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Solubility and Synergistic Extraction Equilibria for [4-(2-Pyridylazo)resorcinolato] Nickel(II) Complexes

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The nickel(II) complex of 4-(2-pyridylazo)resorcinol (PAR, H_2L) is known to show somewhat anomalous and complicated behavior in solution. In this regard, the solubility and the synergistic extraction equilibria of the above complex are studied in connection with acid dissociation reactions. The intrinsic solubility and the acid dissociation constants are determined to be, $S_0=[[Ni(HL)_2]]=10^{-6.2\pm0.1}$ mol dm^{-3}, $K_{a1}=[[Ni(HL)L]^-][H^+][[Ni(HL)_2]]^{-1}=10^{-6.2\pm0.1}$, and $K_{a2}=[[NiL_2]^{2-}][H^+][[Ni(HL)L]^-]^{-1}=10^{-7.1\times0.1}$, respeactively in the solution with the ionic strength of 0.10 (Na_2SO_4) at 298 K. Using the above constants, the extraction constant of the neutral complex with trioctylphosphine oxide (TOPO) into chloroform is evaluated as $K_{ex}=[[Ni(HL)_2(TOPO)_2]]_o[[Ni(HL)_2]]^{-1}[TOPO]_o^{-2}=10^{3.1\pm0.2}$, where the subscript o denotes the organic phase. An equilibrium diagram for the nickel(II)–PAR complexes is proposed.

A well-known sensitive reagent, 4-(2-pyridylazo)-resorcinol (PAR, H_2L) has been used for the trace determination of nickel(II) ion.[1–4] In our previous studies[5–8] of the ion pair extraction of anionic PAR complexes with a quaternary ammonium salt (QCl),[9] it was shown that the nickel(II) ion yields the PAR complex having somewhat unusual properties in sharp contrast to those of other divalent ions, Fe(II), Cu(II), Zn(II), and Cd(II). (1) The ion pair of the mononegative complex, Q[Ni(HL)L] has much poorer extractability than that of the dinegative one, $Q_2[NiL_2]$. This seems to be contrary to the general rule found in ion pair extraction, *i.e.*an increase in the charge number of the anion leads to a decrease in the extractability. (2) The neutral complex, $[Ni(HL)_2]$ is slightly soluble in water as well as in chloroform or nitrobenzene, whereas the correponding iron(II) complex is partly distributed into these solvents. The neutral nickel(II) complex can be extracted synergistically with trioctylphosphine oxide (TOPO) as $[Ni(HL)_2(TOPO)_2]$, which is not an unusual matter as compared with the other neutral PAR complexes.[7,10]

These observations have prompted a more thorough investigation of the solubility, acid dissociation, and synergistic extraction equilibria of the nickel(II)–PAR complexes. This was expected to be an approach to interpret the somewhat anomalous and complicated behavior of the complexes in solutions, especially in the solvent extraction systems.

In this paper is established the equilibrium relation between nickel(II)–PAR complexes which has been sometimes ambiguous and inconsistent,[6,11–13] and the results are discussed in comparison with those of the other metal ion complexes.

Experimental

Apparatus and Reagents. A Hitach model 124 double beam recording spectrophotometer with 1 cm glass cells and a Horiba M-5 pH meter were used. In extraction procedures, samples were shaken in an Iwaki KM-type reciprocating shaker. A Yamato Coolnics Circulator model CTR200/CTE220 water bath was used at a constant temperature of 298 K.

TOPO, as obtained from Dojindo Lab. (Kumamoto, Japan) was dissolved in chloroform which was purified by distillation and saturated with water. Nickel(II)–PAR complex ($[Ni(HL)_2]\cdot2H_2O$) was prepared as described by Corsini *et al.*[14] The concentration of the PAR complex stock solution (pH 8) was determined spectrophotometrically.

All other reagents used were of analytical grade.

Procedure. *Solubility Measurements*: About 50 cm^3 of a phosphate buffer solution (2×10^{-3} mol dm^{-3}) containing nickel(II)–PAR complex (initially 10^{-3}—10^{-4} mol dm^{-3}) and sodium sulfate (0.033 mol dm^{-3}, I=0.10) with 5 cm^3 of chloroform was allowed to stand at 298 K for at least 5 h with occasional shaking. Sodium sulfate was used to maintain a constant ionic strength in conformity with the ion pair extraction study.[6] The initial pH of the solution was roughly adjusted with the buffer, dilute sulfuric acid and sodium hydroxide solutions. The pH range of 6 to 8 was chosen in order to prevent the decomposition of the complex due to protolysis and hydrolysis reactions. The concentration of the nickel complex in aliquots of the saturated solutions was determined spectrophotometrically after filtration through a G-4 sintered glass filter. The pH of the filtrate solution was measured. Because of the inert nature of the nickel(II)–PAR complexes, sulfate and phosphate ions in the solution had no significant effect on the above experiments. Partition of the neutral and the anionic complexes into chloroform phase occurs to a slight extent. However, such a phenomenon has no effect on the solubility measurements under the conditions where the precipitate is present in the system.

TOPO Extraction: Ten cm^3 of an aqueous solution containing phosphate buffer (2.5×10 mol dm^{-3}), sodium sulfate (I=0.10), and nickel(II)–PAR complex were equilibrated by shaking with an equal volume of chloroform containing an appropriate concentration of TOPO in a glass sample tube (50 cm^3), and allowed to stand in a thermostated bath at 298 K for more than 5 h with occasional shaking. Aliqouts of the organic phase were taken and the absorbance at 535 nm was measured (the molar absorption coefficient is 3.57×10^4 dm^3 mol^{-1} cm^{-1}).

Results and Discussion

The equilibrium saturation with respect to the nickel(II)-PAR complex was attained after 4 h; this was confirmed by the solubility-time curve obtained by heating the samples to 313—323 K followed by rapid cooling to the final temperature, 298 K.

The solubility-pH curve for the nickel(II)-PAR complex in water saturated with chloroform is shown in Fig. 1. Above pH 6, the complex is in part soluble as the anionic species of $[Ni(HL)L]^-$ and $[NiL_2]^{2-}$. Decomposition of the complex was negligible. The solubility equilibria can be expressed by the following reactions; the intrinsic solubility S_0 of the neutral complex is given by

$$[Ni(HL)_2]_s \rightleftharpoons [Ni(HL)_2], \quad S_0 = [[Ni(HL)_2]] \qquad (1)$$

where the subscript s denotes the solid phase, and the acid dissociation constants are represented as

$$[Ni(HL)_2] \rightleftharpoons [Ni(HL)L]^- + H^+,$$

$$K_{a1} = \frac{[[Ni(HL)L]^-][H^+]}{[[Ni(HL)_2]]} \qquad (2)$$

$$[Ni(HL)L]^- \rightleftharpoons [NiL_2]^{2-} + H^+,$$

$$K_{a2} = \frac{[[NiL_2]^{2-}][H^+]}{[[Ni(HL)L]^-]} \qquad (3)$$

The solubility, S of the complexes is given by

$$S = [[Ni(HL)_2]] + [[Ni(HL)L]^-] + [[NiL_2]^{2-}] \qquad (4)$$

From Eqs. 1—4 the following equation is obtained,

$$\left(\frac{S}{S_0} - 1\right)[H^+]^2 = K_{a1}[H^+] + K_{a1}K_{a2} \qquad (5)$$

The intrinsic solubility, S_0 was obtained by extrapolation on the solubility-pH curve shown in Fig. 1 (dashed line).

$$\log S_0(\text{mol dm}^{-3}) = -6.2 \pm 0.1 \quad [I = 0.10(Na_2SO_4),\ 298\ K]$$

From the plots of Eq. 5 given in Fig. 2, the values of K_{a1} and K_{a2} were determined to be

$$pK_{a1} = 6.2 \pm 0.1, \quad pK_{a2} = 7.1 \pm 0.1$$
$$[I = 0.10(Na_2SO_4),\ 298\ K]$$

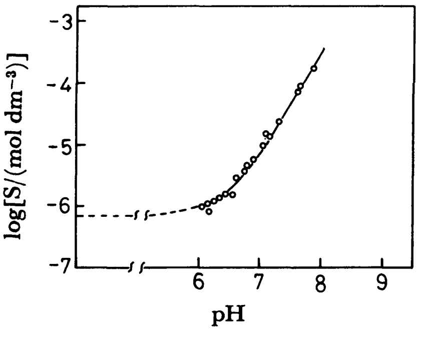

Fig. 1. Solubility *vs.* pH curve for Ni(II)-PAR complex at 298 K.
I=0.10 (Na_2SO_4), $C_{Phosphate} = 2.0 \times 10^{-3}$ mol dm^{-3}.

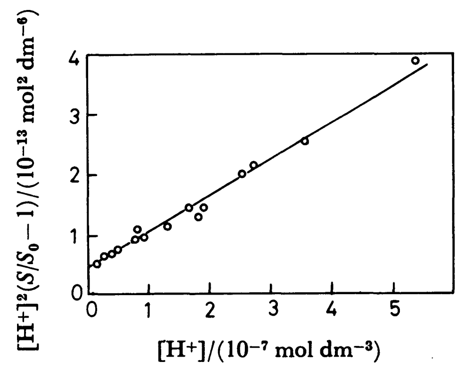

Fig. 2. Plots of Eq. 5.

The calculated log S *vs.* pH curve shown in Fig. 1 as the solid line is in good agreement with the experimental points.

The value of S_0 for the nickel(II)-PAR complex is very small. Although no quantitative solubility data of the other metal-PAR complexes are available, there is no evidence for the precipitation of the complexes at concentrations below 5×10^{-6} mol dm^{-3} in a similar medium. The iron(II) complex, $[Fe(HL)_2]$ was partly distributed into chloroform and still more so into nitrobenzene.[8] This fact demonstrates an interesting contrast between the nickel and iron PAR complexes.

The acid dissociation constants of 1-hydroxyl groups (para position to azo group) in the nickel(II)-PAR complex in 50% aqueous dioxane solution were reported by Corsini *et al.*[15] as pK_{a1}=7.7 and pK_{a2}=9.2. As these values were obtained in quite a different medium, these are not considered in greater detail. The values obtained here agree within a similar order of magnitude with those of the PAR complexes of divalent ions, iron(II); pK_{a1}=6.47, pK_{a2}=7.66 (I=0.10, 293 K),[8] copper(II); 6.54, 7.64 (I=0.10, 298 K),[16] zinc(II); 6.45, 7.55 (I=0.10, 298 K),[17] and cadmium(II); 6.67, 7.84 (I=0.10, 298 K),[18] respectively. The parallel order between the acidity of 1-hydroxyl groups and the stability of PAR complexes suggested by Corsini *et al.*[15] does not seem to be valid in the light of these data as the stability order may be $Fe^{II} > Ni^{II} > Cu^{II} > Zn^{II} > Cd^{II}$.[8,16–18]

At the pH condition for the photometric determination of nickel (pH 9.2, borate buffer)[2,3] the predominant species (99%) is, thus, the dianion, $[NiL_2]^{2-}$ which has the largest molar absorption coefficient of $(7.2-7.8) \times 10^4$ dm^3 mol^{-1} cm^{-1} at 495 nm as compared with the other protonated ones.

Besides TOPO, typical monodentate adduct formers such as pyridine, pyridine *N*-oxide, and tributyl phosphate are effective for the extraction of the neutral complex $[Ni(HL)_2]$, while the bidentate ones, 1,10-phenanthroline, 2,2′-bipyridine, and ethylenediamine, fail to work.

The extraction with TOPO is represented by

$$[Ni(HL)_2] + 2TOPO_{(o)} \rightleftharpoons [Ni(HL)_2(TOPO)_2]_{(o)} \qquad (6)$$

$$K_{ex}=\frac{[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o}{[[\mathrm{Ni(HL)_2}]][\mathrm{TOPO}]_o^2} \tag{7}$$

where the subscript o is used for the species in the organic phase. Using the total concentration of the complex species in the aqueous phase, $C_{a,Ni}$, Eq. 7 is rewritten as

$$K_{ex}=\frac{[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o}{C_{a,Ni}[\mathrm{TOPO}]_o{}^2}\left(1+\frac{K_{a1}}{[\mathrm{H^+}]}+\frac{K_{a1}K_{a2}}{[\mathrm{H^+}]^2}\right) \tag{8}$$

where the aqueous concentration of $[\mathrm{Ni(HL)_2(TOPO)_2}]$ is neglected. When the precipitate is present, $C_{a,Ni}$ is equal to the solubility, S(Eq. 4). At constant pH, the plots of $\log\{[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o(C_{a,Hi})^{-1}\}$ *vs.* log $\{[\mathrm{TOPO}]_o\}$ give a straight line of a slope 2 as shown in Fig. 3. Because of the upward deviation at low organic concentration of TOPO ($<0.05\ \mathrm{mol\ dm^{-3}}$, curve 1 in Fig. 3), the calculation of the K_{ex} value was made using the experimental points on the straight line portion. Under the conditions where the precipitate is in the system at pH≤7.05, the concentration of $[\mathrm{Ni(HL)_2}]$ is held constant according to Eq. 1, thus,

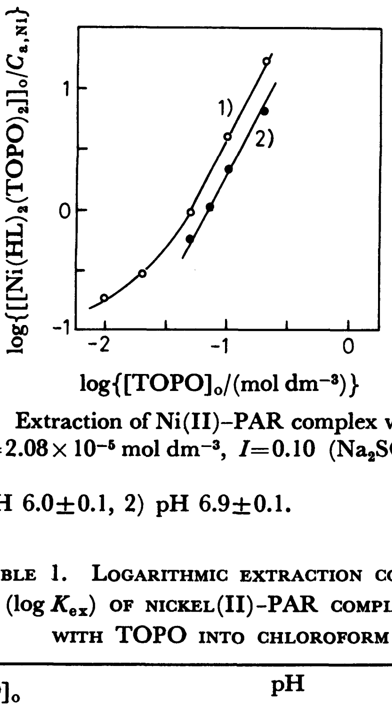

Fig. 3. Extraction of Ni(II)-PAR complex with TOPO. $C_{Ni}=2.08\times10^{-5}\ \mathrm{mol\ dm^{-3}}$, $I=0.10$ ($\mathrm{Na_2SO_4}$), at 298 K.
1) pH 6.0±0.1, 2) pH 6.9±0.1.

Table 1. Logarithmic extraction constant ($\log K_{ex}$) of nickel(II)-PAR complex with TOPO into chloroform

$[\mathrm{TOPO}]_o$ mol dm^{-3}	pH 6.00	6.18	6.41	6.50	6.71	6.80	6.81
0.05	2.9		2.9		3.0	3.1	
0.10	2.9	3.2		3.3			3.2
0.20	2.9						

$[\mathrm{TOPO}]_o$ mol dm^{-3}	pH 6.90	7.05	7.40	7.42	7.47	7.50
0.05	3.3	3.2	3.1	3.2		
0.07	3.3					
0.10	3.2				3.2	3.2
0.20	3.0					

$\log K_{ex}=3.1\pm0.2$ [$I=0.10$ ($\mathrm{Na_2SO_4}$), at 298 K] (averaged value of 18 runs).

$$K_{ex}=\frac{[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o}{S_0[\mathrm{TOPO}]_o^2} \tag{9}$$

Under higher pH conditions (pH≥7.40) where no precipitate is in the system, Eq. 8 is used for calculation of the K_{ex} value, where $C_{a,Ni}$ is given by $C_{a,Ni}=C_{Ni}-[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o$, ($C_{Ni}$ is the total concentration of the nickel(II)-PAR complexes). The calculated values of log K_{ex} at various pH and TOPO concentrations are shown in Table 1. The mean value was determined to be,

$$\log K_{ex}=3.1\pm0.2\quad [I=0.10(\mathrm{Na_2SO_4}),\ 298\ \mathrm{K}]$$

A few reports have dealt with this type of extraction of neutral PAR complexes.[7,19,20] Only one comparable datum is the extraction constant for the vanadium(V)-PAR-TOPO complex, $K_{ex}=[[\mathrm{VO_2(HL)(TOPO)}]]_o[[\mathrm{VO_2(HL)}]]^{-1}[\mathrm{TOPO}]_o^{-1}=10^{2.17}$.[7] In general, in TOPO synergistic extraction systems, over-all extraction constants (including formation of parent complexes) and adduct formation constants in the organic phase have been most frequently used to describe the extraction processes.[21] However, they can not be directly compared with the data obtained in this work. The adduct formation constant in chloroform, $\beta_2=[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o[[\mathrm{Ni(HL)_2}]]_o^{-1}[\mathrm{TOPO}]_o^{-1}$ was roughly estimated as follows: when the distribution ratio, D_{Ni} is defined as $D_{Ni}=\{[[\mathrm{Ni(HL)_2}]]_o+[[\mathrm{Ni(HL)_2(TOPO)_2}]]_o\}(C_{a,Ni})^{-1}$, by extrapolating the $[\mathrm{TOPO}]_o$ term (curve 1 in Fig. 3, pH 6.0) to zero, $D_{Ni}\approx[[\mathrm{Ni(HL)_2}]]_o(C_{a,Ni})^{-1}\approx10^{-1}$ is obtained, and from Eq. 8, $\beta_2=K_{ex}\{D_{Ni}(1+K_{a1}/[\mathrm{H^+}]+K_{a1}K_{a2}/[\mathrm{H^+}]^2)\}^{-1}\approx10^{3.9}$. It is clearly recognized that this β_2 value is smaller by some order of magnitude than those for the other TOPO adducts in chloroform, in which TOPO molecules are directly bound to the central metal ions replacing aqua ligands, *i.e.* mixed ligand complex (for example, some β-diketone complex systems).[21,22] In the nickel(II)-PAR system, therefore, there is a little doubt about the possibility of a mixed ligand complex. It is also likely that two TOPO molecules are bound to each of two 1-hydroxyl groups on the PAR ligands *via* hydrogen bonding, which causes an increase in hydrophobicity of the parent PAR complex. This possibility seems to be supported by the fact that the complex is well distributed into some polar solvents having hydrogen bonding ability, alcohols, esters, and ketones. It is important to observe that the coordination mode of the PAR ligands (bidentate or tridentate) would decide between the alternative possibilities depending upon whether the complex is "coordinatively saturated" with two tridentate $\mathrm{HL^-}$ or "unsaturated" having two bidentate $\mathrm{HL^-}$ and two aqua ligands. Kawamoto *et al.* re-

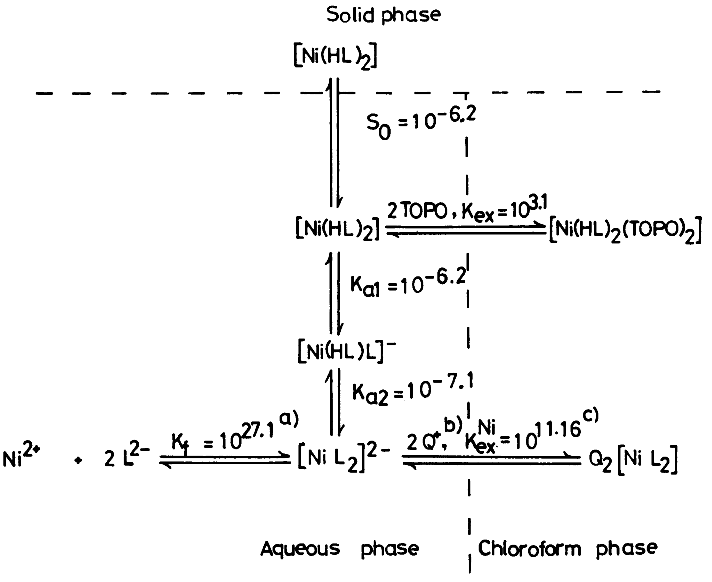

Fig. 4. Equilibrium diagram of Ni(II)–PAR system.
a) Ref. 3), b) Q^+, Ref. 9), c) Ref. 6), $K_{ex}^{Ni}=[Q_2[NiL_2]]_o[Q^+]^{-2}[[NiL_2]^{2-}]^{-1}$.

cently found the nickel(II)–PAR complex having the 1:3 stoichiometry in the ion pair extraction system with a highly lipophilic quaternary ammonium salt.[11] Detailed discussion of the extraction mechanism, in all events, will be the emphasis of a future study which will provide valuable information on the chemistry of PAR complexes.

Finally, several nickel(II)–PAR complex species in solutions and their equilibrium constants were verified as summarized in Fig. 4. These data serve as a quantitative basis for understanding and designing of the conventional spectrophotometric systems and the ion pair solvent extraction for the nickel determination.

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