BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (8), 2108—2110 (1976)

The Synergistic Extraction of Cobalt Ion Fixed on the Ion Exchange Resin with a Mixture of 2-Thenoyltrifluoroacetone and Pyridine Bases

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(Received March 25, 1976)

The extraction of cobalt(II) on the ion exchange resin into a mixture of 2-thenoyltrifluoroacetone(Htta) with pyridine bases in various organic solvents has been studied. In the presence of pyridine bases(B), cobalt ions were extracted from the resin into the organic phase in the form of base adducts, $Co(tta)_2B_n$. The synergistic effect decreased in the order: pyridine > β-picoline > γ-picoline > α-picoline > γ-collidine ≃ isoquinoline ≃ piperidine > 4-benzoylpyridine. This trend was related to its structure, particularly the steric effect of the *ortho*-substituent.

The synergistic effects of neutral ligands have been widely studied in the extraction of a metal ion with β-diketone.[1,2] The effect is well explained by the formation of the base adduct. Akaiwa *et al.* reported that nickel(II) and cobalt(II) ions were extracted synergistically by a mixture of 2-thenoyltrifluoroacetone(Htta) and pyridine base and that the extractability of their metal ions was dependent on the basicity of pyridine bases and the steric effect of their *ortho*-substituent.[3-5]

On the other hand, 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 has been studied.[6] The authors have reported that iron(III),[7] copper(II),[8] and nickel(II)[9] ions on Amberlyst 15 were quantitatively extracted with acetylacetone or Htta into organic medium by the aid of a small amount of pyridine–water mixture. The present paper deals with the synergistic extraction of cobalt ions fixed on Amberlyst 15 with Htta in the presence of pyridine bases.

Experimental

Apparatus and Reagents. A Hitachi 508 atomic absorption spectrophotometer was used for the cobalt absorption measurement at 240.1 nm in air-acetylene flame. Thenoyltrifluoroacetone, β-picoline, and trimetyl phosphate were obtained from Wako Pure Chemical Inc. (Tokyo) and used without further purification. Pyridine, α-picoline, γ-picoline, γ-collidine, isoquinoline, piperidine, 4-benzoylpyridine, tributyl phosphate and all other materials used were of guaranteed grade.

Preparation of Cobalt(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 Co(II)-form by treatment with a 0.1 M solution of cobalt nitrate and washed with water until the washings showed no color reaction with 1-nitroso-2-naphtol and dried over silica gel. The cobalt ions on the air-dried Co(II)-form resin were eluted by 4 M hydrochloric acid and determined by EDTA titration. It was found that 3.19±0.02 meq of cobalt ions were adsorbed onto 1.00 g of the air-dried Co(II)-form resin. The ratio of exchange capacity of cobalt ion to proton was 0.965 and so the cobalt ions were expected to be adsorbed on the resin in the form of Co^{2+}.

General Procedure. A portion of 5 cm^3 of 0.1 M Htta in organic medium was poured onto the 25 mg of air-dried Co(II)-form resin in a eggplant flask and varying amounts of pyridine were added. The mixture was shaken mechanically for 10 min at room temperature. After filtration, the resin was washed with ethanol and water. The cobalt ions remaining on the resin were eluted by 4 M hydrochloric acid and determined by atomic absorption spectrophotometry in air-acetylene flame.

Results and Discussion

Effect of Pyridine and Solvents. It was found that Htta or pyridine could not remove the cobalt ions fixed on the resin into organic medium, however, the mixture of them was highly effective, as Fig. 1 shows. Upon addition of pyridine, the red color was immediately developed in the organic phase, indicating the formation of a base adduct, $Co(tta)_2py_n$. Cobalt ions were quantitatively extracted into Htta-carbon tetrachloride and Htta-benzene solutions in the presence of pyridine of 4—14% and 4—6% (v/v), respectively. But in the case of Htta–chloroform solution, the extractability was less than 98%. The poor extraction of cobalt ions in ethanol is due to a probable interaction between the solvent and Htta. After all, the effect of the solvent natures on the extraction of cobalt ions from the resin decreased in the order: carbon tetrachloride > benzene > chloroform > ethanol. Except ethanol, this order agreed with that found in the solvent extraction study of cobalt–Htta–pyridine system by Akaiwa *et al.*[5]

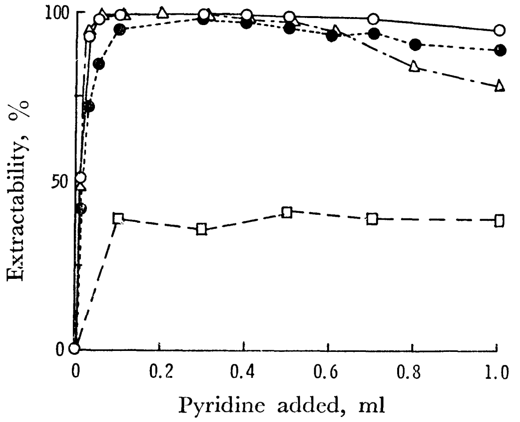

Fig. 1. Extractability of cobalt ions from the resin with 0.1 M Htta solutions in various solvents. Ethanol (□), chloroform (●), benzene (△), and carbon tetrachloride (○).

Composition of the Extracted Species. The composition of the extracted species in benzene was determined by the mole ratio method in the presence of pyridine and found to be Co(II) : Htta = 1 : 2. The determination of the composition of a pyridine adduct was unsuccessful, because a considerable amount of pyridine might be adsorbed on the resin matrix.

Effect of Pyridine Bases. In place of pyridine, other neutral ligands were used as synergist. The extractability of cobalt ions from the resin with 0.1 M Htta and 0.245 M neutral ligands in benzene is given in Fig. 2, as a function of the shaking time. Pyridine was most effective and picolines except α-picoline followed it. The effect of α-picoline was inferior to that of other picolines. Pyridine bases such as γ-collidine, isoquinoline, piperidine, and 4-benzoylpyridine were less effective. In the case of trimethyl phosphate and tri-*n*-butyl phosphate, the extractability of cobalt ions was only about 10% after the 60-min shaking. Consequently, it is concluded that 2-substituted pyridine bases such as α-picoline and γ-collidine and those having a bulky structure such as isoquinoline and 4-benzoylpyridine were not effective. The synergistic effect of the neutral ligands on the ion exchange extraction decreased in the order of pyridine > β-picoline > γ-picoline > α-picoline > γ-collidine ≃ isoquinoline ≃ piperidine > 4-benzoylpyridine > trimethyl phosphate ≃ tri-*n*-butyl phosphate. On the other hand, it is reported that the synergistic effect of the pyridine bases on the solvent extraction of Ni(II)–Htta–benzene system decreases in the order of γ-picoline > β-picoline > pyridine > α-picoline, which is accordant with that of the basicity of pyridine bases.[3] The analogous conclusion is reported in the case of the solvent extraction of nickel(II) and cobalt(II) with thiodibenzoylmethane and *N*-phenyl-β-mercaptocinnamamide in the presence of pyridine bases.[10] It is explained that the poor effectiveness of α-picoline may be due to the steric influence by the *ortho*-methyl group. The disagreement of the results between ion exchange extraction and solvent extraction can be explained by the steric influence of the resin matrix with pyridine bases in the case of the ion exchange extraction. Namely, provided that the reaction occurs around cobalt ions on the resin, the pyridine bases must diffuse into the resin hole and so there appears a steric hinderance of the resin matrix with the large size molecule. The stability of adduct is related to the basicity of pyridine bases and has also an influence on the extractability of cobalt ions.

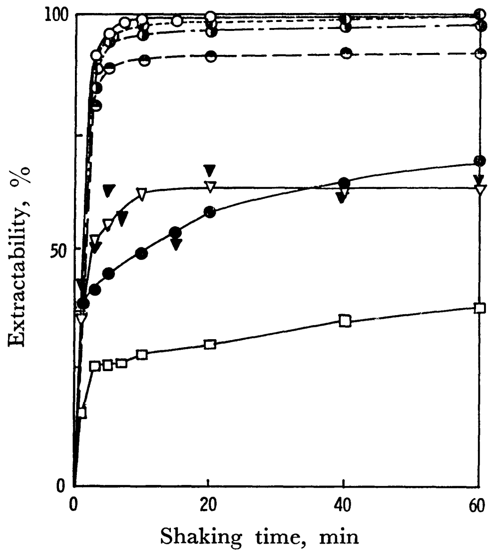

Fig. 2. Effect of shaking time on the synergism of the pyridine bases on the extraction of cobalt ions from the resin with 0.1 M Htta solutions in benzene, containing 0.245 M of pyridine (○), γ-picoline (◑), β-picoline (◐), α-picoline (◓), piperidine (●), isoquinoline (▲), 4-benzoylpyridine (□), and γ-collidine (△).

Effect of the Mesh Size of Co(II)-Form Resin. The Co(II)-form resins of 100—120 and 120—150 mesh ranges were prepared and the extractability of cobalt ions from each of them was compared with that from 60—80 mesh range. The γ-collidine having the *ortho*-substituent to the nitrogen atom of pyridine ring was used as synergist. The result is shown in Fig. 3. Though the extraction rate increased with decreasing mesh size of the resin, the extractability of cobalt ions after 10-min shaking was independent of the mesh size of the resin.

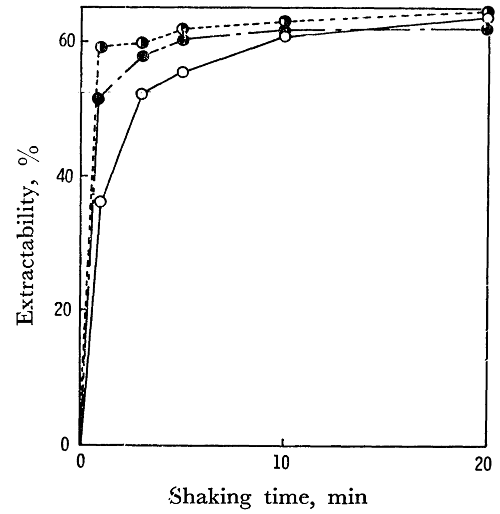

Fig. 3. Effect of the mesh size of Co(II)-form resin on the extraction of cobalt ions with a 0.1 M Htta solution in benzene, containing 0.245 M γ-collidine. The mesh range is 60—80 (○), 100—120 (●), and 120—150 mesh (◑).

Effect of Water Adsorbed to the Co(II)-Form Resin. It has been pointed out that the water played an important role in the reaction of β-diketone with metal ions fixed on the resin.[7–9] In the present case, the difference of the reactivities between the air-dried Co(II)-from resin and the oven-dried one, the latter being prepared by drying the former at 110 °C for 3 h, was investigated. After the 3 h drying at 110 °C. the color of the Co(II)-form resin changed from pink to violet. The water content on the air-dried Co(II)-form resin was determined by the thermogravimetric analysis. It was found that the air-dried Co(II)-form resin adsorbed eight moles of water to

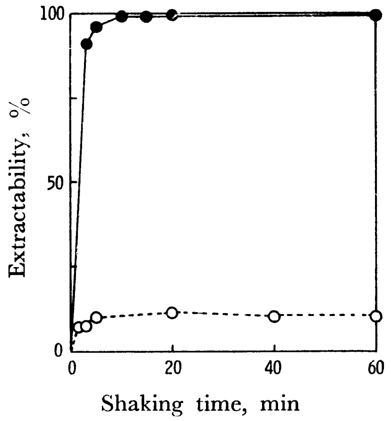

Fig. 4. The difference of the extractabilities between the air-dried Co(II)-form resin (●) and the oven-dried one (○). The extraction of cobalt ions from the resin was carried out with a 0.1 M Htta solution in benzene, containing 0.245 M pyridine.

a mole of cobalt ion on it, and six moles of those were removed by drying at 110 °C. Consequently, the form of the oven-dried Co(II)-form resin is expected to be $(RSO_3)_2Co \cdot 2H_2O$. It is supposed that this color change of the Co(II)-form resin is based on the removal of water molecules from cobalt ions. The use of oven-dried Co(II)-form resin gave a lower extractability in comparison with that of air-dried one, as Fig. 4 shows. Although the role of water remains not clarified, this indicates an importance of trace amounts of water in the extraction of cobalt ion fixed on the ion exchange resin with Htta into the organic medium.

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