Extraction Behavior of Arsenic, Selenium, and Antimony Using Cyclopentyl Methyl Ether from Acidic Chloride Media

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(Received December 28, 2018; Accepted February 15, 2019)

Solvent extraction is one of the efficient separation techniques for the removal of toxic chemical species from aqueous media, as well as their enrichment for microanalysis. In this study, extraction of the toxic elements, arsenic, selenium, and antimony from acidic chloride media using the oxygen-containing compounds cyclopentyl methyl ether (CPME), dibutyl carbitol (DBC), and methyl isobutyl ketone (MIBK) was compared. Extraction of As(III) increases with increasing hydrochloric acid concentration and the extractability using CPME, DBC, and MIBK was similar. On the other hand, As(V) was not extracted at all using these extractants. Sb(V) and Se(VI) were extracted at high hydrochloric acid concentration. The order of extractability for Se(IV) in acidic chloride media was MIBK > DBC > CPME. The extraction of As(III) using CPME was examined under various conditions. As As(III) was extracted only at high hydrochloric acid concentration, arsenic trichloride (AsCl₃) was suggested as the extracting species. CPME was not saturated with As(III) under the extraction conditions used in this study. As(III) can be enriched by the combination of extraction using CPME followed by back extraction using a small volume of distilled water.

1. Introduction

Arsenic (As), selenium (Se), and antimony (Sb) are present as stable hydroxides under neutral condition and are toxic chemical species. Overexposure to arsenic via drinking water causes in excess risk of mortality from lung, bladder and kidney cancer [1,2]. The International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as carcinogenic to humans. Ingestion of a high level of selenium causes gastrointestinal disturbances (vomiting, diarrhea), hair and nail changes, and neurologic manifestations [3,4]. Exposure to antimony causes respiratory irritation, pneumoconiosis, antimony spots on the skin, and gastrointestinal symptoms [5,6]. Because of their toxicity, these chemical species should be removed from aqueous environments. Additionally, their enrichment is also an important subject with regard to microanalysis.

Solvent extraction is likely to be a powerful separation and/or enrichment method for these toxic species. As arsenic (As(III) and As(V)) is present as a stable oxoanion species, ammonium type extractants which can act as ion exchangers should be effective for its extraction. A quaternary ammonium extractant, Aliquat 336, is found to be an effective extractant for As(III) and As(V) [7-9]. Transport of As(V) with polymer inclusion membranes (PIMs) using Aliquat 336 as a carrier has also been studied [10]. Aliquat 336 can be used also for the extraction of Sb(V) [11]. Also, the extraction of As(V) and As(III) using
trialkylphosphine oxide compounds Cyanex 921 and Cyanex 923 has also been studied [12-14].

Morris and Khan reported the extraction of As(III) using dibutyl carbitol (DBC) [15]. In acidic chloride media (1-7 mol/dm³), the extraction percentage of As(III) increases with increasing concentration of hydrochloric acid. Sn(IV), Fe(III), Sb(III) and Sb(V) were also extracted from an acidic solution using DBC. The oxygen-containing compound DBC is known as a good extractant for Au(III) in acidic chloride media [16], but it could also be an extractant for the toxic elements, arsenic, selenium, and antimony. In the present study, the extraction behavior of the toxic elements using oxygen-containing compounds in acidic chloride media was investigated. The compounds (Figure 1) which can extract Au(III) were chosen as the extractants. Methyl isobutyl ketone (MIBK) is a very effective extractant for Au(III) [17]. Recently, cyclopentyl methyl ether (CPME) (Figure 1) was found to extract Au(III) [18]. CPME can load large quantities of Au(III) like DBC and MIBK. CPME has been developed as an alternative solvent for a variety of applications in process chemistry and is available commercially [19-21]. The extraction behavior of the toxic species using DBC, MIBK and CPME was compared. The extraction of As(III) using CPME was studied in detail by extraction tests under various conditions. Back extraction of As(III), extracted using CPME, was also examined.

![Figure 1. Structures of DBC, MIBK, and CPME.](image)

2. Experimental

2.1 Reagents

Analytical grade sodium dioxoarsenate, disodium hydrogenarsenate heptahydrate, antimony(III) chloride, potassium hexahydroxoantimonate(V), sodium selenite(IV) and sodium selenate(VI) (Wako Pure Chemical Ind. Ltd., Japan) were used to prepare test solutions. Analytical grade CPME for the extraction tests was supplied by Zeon Corporation and used without further purification. All other reagents and solvents were of analytical grade and were used as received.

2.2 Extraction of the extract species using DBC, MIBK, and CPME in hydrochloric acid media

Liquid-liquid extraction tests were conducted by the batchwise method and a typical procedure was as follows: an aqueous solution was prepared by dissolving As(III), As(V), Sb(III), Sb(V), Se(IV) or Se(VI) to form $1.0 \times 10^{-4}$ mol/dm³ solutions in hydrochloric acid. The initial concentration of hydrochloric acid was adjusted from 0.1 – 8.0 mol/dm³. CPME, DBC or MIBK were used as the organic phases. Equal volumes (10 cm³) 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 (Kyoto Electronics Manufacturing AT-700). The initial and equilibrium concentrations of the extracted species in the aqueous phases were determined using a polarized Zeeman atomic absorption spectrometer (HITACHI Z-2310). The extraction percentage of the
extracted species and their distribution ratios \((D)\) were calculated according to Equations (1) and (2); 

\[
\text{Extraction} \,[\%] = \frac{[S]_{\text{org,eq}}}{[S]_{\text{aq,init}}} \times 100 = \frac{[S]_{\text{aq,eq}} - [S]_{\text{aq,eq}}}{[S]_{\text{aq,init}}} \times 100
\]  

\[
D = \frac{[S]_{\text{org,eq}}}{[S]_{\text{aq,eq}}} = \frac{[S]_{\text{aq,init}} - [S]_{\text{aq,eq}}}{[S]_{\text{aq,eq}}}
\]

where \([S]_{\text{aq,init}}\) and \([S]_{\text{aq,eq}}\) represent the initial and equilibrium concentrations of the extracted species in the aqueous phase. \([S]_{\text{org,eq}}\) is the total concentration of extracted species in the organic phase after equilibrium, which was calculated from the decrease in concentration of the extracted species in the aqueous phase after equilibrium.

Extraction using a mixture of dodecane and CPME was also conducted in the similar manner as shown above. Furthermore, the extraction capacity of As(III) into CPME was investigated by contacting an aqueous solution (10 cm³) containing \(1 \times 10^{-4} – 1 \times 10^{-2}\) mol/dm³ As(III) in 7 mol/dm³ HCl and CPME.

2.3 Back extraction of As(III), Se(IV) or Se(VI) extracted using CPME

The forward extraction of \(1.0 \times 10^{-4}\) mol/dm³ As(III), Se(IV) or Se(VI) using CPME from hydrochloric acid (7 mol/dm³ for As(III), 7.5 mol/dm³ for Se(IV), and 8 mol/dm³ for Se(VI)) was performed by contacting aqueous and organic phases (100 cm³/100 cm³) in a similar manner as described above. The organic phase containing As(III), Se(IV) or Se(VI) was divided into 10 cm³ portions, and each portion was contacted with a 10 cm³ distilled water, hydrochloric acid or nitric acid. Both phases were mixed and shaken at 30°C for 24 h. The stripping solution was separated from the organic phase and the back extraction percentage \((B.E. \,[\%])\) was calculated according to Eq. (3);

\[
B.E. \,[\%] = \frac{[S]_{\text{aq,strip}}}{[S]_{\text{org,init}}} \times 100
\]

where \([S]_{\text{org,init}}\) represents the initial concentration of extract species in the organic phase and \([S]_{\text{aq,strip}}\) is the total concentration of the extract species in the aqueous phase after stripping.

2.4 Enrichment of As(III) by extraction using CPME

The forward extraction of \(1.0 \times 10^{-4}\) mol/dm³ As(III) from hydrochloric acid (7 mol/dm³, 15 cm³) was performed using CPME (15 cm³). After shaking the mixture at 30 °C for 1.0 h, a 10 cm³ portion of the organic phase containing As(III) was contacted with 1.0 cm³, 2.0 cm³, or 5.0 cm³ of distilled water. Both phases were shaken at 30°C for 1.0 h. The stripping solution was separated from the organic phase and the concentration of As(III) in the stripping solution was analyzed. The enrichment ratio [-] was calculated from the concentration of As(III) after stripping from CPME (\([\text{As(III)}]_{\text{aq,strip}}\)) to that before forward extraction (\([\text{As(III)}]_{\text{aq,ini}}\)).
3. Results and Discussion

3.1 Rate of As(III) extraction and back extraction using CPME

In previous work, the extraction of As(III) using DBC was studied [15]. However, the operational condition was not described in detail. Figure 2 shows the extraction rate of As(III) using CPME as well as the back extraction from CPME using distilled water. Extraction of As(III) using CPME reaches equilibrium within 10 min. The fast As(III) extraction is similar to that of Au(III) extraction in a previous study [18]. Back extraction of As(III) from CPME is also fast. As(III) is quantitatively stripped within 10 min. For operational convenience, most of the extraction experiments in this study were conducted by contacting both phases for 24 h.

3.2 Extraction of As, Se, and Sb using CPME, DBC and MIBK in hydrochloric acid media

Figure 3 shows extraction profiles for arsenic ((a); As(III), As(V)), antimony ((b); Sb(III), Sb(V)), and selenium ((c); Se(IV), Se(VI)) using CPME, DBC and MIBK as a function of hydrochloric acid concentration. The extraction behavior of arsenic is quite similar with the different extractants. When the hydrochloric acid concentration is more than 4 mol/dm$^3$, the extraction of As(III) using CPME, DBC and MIBK increases with increasing the hydrochloric acid concentration.

Figure 2. Rate of As(III) extraction using CPME and back extraction of As(III) using distilled water. $[\text{As(III)}] = 1.0 \times 10^{-4} \text{ mol/dm}^3$, $[\text{HCl}] = 7.0 \text{ mol/dm}^3$.

Figure 3. Extraction profiles of arsenic (a), antimony (b), and selenium (c) using CPME, DBC and MIBK as a function of hydrochloric acid concentration.
Similarly, As(III) is extracted using aromatic compounds at high HCl concentration [22-24]. The extraction percentages of As(III) using each extractant is almost the same. Sella et al. reported aqueous species fractions for As(III) as a function of HCl concentration (Figure 4) [24]. When the hydrochloric acid concentration is more than 4 mol/dm$^3$, AsCl$_2$(OH) and AsCl$_3$ are the major chemical species. In particular, the mole fraction of AsCl$_3$ considerably increases at more than 6 mol/dm$^3$ hydrochloric acid concentration. Therefore, the chemical species of As(III) extracted using the oxygen-containing extractants seems to be AsCl$_3$. On the other hand, As(V) is not extracted at all using any of the extractants. Therefore, As(III) and As(V) can be separated using the extractants at high hydrochloric acid concentration.

The extraction of Sb(III) using CPME, DBC and MIBK shows different behaviors. The extraction of Sb(III) using CPME and DBC increases with increasing hydrochloric acid concentration, but decreases at very high hydrochloric acid concentration: The extraction percentages show a maximum value at 2 mol/dm$^3$ hydrochloric acid. In contrast, the extraction of Sb(III) using MIBK increases at high hydrochloric acid concentration. At 5.5 mol/dm$^3$ hydrochloric acid, extraction of Sb(III) using MIBK was more than 99%. Sb(V) is not extracted at all under the condition of low hydrochloric acid concentration, but the extraction increases with increasing hydrochloric acid concentration. The order of extractability for Sb(V) is MIBK > DBC, CPME. As Sb(V) is present as SbCl$_6^-$ [25], the anionic chloride complex is most likely to be the species extracted using the oxygen-containing extractants.

Recently, Gupta and Moats reported the extraction of selenium using DBC [26]. The extraction of selenium using tributyl phosphate was also studied [27]. However, studies of selenium extraction in acidic chloride media are still limited. Extraction profiles of Se(IV) and Se(VI) using CPME, DBC and MIBK are shown in Figure 3 (c). Se(VI) is not extracted at all at lower hydrochloric acid concentration, but the extraction significantly increases at HCl concentrations of more than 6 mol dm$^3$. The extraction behavior of Se(VI) using MIBK, DBC, and CPME is similar. Se(IV) is extracted at lower HCl concentrations compared with Se(VI). The order of Sb(IV) extraction is MIBK > DBC > CPME. Se(IV) and Se(VI) can be separated using MIBK by controlling the HCl concentration. Selenium would also be present as a chloride complex, however, the chemical species are not clear. From the results, it was found that many types of toxic species can be extracted using CPME at high HCl concentration. The extraction of arsenic using CPME is discussed in the next section.

3.3 Extraction of As(III) and As(V) in nitric acid and sulfuric acid media

Extraction of As(III) and As(V) using CPME was examined from nitric acid and sulfuric acid media (Figure 5). As(III) and As(V) are not extracted at all from nitric acid and sulfuric acid media. As(III) is
extracted using the ethereal compounds only from hydrochloric acid media. The result supports the conclusion that As(III) is extracted using CPME as a chloride complex.

3.4 Effect of the chloride ion concentration on the extraction of As(III)

Figure 6 shows the effect of the concentration of chloride ion on the distribution of As(III) using CPME. The chloride concentration was controlled by the concentration of HCl (open circles, the data is based on Figure 3 (a)) or LiCl (filled circles). The log\(D\) value increases with an increase in the concentration of chloride ions. As the addition of lithium chloride increased the log\(D\) value under same HCl concentrations, the chloride ion is a key factor for the extraction of As(III) using CPME. The results in Figures 5 and 6 confirm that As(III) is extracted as a chloride complex. The slope of the relationship between log\(D\) versus the equilibrium pH is about 6. However, it is not clear what this means because CPME seems to extract As(III) by a solvation mechanism.

3.5 Effect of CPME concentration on the extraction of As(III) in hydrochloric acid media

Figure 7 shows the extraction of As(III) using a mixture of dodecane and CPME in 7.0 mol/dm\(^3\) HCl. The extraction of As(III) using pure dodecane is 7.6%. The extraction increases with increasing CPME concentration. The extraction of As(III) using pure CPME is 74.0%. A similar extraction profile for the extraction of Au(III) using a mixture of dodecane and CPME in hydrochloric acid media has been reported [18]. A molar concentration of pure CPME corresponds to 8.6 mol/dm\(^3\), which is much higher than that of As(III) (1.0\(\times\)10\(^{-4}\) mol/dm\(^3\)).
3.6 Extraction capacity of As(III) using CPME

Figure 8 shows the extraction profile of As(III) using CPME as a function of the As(III) concentrations. The extraction percentage is in the range of 69.7-90.4%. The extraction amount of As(III) increases on increasing the initial concentration of As(III) and is not saturated. CPME can load to at least 10 mM (0.749 g/dm³) As(III). The high extraction capacity for As(III) is similar to that for Au(III) as reported in a previous study [18]: CPME can load to 4.74 mM (0.934 g/dm³) Au(III). The results suggest that CPME can be applied for the extraction of As(III) over a wide range of As(III) concentration.

3.7 Back Extraction of As(III) and Se(IV, VI) from CPME

Table 1 shows the back extraction percentage of As(III), Se(IV), and Se(VI), which were extracted using CPME. As(III) is quantitatively recovered from CPME using distilled water. Addition of 0.1-1.0 mol/dm³ HCl does not influence the back extraction. On the other hand, the back extraction of Se(IV) and Se(VI) using distilled water and hydrochloric acid solution is very small. Nitric acid is effective for their back extraction. Se(IV) and Se(VI) are quantitatively recovered using 1.0 mol/dm³ HNO₃.

As shown above, As(III) seems to be extracted as arsenic trichloride. After contacting with distilled water, the chemical species of As(III) would be changed by hydrolysis. The resulting species would not be stable in CPME and is stripped into the aqueous phase. Selenium should also be extracted as chloride complexes but is not stripped by contacting with distilled water. Contact with nitric acid might change the chemical species of Se(IV) and Se(VI) which are extracted using CPME, however, the mechanism is not clear.

| Stripping solution | B.E. [%] |
|--------------------|---------|
|                    | As(III) | Se(IV) | Se(VI) |
| distilled water    | 100     | 10.8   | 14.6   |
| 0.1 mol/dm³ HCl    | 100     | 13.9   | 17.1   |
| 1.0 mol/dm³ HCl    | 100     | 16.7   | 20.0   |
| 0.1 mol/dm³ HNO₃   | Not examined | 88.0 | 88.6 |
| 1.0 mol/dm³ HNO₃   | Not examined | 100 | 100 |

3.8 Enrichment of As(III) by extraction using CPME

Enrichment of As(III) based on the extraction using CPME followed by back extraction using distilled water was examined. As(III) can be enriched using a smaller volume of stripping solution. The results are summarized in Table 2. The amount of forward extraction of As(III) using CPME from 7 mol/dm³ HCl is
86.7%. After stripping using distilled water, the concentration of As(III) increased compared with the initial solution. The enrichment ratios are smaller than those estimated because the forward extraction is not quantitative. However, the results suggest that As(III) can be enriched by the extraction using CPME followed by stripping, and the process can be applied for microanalysis.

| Volume of stripping solution (estimated enrichment ratio) |
|----------------------------------------------------------|
| 5 cm$^3$ (3.0) | 2 cm$^3$ (7.5) | 1 cm$^3$ (15) |
| [As(III)]$_{aq,in}$ [$\times 10^{-3}$ mol/dm$^3$] | 0.104 |
| [As(III)]$_{aq,strip}$ [$\times 10^{-3}$ mol/dm$^3$] | 0.201 | 0.505 | 11.29 |
| Enrichment ratio [-] | 1.9 | 4.8 | 9.8 |

4. Conclusion

Oxygen-containing compounds CPME, DBC, and MIBK were found to extract toxic chemical species such as arsenic, selenium, and antimony in acidic chloride media. The extractability of As(III) and Se(VI) compounds was similar, while the amount of extraction of Sb(V) and Se(IV) using MIBK was greater than that for CPME and DBC. As(III) seems to be extracted as a chloride complex using CPME similar to Au(III) [18]. Studies of arsenic extraction using oxygen-containing extractants are very limited. The results in this study should be informative for the extraction and/or enrichment of toxic elements from acidic media. The solvent extraction process can be applied for enrichment of trace toxic species. Additionally, the results should be informative for mining processes, because the quality of ore is getting poorer and the content of impurities such as arsenic is increasing.

Acknowledgement

This research was partly supported by Adaptable and Seamless Technology transfer Program through Target-driven R&D (A-STEP) from Japan Science and Technology Agency (JST).

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