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# Liquid-liquid extraction behavior of arsenic using ethereal compounds in acidic media

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#### Abstract

Management of the quantity of toxic arsenic in water as well as in the industrial field is an important issue for human health. Liquid-liquid extraction is one of the most efficient separation techniques to remove toxic chemical species from aqueous media. In this study, extraction of As(III) and As(V) from acidic media was studied using ethereal compounds cyclopentyl methyl ether (CPME) and dibutyl carbitol (DBC). The extraction test was carried out by the batchwise method. An aqueous solution containing 0.1 mM arsenic [As(III) or As(V)] was prepared using 0.1–8.0 M mineral acid (hydrochloric acid, nitric acid or sulfuric acid). Equal volumes of the aqueous solution and CPME (10 cm<sup>3</sup>) were mixed and shaken for 24 h at 30 °C. After phase separation, the concentration of arsenic in the aqueous phase was determined using an atomic absorption photometer to calculate the extraction percentage. In the hydrochloric acid. Conversely, As(III) was not extracted at all in nitric acid and sulfuric acid. Additionally, As(V) was not extracted at all in any acidic medium. The extraction behavior of CPME was compared with that of the commercial ethereal extractant DBC.

Keywords: Liquid-liquid extraction, cyclopentyl methyl ether, arsenic, mineral acid

#### 1. INTRODUCTION

Arsenic (As) is extremely toxic and is lethal in trace amounts. The presence of As in the environment is a threat to human health, thus concentration

monitoring via microanalysis and removal of As in water treatment are especially important. One of the most efficient techniques for As removal is a liquid-liquid extraction



Fig. 1. Molecular structure of CPME.

method. In this extraction method, the commercial use of the ether compound dibutyl carbitol (DBC) to extract As requires a hydrochloric acid medium of high concentration. Therefore, attention has been turned to the development of the ether compound cyclopentyl methyl ether (CPME) in recent years. CPME is a solvent developed with consideration of its environmental impact because regulations on the use of organic solvents have become stricter over the years. Compared with other ether solvents, CPME has a low solubility in water because of its high hydrophobicity and is relatively stable against acids and bases.

In this study, the extraction behavior of As(III) and As(V) in the acidic medium (hydrochloric acid, sulfuric acid, nitric acid) was studied using CPME and DBC.

#### 2. EXPERIMENTS

Liquid-liquid extraction tests were conducted by the batchwise method and a typical procedure is as

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follows: an aqueous solution was prepared by dissolving metal ions As(III) or As(V) to form 0.1 mM solutions in hydrochloric acid. The initial concentration of hydrochloric acid was adjusted to 0.1-8.0 M. CPME, DBC or methyl isobutyl ketone (MIBK) was used as the organic phase. Equal volumes (10 cm<sup>3</sup>) of the aqueous and organic phases were mixed in a stoppered Erlenmeyer flask and shaken (120 rpm) in a thermostated water bath at 30 °C. After shaking for 24 h to attain equilibrium, the phases were separated. The equilibrium concentration of hydrochloric acid in the aqueous solution was determined by acid-base titration using an automatic potentiometric titrator. The initial and equilibrium concentrations of metal ions in the aqueous phases were determined using a polarized Zeeman atomic absorption spectrometer. The extraction percentage of metal ions was calculated according to Equation (1):

$$Extraction[\%] = \frac{[M]_{org,eq}}{[M]_{aq,init}} \times 100 = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,init}} \times 100$$
(1)

where  $[M]_{aq,init}$  and  $[M]_{aq,eq}$  represent the initial and equilibrium concentrations of metal ions in the aqueous phase.  $[M]_{org,eq}$  is the total concentration of metal ions in the organic phase at equilibrium, which is calculated from the decrease in concentration of metal ions in the aqueous phase at equilibrium.

#### 3. RESULTS AND DISCUSSION

### **3.1** Extraction selectivity of metal ions using CPME, DBC or MIBK with hydrochloric acid

The extraction selectivity of metal ions using CPME, DBC or MIBK with hydrochloric acid was examined using As(III) and As(V), and the results are shown in Figure 2. The extraction of As(III) using CPME, DBC or MIBK increased with the increase of hydrochloric acid concentration. The extraction capacity of each extractant for As(III) is almost the same. Conversely, As(V) was not extracted at any hydrochloric acid concentration with any of the extractants.

Therefore, As(III) and As(V) can be separated using any of the extractants at high hydrochloric acid concentrations.

## **3.2** Extraction selectivity of metal ions using CPME with nitric acid or sulfuric acid.

The extraction selectivity of metal ions using CPME with nitric acid and sulfuric acid was

examined using As(III) and As(V), and the results are shown in Figure 3. As(III) and As(V) were not extracted at all in a nitric acid or sulfuric acid medium.

It is therefore speculated that As(III) is extracted into the acidic medium via a chloride complex.



Fig. 2 Extraction profiles of As(III) and As(V) using CPME, DBC or MIBK as a function of hydrochloric acid concentration.



Fig. 3 Effects of concentration of nitric acid and sulfuric acid on the extraction percentage of metal ions with CPME.

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#### 4. REFERENCES

- D. F. C. Morris, M. Ali Khan, *Talanta*, **15**, 1301-1305 (1968)
- 2) C.Sella, Navarro Mendoza and D.Bauer, Hydrometallugry, 27(1991) 179-190
- T. Oshima, I. Fujiwara, Y. Baba, Solvent Extr. Res. Dev. Jpn., 22, 119-125 (2015)
- T. Oshima, N. Ohkubo, I. Fujiwara, T. Horiuchi, T. Koyama, K. Ohe, Y. Baba, *Solvent Extr. Res. Dev. Jpn., in press* (2017)