Synergistic Effect of Pyridine and Ammonia in the Extraction of Copper(II) Fixed on the Ion Exchange Resin with 2-Thenoyltrifluoroacetone

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The composition of hydrated copper(II), copper-pyridine, and -ammine species fixed on the cation exchange resin was determined by chemical and thermogravimetric analyses. Provided that all the water and bases were coordinated to copper(II) ion, the species on the resin were estimated to be $[Cu(H_2O)_5]^{2+}$, $[Cu(py)(H_2O)_3]^{2+}$, and $[Cu(NH_3)_3(H_2O)_3]^{2+}$, respectively. The removal of copper(II) ion from the resin with 2-thenoyltrifluoroacetone (Htta) was studied in various organic solvents. The rate of reaction was accelerated with the replacement of water molecules coordinated to the metal ion with pyridine or ammonia.

The reaction of metal ion fixed on the ion exchange resin with β-diketone in the organic phase has been investigated.[1-3] The quantitative removal of copper(II) ion fixed on Amberlyst 15 by acetylacetone was first achieved by the addition of a small amount of pyridine.[2] The effect of pyridine in the above system is considered to be similar to that observed in the solvent extraction system, *i.e.*, the rate-promoting synergistic effect.[4,5] Akaiwa *et al.* investigated the kinetics of synergistic extraction with nickel(II)- and cobalt(II)-Htta-pyridine base systems, and reported that the formation of the mono(tta) complex is accelerated by the pyridine base, which seemingly facilitates the release of a water molecule bound to metal ion.[5]

In the present work, it is shown that the reaction of copper(II) ion fixed on the resin with Htta is increased by replacement of some of the coordinated water molecules by unidentate neutral ligands, such as pyridine and ammonia.

Experimental

Apparatus and Reagents. Thermogravimetric curves were recorded with a Shimadzu thermal micro-balance TGA-20 with 5 mg sample at a heating rate 5 °C min^{-1} in the air. A Hitachi 508 atomic absorption spectrometer was used for the determination of copper and for the flame photometric determination of sodium. Visible absorption spectra were measured with a Hitachi 356 two-wavelength double beam spectrophotometer. 2-Thenoyltrifluoroacetone (Wako Pure Chemicals, Inc.) was used without further purification. Chloroform was purified by distillation after washing. Copper(II) sulfate and the other materials used were of guaranteed grade.

Preparation of Copper(II) Form Resin. Macroreticular resin Amberlyst 15 (Rohm and Haas Co.) was used. The dry resin was sized into the 60—80 mesh range, washed with ethanol, cleaned and recycled several times between hydrogen and sodium forms, ending in the latter. It was converted, in a column, into the copper-ammine form with 1.0 M ($M = mol\ dm^{-3}$) aqueous ammonia solution containing a total copper(II) concentration of 1.0×10^{-2} M, and washed with a dilute ammonia solution until the effluent became colorless. The copper-py form resin was also prepared using the copper(II) solution containing a large excess of pyridine. The copper(II)-aqua form resin was prepared as usual. The resins were air- and oven-dried at 105 °C for 3 h to purge free base and moisture, and then stored in a desiccator over silica gel for six months. The resin has a characteristic color; namely, Cu-ammine form light blue, Cu-py form grayish green, and Cu-aq form grey, respectively.

Chemical Analysis of the Species on the Resin. The column packed with a known amount of each form of resin was prepared, and the metal ion on the resin was eluted with 2 M hydrochloric acid, and then the column was washed free from the acid with water. The content of hydrogen ion in the resulting resin was determined by titration and the exchange capacity of the resin was evaluated. The analysis of the eluate was carried out as follows. The copper(II) content was determined by EDTA titration. Sodium was determined by flame photometry and the ion exchange sites which have not been displaced by copper(II) were found. Ammonia was determined by back titration; namely, after masking the copper(II) ion with EDTA, a known excess of a standard sodium tetraphenylborate was added to the sample solution, the resulting precipitate was filtered, and then the unreacted precipitant was determined with a standard solution of zephiramine (benzyldimethyltetradecylammonium chloride). The pyridine content was successfully determined spectrophotometrically with potassium thiocyanate-1-phenyl-3-methyl-5-pyrazolone.[6] It was found from the preliminary experiments carried out with synthetic samples that the interference by copper(II) ion could easily avoided with EDTA.

Results and Discussion

Chemical Analysis. The analytical data are given in Table 1. Provided that all the bases found on the resin were coordinated to copper(II), the mole ratio of copper to ammine and that of copper to py in the complexes are 1 : 3 and 1 : 1, respectively. The proportion of the ion exchange sites occupied by the copper(II) species to the exchange capacity was found to be as follows: Cu-aq form resin 100%, Cu-ammine 86%, and Cu-py 66%. The total amounts of copper(II) and sodium ions were less than the exchange capacity in the case of Cu-ammine and Cu-py form resins. Remaining sites on the resins may be occupied by hydrogen ions as a result of the probable decomposition of formerly adsorbed ammonium or pyridinium ions during the course of oven drying.

Thermogravimetric Analysis. It was found from preliminary experiments that a considerable amount of water had been adsorbed on the resin during six months' storage over silica gel in a desiccator. The thermogravimetric analysis was applied to the determination of water content in the resin. The resin matrix begins to decompose at around 300 °C as shown in Fig. 1. Upon further heating, it decomposes rapidly leaving a black residue. Only one step was found on the thermogravimetric curve of the Cu-aq form resin

Table 1. Results of analysis the species on the resin

Complex on the resin	Weight of resin taken (mg)	Cu found (μmol)	Base found (μmol)	Na found (μmol)	H^+ found after conversion to H-form (μmol)	Water found[a] (μmol)
$[Cu(H_2O)_5]^{2+}$	504.5	914			1832	
	5.0	9.1				45
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	492.0	742	2273		1799	
	504.3	789	2312		1847	
	496.5	784		7.0	1824	
	5.0	7.8	23.6			23.6
$[Cu(py)(H_2O)_3]^{2+}$	511.7	608	646		1822	
	502.7	592		478.3	1793	
	5.0	5.9	5.8			19.4

a) Results of thermogravimetric analysis.

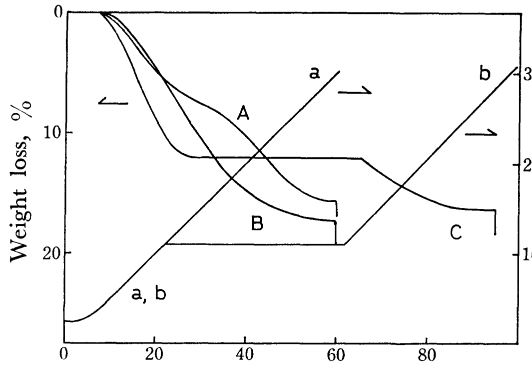

Fig. 1. Thermogravimetric curves of (A) copper-py, (B) copper-ammine, and (C) copper-aq form resin. The curves a and b indicate the heating rate.

at the constant heating rate of 5 °C min^{-1}. The mole ratio of water to copper content on the resin was found to be 5 : 1. On keeping the temperature at 110 °C, the Cu-aq form resin was found to show a constant weight after losing 4 molecules of water (curve C, Fig. 1). Thus, the copper species on the resin at 110 °C was expected to be $[Cu(H_2O)]^{2+}$, which agrees with the result of previous investigation.[2] The copper-py form resin gave two steps before 300 °C. The first step in the temperature range 40—110 °C was assumed to be due to the loss of water, and the second in the range 110—300 °C due to the loss of pyridine. The ratio of pyridine to copper content was found to be 1 : 1, which is consistent with the result of chemical analysis (Table 1), the ratio of water to copper content being 3 : 1. On keeping the temperature at 110 °C, the weight loss reached a constant and definite value, the resulting copper species being found to be $[Cu(py)]^{2+}$. The copper-ammine form resin decomposed in one step before decomposition of the resin matrix. The water content was calculated from the weight loss and analytical data of resin, the weight loss being assumed to be caused by the loss of water and ammonia. The ratio of water to copper content on the resin was found to be 3 : 1.

Copper Species on the Resin. Provided that all the water and base molecules determined by chemical and thermogravimetric analysis are bound to copper(II), the composition of copper species on the resin was found to be $[Cu(H_2O)_5]^{2+}$, $[Cu(py)(H_2O)_3]^{2+}$, and $[Cu(NH_3)_3(H_2O)_3]^{2+}$.

Reaction of Copper Species on the Resin with Htta. A weighed portion of the resin containing 2 mg of copper(II) was taken into an eggplant type flask and a 10-ml portion of 0.1 M Htta solution was added. After mechanical shaking for a certain time at room temperature, the resin was separated by filtration, washed with a small amount of ethanol, and then with water. Copper(II) ions remaining on the resin were eluted with 2 M hydrochloric acid solution and determined by atomic absorption spectrometry. The feasibility of extraction of copper(II) from the resin into Htta-benzene and Htta-chloroform solution increased in the order: Cu-aq, Cu-py, and Cu-ammine (Figs. 2 and 3).

More than 99% of copper(II) was removed from Cu-ammine form resin after a 15-min shaking, while *ca.* 50% of copper(II) was extracted from Cu-aq form resin. The mole ratio of copper to Htta in the complex was confirmed to be 1 : 2. However, the formation of an adduct, such as $[Cu(tta)_2py]$, was not found spectrophotometrically. In carbon tetrachloride

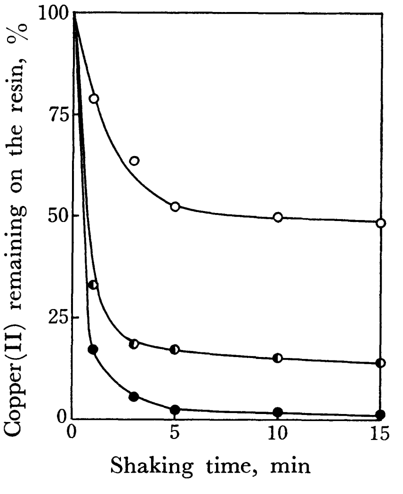

Fig. 2. Effect of shaking time on the removal of copper(II) from the resin into 0.1 M Htta solution in benzene. ○: Copper-aq, ◐: copper-py, ●: copper-ammine form resin.

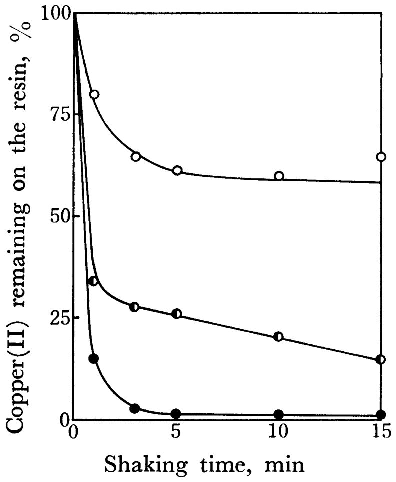

Fig. 3. Effect of shaking time on the removal of copper(II) from the resin into 0.1 M Htta solution in chloro form. The symbols on each curve are the same as in Fig. 2.

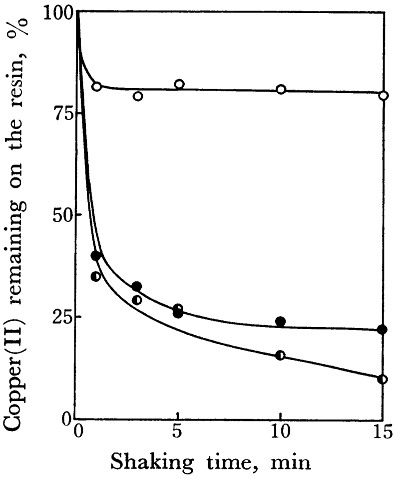

Fig. 4. Effect of shaking time on the removal of copper(II) from the resin into 0.1 M Htta solution in carbon tetrachloride. The symbols on each curve are the same as in Fig. 2.

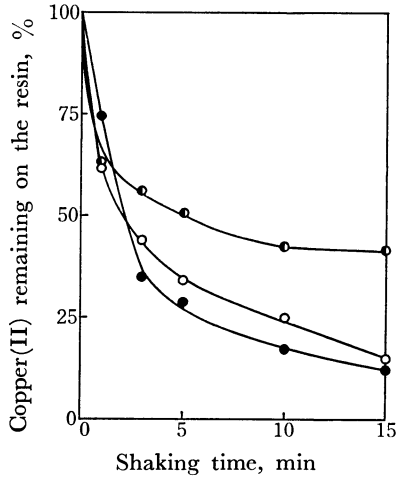

Fig. 5. Effect of shaking time on the removal of copper(II) from the resin into 0.1 M Htta solution in ethanol. The symbols on each curve are the same as in Fig. 2.

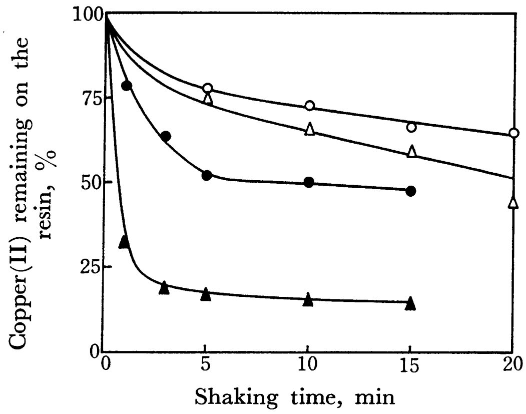

Fig. 6. Effect of water contents on the removal of copper(II) into 0.1 M Htta solution in benzene. Air-dried resin; ●: copper-aq, ▲: copper-py form. Oven-dried resin; ○: copper-aq, △: copper-py form.

solution, Cu-py species was most easily expelled by Htta, whereas Cu-aq species persistently remained on the resin (Fig. 4). In ethanol solution, the rate of conversion of Cu-aq species on the resin into the tta complex was highly increased in comparison with the other solvent systems (Fig. 5). The color of the resulting solution was light green. The absorption maximum at 670 nm suggests the adduct formation between $[Cu(tta)_2]$ and ethanol. Since the phenomenon was characteristic to the aquacopper(II) ion, the first step of the reaction might be assumed to be the displacement of water molecules associated to copper(II) on the resin with ethanol.

Effect of Water. The Cu-aq and Cu-py form resins were dried at 110 °C and cooled for 3 h over silica gel in a desiccator. The copper species on the resin were estimated to be $[Cu(H_2O)]^{2+}$ and $[Cu(py)]^{2+}$, respectively. Evidence for the binding of pyridine to copper(II) was revealed by the light blue color of the resin phase. The results of the removal of copper(II) by Htta in benzene are given in Fig. 6. For the sake of comparison, the results of $[Cu(H_2O)_5]^{2+}$ and $[Cu(py)(H_2O)_3]^{2+}$ in the Htta-benzene system are also illustrated. The reactivity decreases with the removal of some or all water molecules around copper(II).

It can be assumed that the reaction of copper(II) with Htta is accelerated when the coordination sites around the copper(II) ion on the resin are simultaneously occupied by both water and pyridine. The pyridine probably facilitates the release of a water molecule bound to the copper(II) ion when Htta attacks the metal ion to form the mono(tta) complex, and with the progress of complexation the adsorption sites of the resin are competitively occupied by pyridinium and hydrogen ions. The synergistic effect might also hold in the case of the reaction of the copper–ammine complex with Htta and that of aquacopper(II) species with Htta in ethanol.

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