EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) WITH DITHIZONE AND METHYLTRIOCTYLAMMONIUM CHLORIDE

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The mechanism of the synergistic extraction of nickel(II) with a mixture of dithizone(H_2dz) and methyltrioctylammonium chloride($MTOA=R_3R'N\cdot Cl$) was studied. The extraction of nickel(II) in the presence of thiocyanate was clarified to proceed according to the following equations: $Ni(NCS)_2 + R_3R'N\cdot NCS_{org} \rightleftharpoons R_3R'N\cdot Ni(NCS)_3'_{org}$ and $R_3R'N\cdot Ni(NCS)_3'_{org} + H_2dz_{org} \rightleftharpoons R_3R'N\cdot Ni(dz)(NCS)_{org} + 2H^+ + 2NCS^-$, where the subscript org denotes the organic phase. The above reactions have two important features. One is the acceleration of the extraction reaction, and the other is the formation of the reddish colored secondary complex having the absorption maximum at 503 nm. The present system was applied to the spectrophotometric determination of nickel(II).

1. Introduction

It is well known that nickel(II) in weakly acidic solution can be extracted into chloroform with dithizone(H_2dz). However, the extraction system has been scarcely used for analytical purposes, because of the small extraction rate and the complicated absorption spectrum of the resulting brownish colored complex, $Ni(Hdz)_2$. In order to improve the above defects, synergism due to the addition of pyridine or 1,10-phenanthroline was successfully employed¹⁻³). On the other hand, the reddish colored complex, $Ni(dz)$ is extracted from strongly alkaline solution, although its analytical application has not been reported so far. Generally speaking, analytical-chemical use of the secondary dithizonate has been ignored for a long time.

In the work described below, methyltrioctylammonium chloride($MTOA=R_3R'N\cdot Cl$) is shown to be effective for the formation of $Ni(dz)$ and acceleration of the extraction, and as a result, a method for the spectrophotometric determination of nickel(II) with a mixture of dithizone and MTOA is established.

2. Experimental

Reagents:

Standard solution of nickel(II): A stock solution(Ni^{2+} : $500\ \mu g\ cm^{-3}$) was prepared by dissolving a weighed amount of nickel(II) sulfate, $NiSO_4\cdot 7H_2O$ in demineralized water and diluted to the desired concentration.

Dithizone solution: 2.5 g of dithizone was dissolved in $500\ cm^3$ of chloroform and the resulting stock solution was stored in a refrigerator. The purity of dithizone was

confirmed by measuring its molar absorptivity at 608 nm.

MTOA solution: 25 g of Capriquat(=MTOA) was dissolved in 250 cm³ of chloroform.

All reagents obtained from Wako-Pure Chemicals were of guaranteed grade.

Apparatus:

The absorbance of the organic phase was measured with a Hitachi 200-10 type spectrophotometer using 1.00 cm glass cells. The pH measurements were carried out with a Hitachi-Horiba F-7ss type pH meter, and the extraction experiments were conducted by using an Iwaki KM type shaker. Nickel(II) in the aqueous phase was determined with a Hitachi 170-30 type atomic absorption photometer.

Extraction Procedure:

Each 20.0 cm³ of the aqueous solution containing nickel(II), potassium thiocyanate, sodium acetate and acetic acid, and the chloroform solution containing dithizone and MTOA was placed together in a 100 cm³ separatory funnel and shaken vigorously for a definite time. After the phases were allowed to separate, the absorption spectrum of the organic phase and the pH of the aqueous phase were measured. Nickel(II) remaining in the aqueous phase was also determined. All experiments were made at room temperature(ca. 293K).

3. Results and Discussion

The absorption spectrum of the organic phase obtained by using dithizone alone completely agreed with that of the reagent blank, indicating no extraction of nickel(II) under the conditions given in Fig. 1. On the other hand, the addition of MTOA and thiocyanate to the system caused the extraction of the reddish colored dithizonatonicel(II) having an absorption maximum at 503 nm. From the above observation, we recognized that MTOA has an accelerating effect on the extraction of nickel(II) and promotes the formation of the secondary dithizonatonicel(II). The former effect of MTOA has already been shown in the extraction of tris(2-thenoyl-trifluoroacetato)iron(III)⁴⁾, and the latter in the dithizonatopalladium(II) system⁵⁾.

3.1 The extraction of thiocyanatonicel(II) with MTOA

The formation of R₃R'N·Hdz is prevented by the addition of potassium thiocyanate to the system, in which MTOA can be considered to exist as the thiocyanate form, R₃R'N·NCS. At first, the extraction of thiocyanatonicel(II) is assumed to proceed according to the following reaction:

Fig. 1 Absorption spectra of CHCl₃ phase
pH: 5.20, H₂dz: 0.001%, shaking
time: 5 min, KNCS: 5.0%,
reference: CHCl₃
1 - Reagent blank (MTOA: 5.0%,
Ni(II): none)
2 - MTOA: none, Ni(II): 20.0 μg
3 - MTOA: 5.0%, Ni(II): 20.0 μg

where the subscript org denotes the organic phase. The relative concentration of $\text{Ni}(\text{NCS})_2$ in the aqueous phase was calculated by using the equation, $[\text{Ni}(\text{NCS})_2]/[\text{Ni}]_{\text{aq}} = \beta_2 [\text{NCS}^-]^2 / \sum_{x=0}^{\infty} \beta_x [\text{NCS}^-]^x$, where β_x is the formation constant for $\text{Ni}(\text{NCS})_x^{2-x}$ and $\beta_0 = 1$.

The distribution ratio can be written as

$$D^\circ = \frac{[\text{R}_3\text{R}'\text{N}\cdot\text{Ni}(\text{NCS})_3]_{\text{org}}}{[\text{Ni}]_{\text{aq}}} = \frac{K^* [\text{Ni}(\text{NCS})_2] [\text{R}_3\text{R}'\text{N}\cdot\text{NCS}]_{\text{org}}}{[\text{Ni}]_{\text{aq}}} \quad (2)$$

where K^* represents an equilibrium constant for the reaction (1). Taking logarithm, equation (3) can be obtained:

$$\log D^\circ = \log K^* + \log \frac{[\text{Ni}(\text{NCS})_2]}{[\text{Ni}]_{\text{aq}}} + \log [\text{R}_3\text{R}'\text{N}\cdot\text{NCS}]_{\text{org}} \quad (3)$$

The above equation indicates that a logarithmic plot of D° against $[\text{Ni}(\text{NCS})_2]/[\text{Ni}]_{\text{aq}}$ should give a straight line having a slope of unity at a definite concentration of MTOA. The term of $[\text{Ni}(\text{NCS})_2]/[\text{Ni}]_{\text{aq}}$ was calculated by adopting the literature value of $\beta_x^{(6)}$, and the result is given in Fig. 2. The above assumption turns out to be reasonable from Fig. 2 and some deviations at high concentration region of thiocyanate is probably due to the reaction; $\text{Ni}(\text{NCS})_3^- + \text{R}_3\text{R}'\text{N}\cdot\text{NCS}_{\text{org}} \rightleftharpoons \text{R}_3\text{R}'\text{N}\cdot\text{Ni}(\text{NCS})_3_{\text{org}} + \text{NCS}^-$. According to equation (3), a logarithmic plot of D° against the MTOA concentration should give a straight line having a slope of unity, keeping the thiocyanate concentration constant. This is also verified experimentally, as is shown in Fig. 3.

Fig. 2 Logarithmic plot
 H_2dz : none, MTOA: 5.0%
 pH: 4.75, $\text{Ni}(\text{II})$: 5.0 μg

Fig. 3 Logarithmic plot
 H_2dz : none, KNCS: 5.0%, pH: 4.75
 $\text{Ni}(\text{II})$: 5.0 μg

From the foregoing discussion, the extracted species in the absence of dithizone is concluded to be $\text{R}_3\text{R}'\text{N}\cdot(\text{NCS})_3$.

3.2 Extraction scheme of nickel(II) with dithizone and MTOA

The composition of the extracted species in the present system was examined by

Fig. 4 Molar ratio method
 $H_2dz: 3.9 \times 10^{-5} \text{ mol dm}^{-3}$
 MTOA: 5.0%, pH: 4.75, KNCS: 5.0%

the molar ratio method and the results are shown in Fig. 4. Turning point in the absorbance is seen at the molar ratio of nickel(II) to dithizone 1:1, indicating that $Ni(dz)$ may be involved in the composition of the extracted complex. Moreover, a logarithmic plot of the distribution ratio of nickel(II) against the MTOA concentration gives a straight line having a slope of unity (Fig. 5). Therefore, $R_3R'N \cdot Ni(dz)(NCS)$ is reasonably assumed to be extracted, and reaction in the organic phase may proceed as follows:

The distribution ratio of nickel(II) obtained with a mixture of dithizone

and MTOA is written as

$$D = \frac{[R_3R'N \cdot Ni(NCS)_3]_{org} + [R_3R'N \cdot Ni(dz)(NCS)]_{org}}{[Ni]_{aq}} \quad (5)$$

Combining equations (2) and (5), the following equation can be obtained:

$$\log\left(\frac{D}{D^0} - 1\right) = \log K^0 [H_2dz]_{org} + 2pH - 2\log[NCS^-] \quad (6)$$

Fig. 5 Logarithmic plot
 $H_2dz: 0.001\%$, KNCS: 5.0%
 pH: 4.75, $Ni(II): 5.0 \mu g$

where K^0 is an equilibrium constant for the reaction (4). Keeping the terms $[H_2dz]_{org}$ and pH constant, a plot of the value of the left-hand side against $\log[NCS^-]$ gives a straight line having a slope of -2 (Fig. 6), which agrees with that expected from equation (6). Additionally, the pH dependence of $\log(D/D^0 - 1)$ obtained experimentally can be also explained by equation (6), as is shown in Fig. 7. The above facts support the extraction mechanism expressed by equation (4), and it can be concluded that the rate promoting effect of MTOA on the extraction of dithizonatonickel(II) is attributable to the formation of $R_3R'N \cdot Ni(NCS)_3$. However, the reason for the preferential formation of the secondary dithizonatonickel(II) is not clear at the present time.

3.3 Analytico-chemical application

Fig. 6 Logarithmic plot
 H_2dz : 0.001%, MTOA: 5.0%
 pH: 4.75, Ni(II): 5.0 μg

Fig. 7 $\log (D/D^\circ - 1)$ vs. pH
 H_2dz : 0.001%, MTOA: 5.0%
 KNCS: 5.0%, Ni(II): 5.0 μg

Fig. 8 Effects of pH(1) and MTOA concentration(2) on the absorbance
 H_2dz : 0.001%, Ni(II): 5.0 μg
 KNCS: 5.0%
 1 - Absorbance vs. pH, MTOA: 5.0%
 Reference: CHCl_3
 2 - Absorbance vs. [MTOA], pH: 5.2
 Reference: Reagent blank

Since difficulties in the extraction of $\text{Ni}(\text{Hdz})_2$ could be improved by the addition of MTOA, application of $\text{R}_3\text{R}'\text{N}\cdot\text{Ni}(\text{dz})(\text{NCS})$ to practical analysis was examined. The absorption spectrum of the reddish colored mixed complex has an absorption maximum at around 503 nm and stable for at least 1 h. Effect of the pH and the MTOA concentration on the absorbance are given in Fig. 8, and the optimal pH and the reagent concentration were adopted to be 5.2 and 5.0% respectively.

3.3.1 Recommended procedure

A sample solution containing less than 6 μg of nickel(II) is taken in a separatory funnel. After the addition of 5 cm^3 of 10% potassium thiocyanate, the pH of the aqueous phase is adjusted to 5.2 by adding 2 cm^3 of 1.0 mol dm^{-3} acetate buffer solution, and then 10.0 cm^3 of chloroform solution containing 0.001% dithizone and 5% MTOA is placed. The mixture is shaken for 5 min. After the phases are allowed to separate, the

absorbance of the organic phase is measured at 503 nm against chloroform.

3.3.2 Calibration curve

The calibration curve prepared according to the above procedure was linear up to 6.0 μg of nickel(II). The molar absorptivity was estimated to be $24000 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$, the Sandell sensitivity being $0.0020 \text{ } \mu\text{g cm}^{-2}$. The sensitivity of this method is higher than those of the dimethylglyoxime methods⁷⁾. Relative standard deviation of the absorbance measurement for 5.0 μg of nickel(II) was 1.0% (n=10).

3.3.3 Effect of diverse ions

The results are summarized in Table 1. The tolerance limit was set at the amount required to cause $\pm 1.0\%$ error in the nickel(II) recovery. Each 10 μg of copper(II), silver(I), mercury(II) and cadmium(II) interfered seriously with the determination. However, preliminary extraction with 10 cm^3 of 0.01% dithizone at pH 5.2 was found to be quite effective in eliminating the interferences, and each 100 μg of those ions was tolerable.

Table 1. Effect of diverse ions

Tolerance limit/ μg	Diverse ions (Ni(II)= 5.0 μg)
10	Co(II), Fe(II), Pd(II)
50	Sb(III), Sn(II)
100	Mn(II), V(IV), Cu(II)* Cd(II)*, Hg(II)*, Ag(I)*
200	Pb(II)*
500	Zn(II), W(VI)
1,000	Oxal ²⁻ , Cit ³⁻
20,000	F ⁻ , Cl ⁻ , Br ⁻ , S ₂ O ₃ ²⁻ , Tart ²⁻

* Preliminary extraction technique was applied.

4. Conclusion

The co-operative effect of dithizone and MTOA on the extraction of nickel(II) was summarized as follows; (1) acceleration of the extraction and (2) the promotion of the secondary complex formation. By using the above effect, analytical application of the system could be developed.

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