October, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2829—2831 (1975) 2829

Reaction of Nickel Ion Fixed on the Ion Exchange Resin with 2-Thenoyltrifluoroacetone

Kunio Ohzeki, Tooru Tamura, and Tomihito Kambara
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received June 7, 1975)

The reaction of nickel ions fixed on the ion exchange resin with 2-thenoyltrifluoroacetone was investigated in various organic solvents. In the presence of pyridine, nickel ions were quantitatively extracted from the resin into the organic phase in the form of the adducts of nickel(II) chelate with pyridine. The synergistic effect of a series of pyridine bases on the removal of the metal ions from the resin decreased in the order : pyridine> γ-picoline> β-picoline> α-picoline.

Several studies on the conversion of a metal ion fixed on the ion exchange resin to a chelate compound based on the ion exchange reaction in organic medium have been investigated in our laboratory. The authors have reported the quantitative removal of iron(III)[1] and copper(II)[2] ions fixed on Amberlyst 15 by acetylacetone with the aid of a small amount of pyridine–water mixture. In this work, the reaction of the nickel ions fixed on Amberlyst 15 with 2-thenoyltrifluoroacetone(Htta) was investigated in benzene, carbon tetrachloride, chloroform, and ethyl alcohol, and the effects of pyridine bases on the quantitative removal of the nickel ions were discussed.

Experimental

Apparatus and Reagents. Absorption measurements were carried out by the aid of a Shimadzu Spectronic 88 spectrophotometer and a Hitachi 356 two-wavelength double-beam spectrophotometer with 10 mm cells. A Hitachi 508 atomic absorption spectrophotometer was used for the nickel absorption measurement at 231.4 nm in air-acetylene flame. 2-thenoyltrifluoroacetone and β-picoline were obtained from Wako Chemical Inc. and used without further purification. Pyridine, α-picoline, γ-picoline, and all other materials used were of guaranteed grade.

Preparation of Nickel(II)-Form Resin. The resin used was sulfonic acid cation exchanger, Amberlyst 15, with a macroreticular structure. The commercially available Amberlyst 15 was crushed and shieved to a fraction of 60—80 mesh. The resin was converted to Ni(II)-form by treatment with 0.1 mol dm^{-3} solution of nickel nitrate. The resulting Ni(II)-form resin was washed with water until the washings showed no color reaction with dimethylglyoxime and dried over silica gel. The ratio of exchange capacity of nickel ion to proton was 0.996, and that the nickel ions are expected to be adsorbed on the resin in the form of Ni^{2+}. When the air dried Ni(II)-form was dried at 110 °C for 3 hours, the weight loss was found to be about 24%. The infrared spectrum of the resin showed the existence of a small amount of water. The water on the oven dried resin was determined by the method described in the previous paper[2] and it is supposed that two water molecules are coordinated to a nickel(II) ion on the resin, such as $(RSO_3)_2Ni \cdot 2H_2O$. In the following experiments, the air dried resin was used without oven drying.

Determination of Nickel Ions on the Ni(II)-Form Resin. The nickel ions on the air dried Ni(II)-form resin were eluted by 4 mol dm^{-3} hydrochloric acid solution and determined by EDTA titration. It was found that 2.95±0.02 meq of nickel ions were adsorbed onto 1.00 g of the air dried Ni(II)-form resin.

Reaction of Ni(II)-Form Resin. A portion of 5 ml of 0.1 mol dm^{-3} Htta in organic medium was poured onto the 25 mg of air dried Ni(II)-form resin in a test tube and varying amounts of pyridine and/or pyridine–water mixture were added. The mixture was shaken mechanically for 10 min at room temperature (around 19 °C) and for equilibrium study, it was allowed to stand for 24 hours with occasional shakings. After filtration, the resin was washed with ethyl alcohol and water. The nickel ions remaining on the resin were eluted by 4 mol dm^{-3} hydrochloric acid solution and determined by atomic absorption spectrophotometry.

Results and Discussion

Effect of Pyridine. Any portion of the nickel ions fixed on the resin could not be removed by Htta alone into organic medium. But the addition of a small amount of pyridine or pyridine–water mixture was highly effective, as Fig. 1 shows. Upon addition of pyridine to Htta solution in contact with the Ni(II)-form resin, green color was developed in the organic phase, indicating the formation of $Ni(tta)_2py_2$. More than 99% of nickel ions can be removed from the resin by the addition of the 30 : 1 to 100 : 1 pyridine–water mixture, where Htta dissolved in chloroform in 4—14% (v/v) is employed. The resin floated up to the surface of the solvent as the reaction proceeded.

Effect of Solvents. Figure 2 shows the effect of the solvents on the removal of nickel ions from the resin. More than 99% of the nickel ions are extracted into benzene and carbon tetrachloride by the

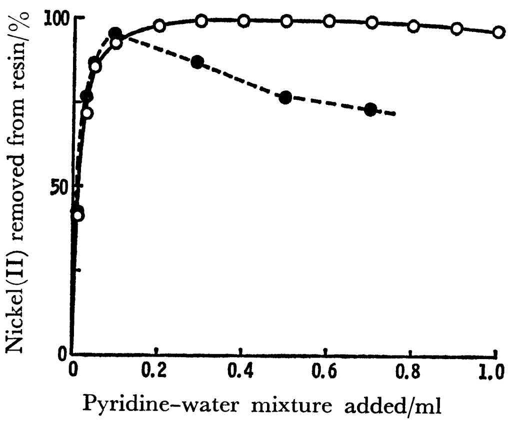
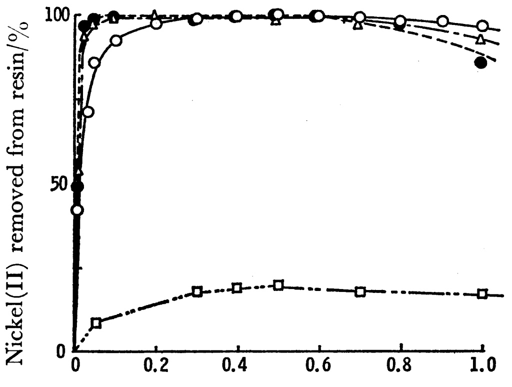


Fig. 1. Effect of the addition of pyridine (●), and pyridine-water (50 : 1) mixture (○) on the removal of nickel ions from the resin with 5 ml of 0.1 mol dm^{-3} Htta solution in chloroform.



Pyridine-water (50 : 1) mixture added/ml

Fig. 2. Removal of nickel ions from the resin with 5 ml of 0.1 mol dm^{-3} Htta solution in various solvents. Ethyl alcohol (□), chloroform (○), benzene (△) and carbon tetrachloride (●).

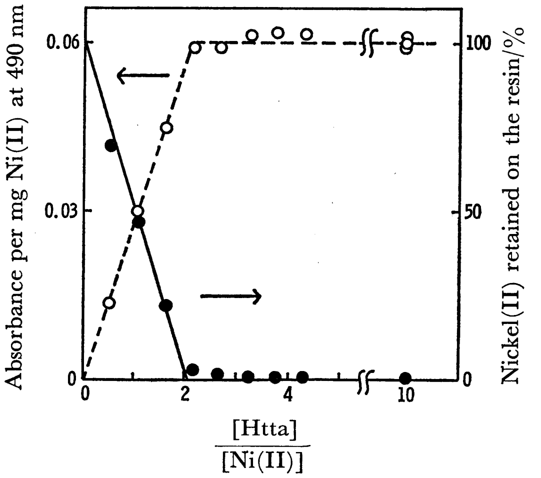


Fig. 3. Effect of Htta concentration in chloroform containing 1.14 mol dm^{-3} pyridine-water (50 : 1) mixture. The absorbance measurement of the organic extract (○), and nickel retained on the resin (●).

addition of pyridine as well as pyridine–water mixture. The poor extraction of nickel ions in ethyl alcohol is due to a probable interaction of the solvent and Htta.

Ion Exchange Extraction Constant. The composition of the complex in chloroform medium was determined by the mole ratio method. The nickel ions remaining on the resin were eluted by 4 mol dm^{-3} hydrochloric acid solution and determined by atomic absorption spectrophotometry and the absorbance of the solution was measured at 490 nm against chloroform. Consequently the composition of the Ni(II)–Htta complex was estimated to be Ni(II) : Htta=1 : 2 as shown by Fig. 3. It is reported that Ni(II)–Htta complex adds two moles of pyridine at high concentration of pyridine[3] and it is reosonable to expect that pyridinium ion is adsorbed on the resin instead of nickel ion[1]. Consequently the following ion exchange extraction equilibrium is proposed.

$$(\mathrm{RSO_3})_2\mathrm{Ni} + 2\,\mathrm{Htta} + 4\,\mathrm{py} \rightleftharpoons 2\,\mathrm{RSO_3Hpy} + \mathrm{Ni(tta)_2py_2} \tag{1}$$

where R denotes the resin matrix.

Now we can define the ion exchange extraction constant $K^{\mathrm{r}}_{\mathrm{ex}}$ as

$$K^{\mathrm{r}}_{\mathrm{ex}} = \frac{[\mathrm{Ni(tta)_2py_2}]_{\mathrm{o}}[\mathrm{pyH^+}]^2_{\mathrm{r}}}{[\mathrm{Ni^{2+}}]_{\mathrm{r}}[\mathrm{Htta}]^2_{\mathrm{o}}[\mathrm{py}]^4_{\mathrm{o}}} \tag{2}$$

where the subscripts r and o denote the chemical species on the resin and in the organic phase, respectively. In this case, the distribution ratio of nickel is shown by

$$D = \frac{[\mathrm{Ni(tta)_2py_2}]_{\mathrm{o}}}{[\mathrm{Ni^{2+}}]_{\mathrm{r}}} \tag{3}$$

Introducing the ion exchange extraction constant shown by the Eq. (2) into the Eq. (3), one obtains.

$$\log D[\mathrm{py}]^{-4}_{\mathrm{o}} = \log K^{\mathrm{r}}_{\mathrm{ex}} + 2\log[\mathrm{Htta}]_{\mathrm{o}}[\mathrm{pyH^+}]^{-1}_{\mathrm{r}} \tag{4}$$

Consequently a plot of $\log D[\mathrm{py}]_{\mathrm{o}}^{-4}$ against $\log [\mathrm{Htta}]_{\mathrm{o}}[\mathrm{pyH^+}]_{\mathrm{r}}^{-1}$ should give a straight line of slope 2. The result is given in Fig. 4. The values of $\log K^{\mathrm{r}}_{\mathrm{ex}}$ obtained are 1.96 in chloroform, 4.81 in benzene, and 4.91 in carbon tetrachloride. In all calculations, the concentration of the species on the resin is expressed as mole per gram of Ni(II)-form resin.

Effect of Pyridine Bases. The relationship between the percentage of nickel ions removed from the resin and the shaking time was examined with various pyridine bases. It is found that picolines are less effective than pyridine and it takes several hours to remove more than 99% of nickel ions from the resin as Fig. 5 shows. The synergistic effect of the pyridine bases on the removal of the nickel ions from the resin decreased in the order of pyridine>γ-picoline>β-picoline>α-picoline. On the other hand, it is reported that the synergistic effect decreases in the order of γ-picoline>β-picoline>pyridine>α-picoline in the solvent extraction of nickel ions with Htta.[3] The disagreement of the results between ion exchange

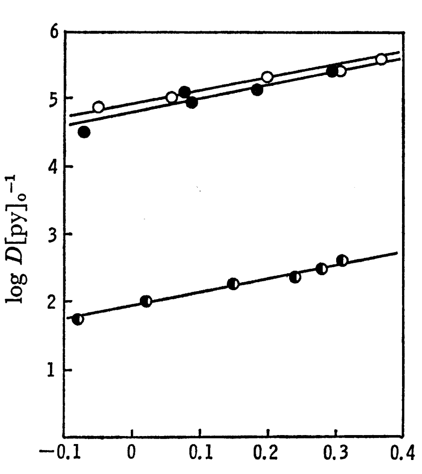


Fig. 4. Effect of ligand concentration on distribution ratio of nickel in the presence of pyridine.
Solution of Htta in carbon tetrachloride (○), benzene (●), and chloroform (◐).

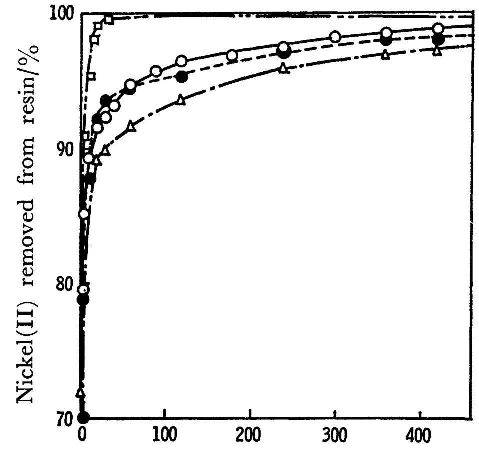


Fig. 5. Synergistic effect of the pyridine bases on the removal of nickel ions from the resin with 0.1 mol dm^{-3} Htta solution in benzene, containing 0.245 mol dm^{-3} of pyridine (□), γ-picoline (○), β-picoline (●), and α-picoline (△).

extraction and solvent extraction may be caused by the steric influence of the resin matrix with methyl group of the picolines.

Comparison of Chelating Reagents. The removal of nickel ions from the resin into benzene with benzoylacetone(Hba) was investigated in the presence of pyridine as the function of the shaking time as Fig. 6 shows. It is found that the reaction rate is much slower in the case of Hba than Htta. This may be due to the difference in the acidity of the chelating reagents, Hba (pK_a=9.8), Htta (pK_a=5.7).

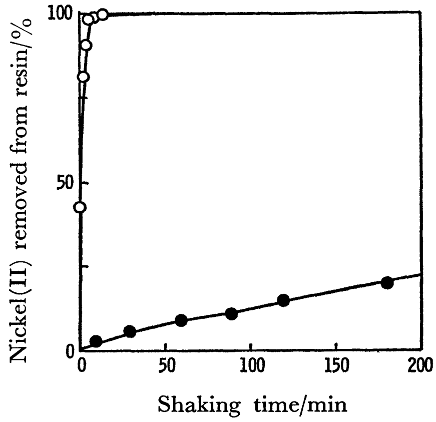


Fig. 6. Comparison of reaction rates.
Htta (○) and Hba (●) in benzene in the presence of pyridine.

References

1) K. Ohzeki, M. Ikeuchi and T. Kambara, This Bulletin, **48**, 67 (1975).

2) T. Okamura, K. Ohzeki and T. Kambara, *ibid.*, **48**, 469 (1975).

3) H. Kawamoto and H. Akaiwa, *J. Inorg. Nucl. Chem.*, **31**, 1141 (1969).