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Kinetics and Mechanism of the Extraction of Nickel(II) with 3-Mercapto-1,5-Diphenylformazan in the Presence of 1,10-Phenanthroline or Pyridine

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The kinetics and mechanism of the extraction of nickel(II) with 3-mercapto-1,5-diphenylformazan (dithizone, Hdz) into chloroform in the presence of 1,10-phenanthroline (phen) or pyridine (py) were studied in the presence of 0.1 mol dm^{-3} or 0.2 mol dm^{-3} $NaNO_3$ at 25 °C. For the nickel(II)–dithizone–1,10-phenanthroline system, the rate-determining steps were the competitive reactions of nickel(II) with dithizonate and with 1,10-phenanthroline in an aqueous phase. The second-order rate constants for the formation of $[Ni(dz)]^+$ and of $[Ni(phen)]^{2+}$ were determined to be $(6.0\pm0.4)\times10^3$ mol^{-1} dm^3 s^{-1} and $(3.4\pm0.2)\times10^3$ mol^{-1} dm^3 s^{-1} respectively. It was suggested that $[Ni(phen)]^{2+}$ is more reactive toward dithizonate than toward 1,10-phenanthroline in an aqueous phase. The formation of $[Ni(phen)_2]^{2+}$ retards the extraction of nickel(II) with dithizone. For the nickel(II)–dithizone–pyridine system, the rate-determining step is probably the reaction of $[Ni(py)]^{2+}$ with dithizonate in an aqueous phase. The second-order rate constant for this reaction was determined to be $(1.7\pm0.3)\times10^5$ mol^{-1} dm^3 s^{-1}.

From the point of view of a selective separation and sensitive determination of metal ions, the synergistic extraction is a remarkably interesting method.[1–4]

Dithizone reacts with many metal ions to give solvent-extractable and highly colored metal complexes, whereas this extractant is less selective for metal ions. The selectivity for the extraction of metal ions with dithizone was improved by the addition of pyridine or 1,10-phenanthroline. For example, cadmium(II) was predominantly separated and determined from a mixture of cadmium(II) and zinc(II) with dithizone in the presence of 1,10-phenanthroline.[5] The extraction of nickel(II) with dithizone in the presence of 1,10-phenanthroline gave an intensely pink adduct, $[Ni(dz)_2(phen)]$, absorbing strongly in the visible range around 520 nm with a molar extinction coefficient of about 5×10^4 mol^{-1} dm^3 cm^{-1}. The above development was utilized for the sensitive determination of nickel(II).[6,7] At a pH lower than 6.0, the extraction rate of $[Ni(dz)_2]$ into chloroform is very small, but it is remarkably accelerated by the addition of 1,10-phenanthroline. In order to clarify the mechanism of the synergistic extraction of the nickel(II) ion with dithizone in the presence of 1,10-phenanthroline or of pyridine, kinetic studies of this method were carried out. The rate-determining step of the extraction of nickel(II) with dithizone was the formation of $[Ni(dz)]^+$ in an aqueous phase.[8–10] On the other hand, the rate-determining steps of synergistic extraction were found to be the competitive extraction of nickel(II) with dithizonate and that with 1,10-phenanthroline in an aqueous phase.

Experimental

Apparatus. For the determinations of the rates of the extraction reactions, the high-stirring apparatus was used.[11] An Iwaki KM shaker was used for shaking a solution in order to study the extraction equilibrium. A Hitachi 170-30 atomic absorption spectrophotometer was used for the determination of the nickel(II) ion in an aqueous phase. A Hitachi 101 spectrophotometer was used for the measurements of the absorbances of $[Ni(dz)_2(phen)]$. All the pH measurements were carried out with a Hitachi-Horiba F-7 pH meter.

Reagents. A 3-mercapto-1,5-diphenylformazan (dithizone) (Kanto Chemical Co., Inc.) was purified according to the method described in a preceding paper.[12] The chloroform solution of dithizone was prepared by dissolving a weighed amount of dithizone into chloroform just before use.

The nickel(II) stock solution was prepared by dissolving a given amount of nickel(II) nitrate hexahydrate in water. A stock solution of 1,10-phenanthroline was prepared by dissolving the weighed amount of reagent-grade 1,10-phenanthroline (Kanto Kagaku) in chloroform. Spectrophotometric-grade pyridine (Kanto Kagaku) was used without purification.

The chloroform was distilled and treated with $NH_2OH\cdot 2HCl$ at pH 8 just before use.

All the other chemicals used were of a reagent-grade quality. Sodium nitrate was used to adjust the ionic strength to 0.10 mol dm^{-3} and 0.20 mol dm^{-3} for the nickel(II)–dithizone–1,10-phenanthroline and nickel(II)–dithizone–pyridine systems respectively. A potassium dihydrogenphosphate-sodium hydroxide buffer solution was used to adjust the pH of the aqueous solution. The concentration of potassium dihydrogenphosphate for the nickel(II)–dithizone–1,10-phenanthroline and nickel(II)–dithizone–pyridine systems were adjusted to 0.01 mol dm^{-3} and 0.1 mol dm^{-3} respectively.

Procedure for the Kinetics of the Extraction. The kinetics was carried out under the pseudo-first order conditions, in which dithizone is present in a large excess with respect to the nickel(II) ion. One hundred-cm^3 portions of an aqueous solution containing nickel(II) and of a phosphate buffer solution were placed in a three-necked flask. Then, a 100-cm^3 portion of a chloroform solution of dithizone containing 1,10-phenanthroline or of pyridine was added carefully using a funnel. Before mixing, both of the solutions were thermostated at 25 °C. The solutions were vigorously stirred, and then equal volumes of two phases were removed in a test tube for a definite time interval. Each sample was centrifuged to separate the phases. The nickel(II) ion in an aqueous phase was determined by means of atomic-absorption spectrophotometry. After stirring, the pH value of an aqueous phase was measured. For the nickel(II)-dithizone–1,10-phenanthroline system, the change of the pH in an aqueous phase during the extraction reaction was within ±0.01 pH unit. The extractions were done at a constant stirring speed of 1500 rpm, because the extraction rate was independent of the stirring speed in the range greater than 1500 rpm.

Procedure for the Extraction Equilibrium. A 25-cm^3 portion of an aqueous phase containing the nickel(II) ion and a 25-cm^3 portion of a chloroform solution containing dithizone and 1,10-phenanthroline were placed in a separatory funnel. The solutions were then shaken vigorously by using an automatic shaker. After phase-separation, the nickel(II) ion remaining in an aqueous phase was determined. For nickel(II)-dithizone–pyridine, we used almost the same procedure as for nickel(II)-dithizone–1,10-phenanthroline.

Distribution Constant of 1,10-Phenanthroline. The distribution constant of 1,10-phenanthroline, K_D between chloroform and water was determined to be $(1.1\pm0.08)\times10^3$ at 25 °C and I=0.10 mol dm^{-3} (NaNO$_3$) by using the same procedure as was used for dithizone.[9]

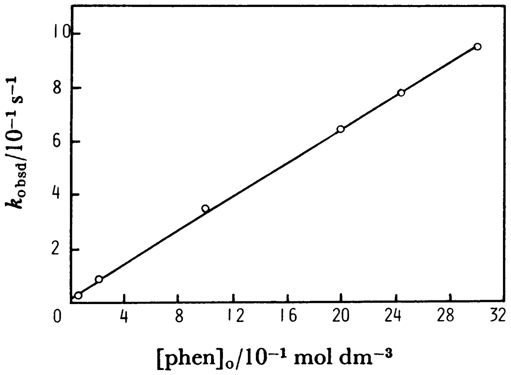

Fig. 1. Relationship between k_{obsd} and 1,10-phenanthroline concentration in the organic phase. [Ni^{2+}]: 1.90×10^{-5} mol dm^{-3}; [Hdz]: 4.80×10^{-4} mol dm^{-3}; pH: 6.0; 25 °C; I: 0.1 mol dm^{-3} (NaNO$_3$).

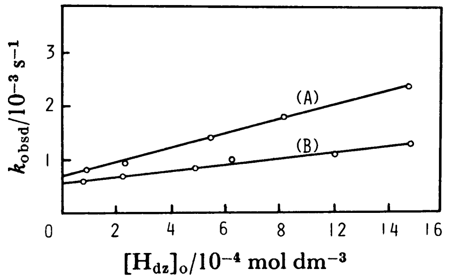

Fig. 2. Relationship between k_{obsd} and dithizone concentration. [phen]: 2.00×10^{-4} mol dm^{-3}; I: 0.1 mol dm^{-3} (NaNO$_3$); (A): pH 6.5; (B): pH 6.0.

The Kinetics of the Extraction of [Ni(dz)$_2$(phen)]. The relationship between log[Ni^{2+}]$_t$ and the extracting time appeared linear. The rate of the extraction of nickel(II) with dithizone in the presence of 1,10-phenanthroline was found to be first-order with respect to the nickel(II) ion. The pseudo first-order rate constant, k_{obsd}, was obtained by plotting log[Ni^{2+}]$_t$ vs. the time, where [Ni^{2+}]$_t$ represents the nickel(II) ion in the aqueous phase at a given time.

As is shown in Fig. 1, a plot of k_{obsd} vs. [phen]$_o$ in the chloroform phase gives a straight line with an intercept. In addition, the value of k_{obsd}, as is shown in Fig. 2, increases linearly with an increase in the dithizone concentration at a given 1,10-phenanthroline concentration. These findings suggest that the rate-determining reactions proceed through two parallel paths in an aqueous phase. One is the reaction between nickel(II) and 1,10-phenanthroline. The other is the reaction of nickel(II) with dithizone.

The rate-determining step for the extraction reaction of nickel(II) with dithizone is the reaction of nickel(II) with dithizonate, dz$^-$, in an aqueous phase. The second-order rate constant, k (rate=k [Ni^{2+}] [dz$^-$]), has been reported to be 6.1×10^3 mol^{-1} dm^3 s^{-1} at 25 °C and I=0.10 mol dm^{-3}.[9]

If they are similar to the extraction of nickel(II) with dithizone, the rate-determining reactions of the synergistic extraction occur in an aqueous phase, and the rate law for the extraction of nickel(II) with dithizone–1,10-phenanthroline system can be expressed by:

$$\frac{-d[\mathrm{Ni}^{2+}]}{dt} = k_{\mathrm{phen}}[\mathrm{Ni}^{2+}][\mathrm{phen}]_w + k_{\mathrm{Hdz}}[\mathrm{Ni}^{2+}][\mathrm{dz}^-]_w. \tag{1}$$

The pseudo first-order rate constant, k_{obsd}, is represented by:

$$k_{\mathrm{obsd}} = k_{\mathrm{phen}}K_D{}^{\mathrm{phen}^{-1}}[\mathrm{phen}]_o + k_{\mathrm{Hdz}}K_a{}^{\mathrm{Hdz}}[\mathrm{Hdz}]_o[\mathrm{H}^+]^{-1} \tag{2}$$

where k_{phen} and k_{Hdz} are the second-order rate constant, and where $K_D{}^{phen}$ $(=1.1\times10^3$ at 25 °C) is the distribution constant of 1,10-phenanthroline between chloroform and water. A 1,10-phenanthroline species distributed into water at pH 6.0 should be predominantly present as a neutral form because of the pK_a of 4.92.[13] The value of k_{Hdz} was determined to be $(6.0\pm0.4)\times10^3$ mol^{-1} dm^3 s^{-1} by using the value of the intercept in Fig. 1 and the following constants: $K_a{}^{Hdz}=4.90\times10^{-5}$ mol dm^{-3}[12] and $K_D{}^{Hdz}=7.94\times10^5$ mol dm^{-3}.[12] The k_{Hdz} value thus obtained is approximately equal to that obtained in the previous work within the limits of experimental error.[9] The k_{phen} value was calculated to be $(3.4\pm0.2)\times10^3$ mol^{-1} dm^3 s^{-1} by using $K_D{}^{phen}=1.1\times10^3$ and the slope of a plot of log k_{obsd} vs. [phen]$_o$ (Fig. 1). The k_{phen} value thus obtained agrees satisfactorily with the second-order rate constant for the formation of [Ni(phen)]$^{2+}$ in an aqueous phase in the absence of dithizone.[14] The k_{Hdz} and k_{phen} values calculated from the intercept and the slope in Fig. 2 were in good agreement with the k_{Hdz} and k_{phen} values respectively obtained from the data shown in Fig. 1. Judging from these results, the first reaction of the synergistic extraction should take place in an aqueous phase. When 1,10-phenanthroline is present in a large excess to dithizone at pH 6.0, the reaction schemes in an aqueous phase are represented as follows:

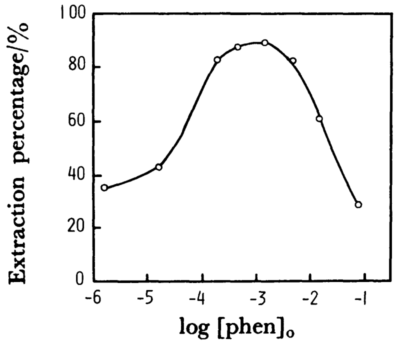

Fig. 3. Relationship between extraction percentage and 1,10-phenanthroline concentration in the presence of dithizone. $[Ni^{2+}]$: 1.90×10^{-5} mol dm^{-3}; [Hdz]: 4.80×10^{-4} mol dm^{-3}; pH 6.0; Shaking time: 30 min; I: 0.1 mol dm^{-3} ($NaNO_3$).

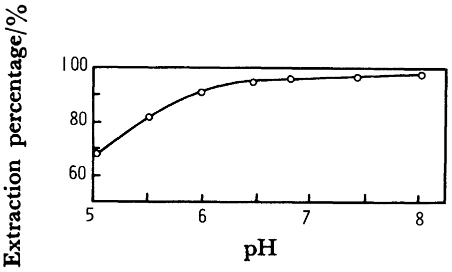

Fig. 4. Relationship between extraction percentage and pH. $[Ni^{2+}]$: 1.90×10^{-5} mol dm^{-3}; [Hdz]: 4.80×10^{-4} mol dm^{-3}; [phen]: 1.60×10^{-3} mol dm^{-3}; 25 °C; Shaking time: 30 min; I: 0.1 mol dm^{-3} ($NaNO_3$).

$$Ni^{2+} + phen \xrightarrow{slow} [Ni(phen)]^{2+} \tag{3}$$

$$[Ni(phen)]^{2+} + dz^- \xrightarrow{fast} [Ni(phen)(dz)]^+ \tag{4}$$

$$[Ni(phen)(dz)]^+ + dz^- \xrightarrow{fast} [Ni(phen)(dz)_2] \tag{5}$$

The reaction of $[Ni(phen)]^{2+}$ with 1,10-phenanthroline should not occur in the presence of dithizone, because $[Ni(phen)_2]^{2+}$ does not react with dithizone. The extraction of nickel(II) with dithizone takes place at a lower pH range in the presence of 1,10-phenanthroline. The acceleration effect of 1,10-phenanthroline was ascribed to the rapid formation of $[Ni(phen)]^{2+}$, based on the small $K_D{}^{phen}$ value compared with the $K_D{}^{Hdz}$ value, and on the lower reactivity of $[Ni(phen)]^{2+}$ toward 1,10-phenanthroline than toward dithizonate. When dithizone is in excess to 1,10-phenanthroline at pH 6.0, the following reactions should be added to Reactions (3)—(5):

$$Ni^{2+} + dz^- \xrightarrow{slow} [Ni(dz)]^+ \tag{6}$$

$$[Ni(dz)]^+ + dz^- \xrightarrow{fast} [Ni(dz)_2] \tag{7}$$

$$[Ni(dz)]^+ + phen \xrightarrow{fast} [Ni(dz)(phen)]^+ \tag{8}$$

$$[Ni(dz)_2] + phen \xrightarrow{fast} [Ni(dz)_2(phen)] \tag{9}$$

At pH 8.0, the predominant reaction path may be Reaction (6) because of the high concentration of the dithizonate distributed into an aqueous phase, even when an excess of 1,10-phenanthroline is present.

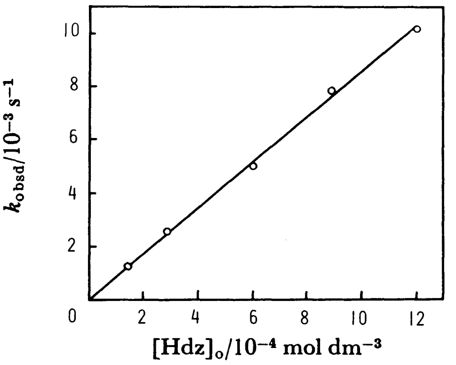

Fig. 5. Relationship between k_{obsd} and dithizone concentration. $[Ni^{2+}]$: 1.90×10^{-5} mol dm^{-3}; [py]: 0.20 mol dm^{-3}; pH: 6.0; 25 °C, I: 0.20 mol dm^{-3} ($NaNO_3$).

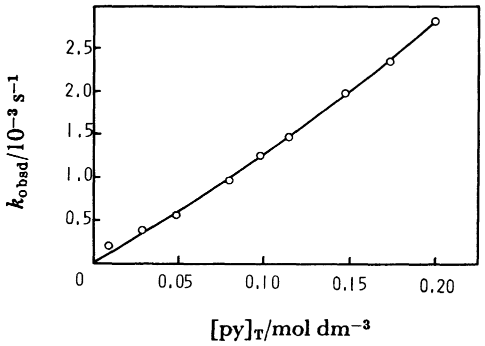

Fig. 6. Relationship between k_{obsd} and pyridine concentration. $[Ni^{2+}]$: 1.90×10^{-5} mol dm^{-3}; [py]: 0.2 mol dm^{-3}; pH: 6.0; 25 °C; I: 0.20 mol dm^{-3} ($NaNO_3$).

Reactions (6)—(8) should take place in an aqueous phase. The formation reaction of $[Ni(dz)_2(phen)]$ may occur in an aqueous phase and/or in an organic phase.

The effect of the 1,10-phenanthroline concentration and of the pH on the extraction of nickel(II) are shown in Figs. 3 and 4 respectively. The extraction percentage increases with an increase in the 1,10-phenanthroline concentration and the pH. In the presence of more than 1×10^{-3} mol dm^{-3} of 1,10-phenanthroline at pH 6.0, the extraction percentage decreases with an increase in the concentration of 1,10-phenanthroline. The small extraction percentage is probably to be ascribed to the formation of $[Ni(phen)_2]^{2+}$.

The Kinetics of the Extraction of $[Ni(dz)_2(py)]$. The relationship between the pseudo first-order rate constant, k_{obsd}, and the concentration of dithizone, as shown in Fig. 5, gives a straight line without an intercept, indicating that the extraction rate is first-order with respect to the concentration of dithizone. Though a plot of k_{obsd} vs. the concentration of pyridine does not give a straight line, the extraction rate increases with an increase in the concentration of pyridine (Fig. 6).

The effect of the pH on the rate for the extraction reaction of nickel(II) with dithizone in the presence of pyridine is represented by Curve (A) of Fig. 7. The dotted line (Curve (B) in Fig. 7) shows the theoretical line calculated by assuming that the rate-determining step of the extraction of nickel(II) with dithizone in the absence of pyridine is the reaction of nickel(II) with dithizonate in an

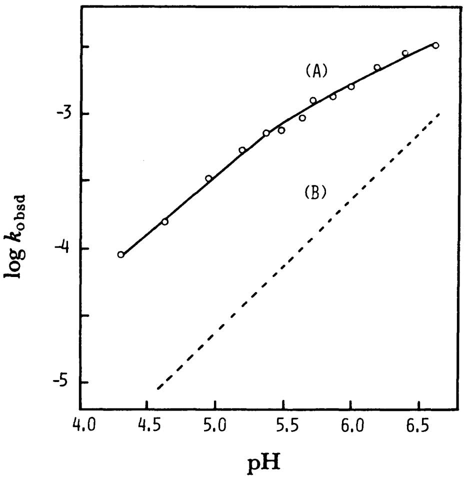

Fig. 7. Relationship between k_{obsd} and pH. [Ni^{2+}]: 1.90×10^{-5} mol dm^{-3}; [Hdz]: 8.90×10^{-4} mol dm^{-3}; [py]: 0.10 mol dm^{-3}; 25 °C; I: 0.20 mol dm^{-3} ($NaNO_3$). (A): Experimental curve; (B): Theoretical curve.

aqueous phase reacts with nickel(II) to form a nickel(II)-pyridine complex, $Ni(py)_n{}^{2+}$, prior to the extraction of nickel(II) with dithizone. The step-by-step stability constants of $Ni(py)_n{}^{2+}$ have been reported to be K_1=8.32×10,15) K_2=7.08,15) K_3=3.98,15) and K_4=1.35.15) The K_5 and K_6 values, which are unavailable, must be very small. If the rate-determining reaction is the reaction of dithizonate with $[Ni(py)_n]^{2+}$ (n=0—4) in an aqueous phase, the rate equation can be represented by Eq. 10:

$$\frac{-d[Ni^{2+}]}{dt} = \{k_0[Ni^{2+}]+k_1[Ni(py)^{2+}]+k_2[Ni(py)_2{}^{2+}] + k_3[Ni(py)_3{}^{2+}]+k_4[Ni(py)_4{}^{2+}]\}[dz^-] \quad (10)$$

where k_0, k_1, k_2, k_3, and k_4 are the second-order rate constants. The pseudo first-order rate constant is represented as follows:

$$k_{obsd} = \{k_0+k_1K_1\beta+k_2K_1K_2\beta^2+k_3K_1K_2K_3\beta^3+k_4K_1K_2K_3K_4\beta^4\} \times \left\{\frac{K_a{}^{Hdz}\cdot[Hdz]_0}{A\cdot[H^+]\cdot K_D{}^{Hdz}}\right\} \quad (11)$$

where $A=1+K_1\beta+K_1K_2\beta^2+K_1K_2K_3\beta^3+K_1K_2K_3K_4\beta^4$, $\beta=[py]_T\{1+K_D{}^{py}+[H^+]/K_a{}^{py}\}^{-1}$. The values of $K_a{}^{Hdz}/A[H^+]$, $K_1\beta K_a{}^{Hdz}/A\cdot[H^+]$, $K_1K_2\beta^2K_a{}^{Hdz}/A\cdot[H^+]$, $K_1K_2K_3\beta^3K_a{}^{Hdz}/A\cdot[H^+]$, and $K_1K_2K_3K_4\beta^4K_a{}^{Hdz}/A\cdot[H^+]$ were calculated by introducing the following constants: $K_D{}^{py}$=0.80,16) $K_a{}^{py}$=5.89×10^{-6},17) $K_a{}^{Hdz}$=4.90×10^{-5},12) and $K_D{}^{Hdz}$=7.94×10^5,12) Equation 11 shows that a plot of k_{obsd} vs. $[Hdz]_0$ should provide a straight line and that the rate is not first-order with respect to pyridine and the hydrogen-ion concentration. As is shown in Figs. 6 and 7, the results satisfy the above conditions. The value of k_1 which best fitted the log k_{obsd}-pH curve was found to be (1.7±0.3)×10^5 mol^{-1} dm^3 s^{-1} at 25 °C. The value of k_0 was independently determined to be (3.0±0.2)×10^3 mol^{-1} dm^3 s^{-1} at 0.1 mol dm^{-3} potassium dihydrogenphosphate. The value of k_2 is estimated to be (1±0.8)×10^4 mol^{-1} dm^3 s^{-1}. It is safe to conclude that the values of k_3 and k_4 are negligibly smaller than the k_2 value. Also, the paths of the reactions of $[Ni(py)_5]^{2+}$ and $[Ni(py)_6]^{2+}$ with dz^- should be omitted. On the base of these results, the reaction scheme for the synergistic extraction of nickel(II) with dithizone-pyridine can be represented by:

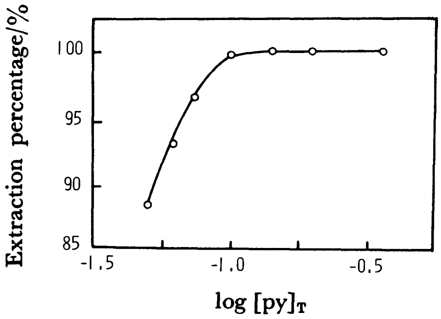

Fig. 8. Relationship between extraction percentage and pyridine concentration. [Ni^{2+}]: 1.90×10^{-5} mol dm^{-3}; [Hdz]: 4.80×10^{-4} mol dm^{-3}; pH 6.9; Shaking time: 30 min.

$$Ni^{2+} + py \xrightarrow{\text{fast}} [Ni(py)]^{2+} \quad (12)$$

$$[Ni(py)]^{2+} + dz^- \xrightarrow{\text{slow}} [Ni(dz)(py)]^+ \quad (13)$$

$$[Ni(dz)(py)]^+ + dz^- \xrightarrow{\text{fast}} [Ni(dz)_2(py)] \quad (14)$$

As the reactivity of $[Ni(py)]^{2+}$ toward dz^- was found to be about 60 times larger than that of aqua Ni^{2+} toward dz^-, the acceleration effect of pyridine on the extraction of nickel(II) with dithizone was ascribed to the formation of $[Ni(py)_n]^{2+}$.3) It was suggested that the rate-determining step for the extraction of nickel(II) with thenoyltrifluoroacetone (tta) in the presence of pyridine was the reaction of tta with aqua Ni^{2+} and $[Ni(py)]^{2+}$ in the pH range from 1.5 to 3.9.18) These facts further support the mechanism proposed for the extraction of nickel(II) with dithizone-pyridine.

Figure 8 represents the effect of the pyridine concentration on the extraction percentage of nickel(II) with dithizone into chloroform. In the presence of more than 0.1 mol dm^{-3} of pyridine, the complete extraction of nickel(II) was achieved with 4.8×10^{-4} mol dm^{-3} of dithizone at pH 6.9. Pyridine does not mask the extraction of nickel(II) with dithizone, even when pyridine is present in a large excess to dithizone.

As has been shown above, the rate-determining steps for the nickel(II)-dithizone-1,10-phenanthroline and nickel(II)-dithizone-pyridine systems are different from each other. This difference should result in a difference in the distribution constant between pyridine and 1,10-phenanthroline. The coordination of pyridine or 1,10-phenanthroline to the aqua nickel(II) ion probably facilitates the removal of water molecules from the central nickel(II) ion, hence accelerating the extraction rate of nickel(II) with dithizone in the presence of 1,10-phenanthroline or pyridine.

1,10-Phenanthroline behaves as a masking reagent for the extraction of zinc(II) with dithizone.11) On the other hand, nickel(II),1) cobalt(II),19) and manganese(II)20) are extracted as an adduct, $[M(dz)_2(phen)]$, with dithizone in the presence of 1,10-phenanthroline. The phenomenon that zinc(II) does not form an adduct can not be reasonably explained by considering the difference in the softness of these metal ions as a Lewis acid. Manganese(II), cadmium(II), and zinc(II) are classified as hard, soft, and middle-class acids respectively.[21,22] Furthermore, there seems to be no relationship between the capability of the adduct formation of metal ions and the stability constants of the metal complex of dithizone and 1,10-phenanthroline. A systematical study of the kinetics of a synergistic extraction of metal ions would perhaps give more valuable guidelines for the development of a new synergistic extraction system.

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