</th>
<th>PAPH</th>
<th>PAQH</th>
<th>QAPH</th>
<th>PA5NPH</th>
<th>DPPH</th>
<th>DPQH</th>
<th>DP5NPH</th>
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<tr>
<td>log $K_d$</td>
<td>2.47±0.01</td>
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<td>(chloroform)</td>
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<tr>
<td>log $K_d$</td>
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<tr>
<td>(benzene)</td>
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<td>log $K_{ex}(Ni)$</td>
<td>−0.25</td>
<td>0.69</td>
<td>−1.82</td>
<td>—</td>
<td>−0.52</td>
<td>0.54</td>
<td>2.86</td>
</tr>
<tr>
<td>(benzene)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Evaluated value obtained by applying regular solution theory (see text).
complex can not be discussed based on a simple extraction equilibrium, such as Eqs. (10), (12) or (13). The distribution diagrams for the extraction of nickel(II)-PAPH and -DPQH complexes are depicted in Fig. 4 as a function of the pH of the aqueous phase. In the PAPH system, nickel(II) ion predominantly forms the Ni(HL)$_2^{2+}$ complex at pH 3 - 5 and the Ni(HL)$_2^{2+}$ complex is quantitatively extracted as the NiL$_2$ complex into chloroform above pH 6.5. In this case the formation of Ni(HL)L$^+$ can practically be neglected (cf. Fig. 4). As the NiL$_2$ complex is extracted at higher pH into benzene, the Ni(HL)L$^+$ complex is formed to some degree (>10%) in the aqueous phase. Plots of log $D_{Ni}$ vs. pH are depicted in Fig. 2. The value of the slope for PAPH in benzene is 1.9, while that for PAPH in chloroform is 2.0. This corroborates the formation of the Ni(HL)L$^+$ complex in the aqueous phase for extraction using benzene as a solvent. In the DPQH system, three species, i.e., Ni$^{2+}$, Ni(HL)$^{2+}$ and Ni(HL)$_2^{2+}$, coexist at pH 1.5 - 2.5 and NiL$_2$ complex is quantitatively extracted above pH 3.5. This corroborates that the region independent of $D_{Ni}$ on the ligand concentration was not observed for the DPQH system in chloroform, as mentioned above.

Stary$^{14}$ described the relationship between $K_{dm}$ and $K_d$ for various organic solvents,

$$\log K_{dm} = n \log K_d + K,$$

(21)

where $n$ is the number of coordinating ligands and $K$ is a constant.

---

**Table 3** Absorption maxima, $A_{max}$ (nm), and molar absorptivities, $\varepsilon_{max}$ (1 mol$^{-1}$ cm$^{-1}$), of NiL$_2$ complexes extracted into chloroform and/or benzene

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PAPH</th>
<th>PAQH</th>
<th>QAPH</th>
<th>PA5NP</th>
<th>PAPH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>474</td>
<td>498</td>
<td>526</td>
<td>56400</td>
<td>496</td>
</tr>
<tr>
<td>Benzene</td>
<td>480</td>
<td>510</td>
<td>536</td>
<td>59700</td>
<td>—</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Chloroform</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPPH</td>
<td>490</td>
<td>501</td>
</tr>
<tr>
<td>DPQH</td>
<td>512</td>
<td>518</td>
</tr>
<tr>
<td>PA5NP</td>
<td>59100</td>
<td>65000</td>
</tr>
</tbody>
</table>

**Fig. 4** Distribution of each species of Ni$^{11}$-hydrazone complexes in a water-chloroform system. (a) PAPH: $C_l=4.0 \times 10^{-4}$ M, $C_n=1.4 \times 10^{-2}$ M; (b) DPQH: $C_l=3.3 \times 10^{-3}$ M, $C_n=1.1 \times 10^{-2}$ M; (1) Ni$^{2+}$, (2) Ni(HL)$_2^{2+}$, (3) Ni(HL)$_2^{2+}$, (4) Ni(HL)L$^+$, (5) NiL$_2$. Dotted line represents the coloring species.

**Fig. 5** Relationship between the distribution constants of NiL$_2$($K_{dm}$) and HL($K_d$). $\circ$, $\bullet$: PAPH, PAQH, QAPH and PA5NP; $\Delta$, $\triangle$: DPPH and DPQH. Open symbols in chloroform, closed symbols in benzene.
constant which depends on the ligands.\textsuperscript{14,15} Plots of log $K_{dm}$ vs. log $K_d$ are depicted in Fig. 5. Although the symbols for different solvents are bonded, two straight lines are evidently obtained; one includes PAPH, PAQH, QAPH and PA5NPH systems, and the other DPPH, DPQH and DP5NPH systems. For the latter ligands with two pyridyl groups on the aldehyde moiety, one of the two pyridyl groups forms an intramolecular hydrogen bond between the imino hydrogen and the pyridine-nitrogen\textsuperscript{10}, which would cause an increase in the $K_d$ of HL.

The spectral properties of NiL$_2$ complexes are listed in Table 3. DPQH gives an uncharged bis complex with the highest $\varepsilon_{\text{max}}$ of the hydrazones without an nitro group. Moreover, the solubilities of DPQH and its metal complexes in organic solvents are satisfactorily large to be used in the spectrophotometric determination of metals and anions.\textsuperscript{4,16} The $\varepsilon_{\text{max}}$ of hydrazone complexes significantly increase by the introduction of a nitro group to the 5-position of pyridine in the hydrazine moiety, the values increasing to over 10$^5$ 1 mol$^{-1}$ cm$^{-1}$ for certain metal complexes.

References


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