
Article

Solvent Extraction Behavior of Copper Ions Using Hydrophobic Silica Gel

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(Manuscript submitted February 15, 2003; accepted May 2, 2003)

Abstract

Solvent extraction of Cu$^{2+}$ metal ions with thenoyltrifluoroacetone in the presence of hydrophobic silica gel system was studied. In this extraction system, the extractability of the Cu$^{2+}$ metal ions has been improved compared to the normal extraction system. Plots of the values of distribution ratio (logD) in logarithm for the Cu$^{2+}$ metal ions as a function of aqueous pH were found to be linear relationship with slopes of almost +2. It was found that extracted metal ions can be transported not only into the organic phase but also into the hydrophobic silica gel phase. We clarified the extraction mechanism of solvent extraction system in the presence of the hydrophobic silica gel. This solvent extraction system may provide a new method with enhancement of extractability for the solvent extraction techniques compared to the normal extraction system.

1 Introduction

There have been reported many methods to collect and separate the metal ions such as the ion-exchange techniques, the solvent extraction methods, etc. The normal solvent extraction method is one of the useful methods to collect the metal ions. The improvements of extractability have been reported [1,2]. To improve the extractability for metal ions, many synergic extraction systems have been studied [3].

New solvent extraction system in the presence of hydrophobic silica gel was suggested to improve the extractability. The gel phase was added to the normal solvent extraction system which consists of an aqueous and an organic phase. By introducing the gel phase, the metal ions can be transported not only into the organic phase but also into the gel phase by which the improvement in the extractability of the metal ions is expected from the aqueous phase. Because of the high extractability, this method provides an efficient and useful technique for extraction of metal ions. Solvent extraction of the Cu$^{2+}$ metal ions with thenoyltrifluoroacetone (TTA) in the presence of hydrophobic silica gel has been studied. In this study, solvent extraction behavior of the Cu$^{2+}$ metal ions with TTA using hydrophobic silica gel is reported.
2 Experimental

The hydrophobic silica gel was synthesized by the procedure shown in Fig. 1. The silica gel of reagent grade was sieved under 270 meshes. The toluene and Octadecyltrichlorosilane was added to the sieved silica gel. After the solution was stirred for 12 h at 423 K, methanol was added in this solution and it was stirred again for 3 h at 373 K. The silica gel was filtered in the mixed solution and washed with the deionized water and then washed with the toluene. After drying the product for 1 day, the hydrophobic silica gel was obtained to which octadecyl-group is introduced and hereafter was abbreviated as the C18g.

In a 30 cm³ centrifuge tube, an aliquot of cyclohexane containing 1.0 x 10⁻² mol dm⁻³ TTA as an extractant was shaken for 23 h with an equal volume of an aqueous phase containing 0.1 mol dm⁻³ of sodium nitrate with 2 x 10⁻² mol dm⁻³ of buffer (monochloroacetic acid) at 298±1 K in the presence of C18g or not. For the solvent extraction reaction in the presence of C18g, the 0.5 g / 10 cm³ of the C18g was added into the solutions. After phase separation by the centrifugation at 3,500 r.p.m. for 10 min., the pH and the metal ion concentration in the aqueous phase were determined with Hitachi-Horiba F-21 pH meter and VARIAN SpectrAA 220FS atomic absorption spectrophotometer, respectively. The metal concentrations in the organic phase were similarly determined after back extraction reaction into 0.1 mol dm⁻³ hydrochloric acid solution.

Fig. 1 Flowchart of synthesis of hydrophobic silica gel (C18g).

3 Results and Discussion

The extraction of metal ions into organic phase with TTA as an extractant is expressed in terms of the distribution ratio, D;

\[ D = \frac{C_{Cu(o)}}{C_{Cu}} \]  

where \( C \) represents total concentration of metal ions and the subscript “\( o \)” denotes the organic phase. Plots of the log\( D \) values for the \( Cu^{2+} \) metal ions as a function of aqueous pH are linear relationship with slopes of almost +2 (Fig. 2). The following reaction can be written on the basis of the findings:

\[ M^{2+} + 2HL(o) \rightleftharpoons ML_2(o) + 2H^+ \]  

where HL represents the TTA. On the other hand, the solvent extraction of the \( Cu^{2+} \) metal ions into the organic phase with TTA in the presence of the C18g is represented in terms of the distribution ratio, \( D' \);

\[ D' = \frac{(C_{Cu(o)} + C_{Cu(g)})}{C_{Cu}} \]  

(370)
where the subscript "g" denotes the gel phase.

The Cu\(^{2+}\) concentrations in the gel phase were calculated from the following equation;

\[
C_{Cu(g)} = C_{Cu(init)} - (C_{Cu(o)} + C_{Cu(g)})
\]  
(4)

where \(C_{Cu(init)}\) means an initial metal concentration in the aqueous phase. In the presence of the C18g, distribution ratio of the Cu\(^{2+}\) metal ions was increased and the extraction ratio was improved compared to normal solvent extraction.

**Fig. 2** Plots of the values of distribution ratio (\(\log D\) and \(\log D'\)) in logarithm as a function of aqueous pH for the extraction of Cu\(^{2+}\) into cyclohexane with TTA;

- ■: In the absence of the C18g;
- □: In the presence of the C18g

**Fig. 3** Flowchart of extraction mechanism in the presence of hydrophobic silica gel.

Figure 3 shows the extraction mechanism in the presence of the C18g. In this figure, the distribution was shown for the metal complex (ML\(_2\)) in the aqueous, organic and gel phases. Figure 4 shows the partition of copper ions by normal solvent extraction (a) and that of the aqueous, organic and gel phases in the presence of the C18g (b) at the pH value of 2.9. It can be seen from the figure that the concentration of the Cu\(^{2+}\) metal ions in the aqueous phase of solvent extraction system in the presence of the C18g is considerably reduced compared to normal solvent extraction system, that is, the extraction ratio has decreased from 42% for the normal extraction system to 24% of the triple phase distribution system in the aqueous phase.
As the result, it was found that the Cu$^{2+}$ metal ions were distributed not only in the aqueous and organic phases but also in the gel phase. The amount of the Cu$^{2+}$ metal ions in the gel phase is the largest compared to the other two phases in the presence of the C18g. The enhancement of extractability is confirmed in method by using hydrophobic silica gel than that of the normal extraction technique.

References