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ARTICLE

Extraction Behavior of Antimony in a TRUEX System

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The extraction behavior of antimony into a transuranic element extraction (TRUEX) solvent containing octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide was investigated. An extraction study with a PUREX solvent was also performed for comparison. Adding oxalic acid into the TRUEX system was quite effective for decreasing the distribution ratio to $\approx 1/4$. In order to clarify possible antimony species in a nitric acid medium, the solubility measurement of antimony oxide was performed. The extraction results and solubility data suggested that the monovalent cationic antimony would be extracted into the TRUEX solvent.

KEYWORDS: antimony, ^{125}Sb , antimonyl, TRUEX, PUREX, solvent extraction, CMPO, nitric acid, solubility, distribution ratio

I. Introduction

Antimony ^{125}Sb is a fission product (FP) with high radioactivity and is found in nuclear spent fuels. Though its half-life is 2.77 years, the reprocessing process without long-term cooling must take account of the dose rate due to ^{125}Sb decay. On a global basis, the reprocessing process is requested as a simplified and low-decontamination process which is effective for minor actinide recovery. If this reprocessing process operates without long-term cooling, decontamination performance for ^{125}Sb will be important. Hence, the extraction behavior of ^{125}Sb from the high activity waste (HAW) should be given more attention.

Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) effectively extracts trivalent actinides from acid solutions. Horwitz and co-workers have developed the transuranic element extraction (TRUEX) process by employing CMPO.¹⁾ A mixture of CMPO and tri-*n*-butyl phosphate (TBP) in *n*-dodecane is one of the possible TRUEX solvents. In our previous study, we tested the extraction of antimony with this solvent, and found that the distribution ratio (D) in the TRUEX system is about 100 times larger than that in the PUREX system.²⁾ Though the preliminary result pointed the importance of the extraction behavior of antimony in the TRUEX system, the extraction experiment has been performed only for five different acidities. Hence, more detailed information on the extraction behavior is required to clarify it. In this study, we investigated the extraction behavior of antimony in detail, most especially its dependence on $[\text{HNO}_3]$, dependence on $[\text{CMPO}]$, and dependence on $[\text{H}^+]$ under a fixed ionic strength. The possibility of antimony spe-

cies in nitric acid solutions was predicted from the solubility measurement of antimony pentoxide. The extraction stoichiometry of antimony in the TRUEX system will be discussed.

II. Experimental

1. Solvent Extraction

The distribution ratio of antimony was radiochemically determined by using a radioactive tracer ^{122}Sb produced by neutron irradiation. 5.7 mg of pure antimony metal (Nilaco, Inc., 99.9999% purity) was irradiated for 20 min in a pneumatic irradiation system with a thermal neutron flux of $\phi_{\text{th}} = 2.75 \times 10^{13} \text{ n/cm}^2/\text{s}$ at the Kyoto University Research Reactor. The irradiated metal was dissolved in 13.5 mol dm^{-3} (M) HNO_3 by gentle heating. This was used as the stock solution.

Portions of the stock solution were dissolved in HNO_3 , and $4.8 \times 10^{-5} M$ antimony in nitric acid solutions. Solutions with various concentrations, from 0.5 to 5 M , were prepared. Solutions of $4.8 \times 10^{-5} M$ antimony in 1 and 3 M HNO_3 with 0.02 M $\text{H}_2\text{C}_2\text{O}_4$, and solutions of $4.8 \times 10^{-5} M$ antimony in mixtures of HNO_3 - CsNO_3 with an ionic strength of 1 M were also prepared. These solutions served as the aqueous phase. Mixtures of CMPO (0.010 to 0.20 M , Strem Chemicals, Inc., 99.7% purity) and 1.0 M TBP diluted with *n*-dodecane were prepared as TRUEX solvents. Each TRUEX solvent was scrubbed twice by using 0.5 M Na_2CO_3 , and then it was pre-equilibrated with fresh nitric acid solutions.

Fifteen mL each of the aqueous solution and the organic solution was mixed by magnetic stirring in a glass centrifuge tube for 20 min at room temperature. After separating two phases by centrifugation (1500 rpm, 1 min), weighed portions of both phases were taken for γ -spectrometric analysis

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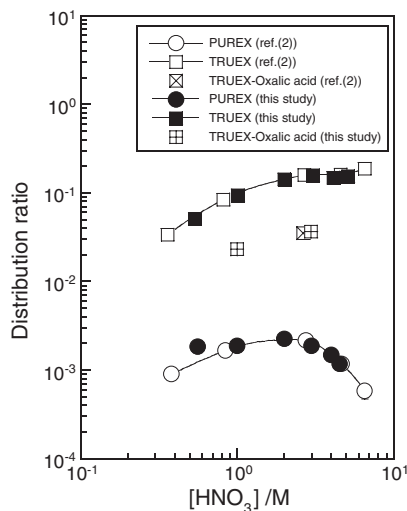


Fig. 1 Distribution ratios of antimony(V) as functions of $[\text{HNO}_3]$

to determine the distribution ratio of ^{122}Sb . The H^+ concentration in the equilibrated aqueous phase was determined by titration with NaOH .

The quantifications of both phases were performed gravimetrically to avoid the large error associated with volumetric treatment. The radioactivity per volumetric unit was converted by using the density of the HNO_3 solutions.

2. Solubility Measurement

Antimony pentoxide (Sb_2O_5 , 99.99% purity) was purchased from Kojundo Chemical Laboratory, Co., Ltd. Nitric acid (reagent grade) was diluted with pure water, and 0.1–10 M HNO_3 solutions were prepared. One mg of antimony pentoxide was placed in a glass vial, and 30 mL of nitric acid solution was added. The vial was sealed with a stopcock. The vial was gently shaken at room temperature, $T = 298 \text{ K}$. After aging, two phases were separated by centrifugation. The supernatant was filtered by a PTFE filter with a $0.20 \mu\text{m}$ pore size. The concentration of antimony in the filtrate was measured by an ICP spectrometer (Shimadzu, ICPS-1000TR). The solubility was measured for periods ranging from 2 h to 4 months by attaining equilibrium between solid and liquid phases. The temperature change during the experiment was $\pm 3 \text{ K}$.

III. Results and Discussion

1. Extraction of ^{122}Sb under the PUREX and TRUEx Conditions

Distribution ratios of antimony are shown in **Fig. 1** as functions of $[\text{HNO}_3]$ (all extraction results in the present study are tabulated in **Table 1**). The extraction results in a previous study²⁾ are also shown in **Fig. 1**. High reproducibility can be recognized. The D values in the TRUEx system are about 100 times larger than those in the PUREX study. The D value in the TRUEx system increases with acidity, and it approaches 0.15. The D values with $\text{H}_2\text{C}_2\text{O}_4$ are about 1/4 of those without $\text{H}_2\text{C}_2\text{O}_4$ for 1 and 3 M HNO_3 . The addition of oxalic acid is quite effective for suppressing the ex-

Table 1 Extraction conditions and results

[TBP] /M	[CMPO] /M	$[\text{HNO}_3]_{\text{aq}}$ /M	$[\text{CsNO}_3]$ /M	$[\text{H}_2\text{C}_2\text{O}_4]$ /M	$D_{\text{Sb}^{\text{a}}}$
1.0	—	0.56	—	—	0.00184(7)
1.0	—	1.0	—	—	0.00187(6)
1.0	—	2.0	—	—	0.00224(6)
1.0	—	3.0	—	—	0.00188(7)
1.0	—	4.0	—	—	0.00148(6)
1.0	—	4.5	—	—	0.00117(4)
1.0	0.20	0.54	—	—	0.0510(13)
1.0	0.20	1.0	—	—	0.0942(24)
1.0	0.20	1.0	—	0.020	0.0231(8)
1.0	0.20	2.0	—	—	0.143(4)
1.0	0.20	3.1	—	—	0.158(4)
1.0	0.20	3.0	—	0.020	0.0364(11)
1.0	0.20	4.1	—	—	0.149(4)
1.0	0.20	5.1	—	—	0.155(4)
0.10	—	1.0	—	—	0.000008(8)
0.25	—	1.0	—	—	0.000063(11)
0.50	—	1.0	—	—	0.000557(21)
1.0	0.010	1.0	—	—	0.00300(11)
1.0	0.025	1.0	—	—	0.00539(19)
1.0	0.050	1.0	—	—	0.0110(4)
1.0	0.10	1.0	—	—	0.0286(10)
1.0	0.2	0.15	0.90	—	0.0344(12)
1.0	0.2	0.34	0.70	—	0.0506(18)
1.0	0.2	0.53	0.50	—	0.0640(22)
1.0	0.2	0.74	0.30	—	0.0742(26)

^{a)}Errors of 1 standard deviation corresponding to γ -counting in the last quoted digits are given in parentheses.

traction of antimony. In other words, the coefficient of separation between trivalent f-elements and antimony can be improved by adding oxalic acid.

2. Dissolved Species of Antimony in Nitric Acid

From the Pourbaix diagram,³⁾ antimony should exist in nitric acid solutions as pentavalent antimony. The major Sb(V) ions are known as cationic SbO_2^+ and anionic Sb(OH)_6^- , whose isoelectric point has been reported to be $\text{pH} = -0.27$.^{3,4)} According to the reported value, both SbO_2^+ and Sb(OH)_6^- are major species under the typical acidity ($\approx 3 \text{ M HNO}_3$) of the TRUEx process. The extraction behavior should take into account the reactions corresponding to these species. However, the isoelectric point³⁾ has been calculated from the solubility⁵⁾ of antimony pentoxide in hydrochloric acid solutions. From the oxidation potential,³⁾ antimony pentoxide dissolved in HCl may have formed Sb(III) species. In order to verify the possible Sb(V) species in the TRUEx system, we analyzed the solubility of antimony pentoxide in HNO_3 solutions.

In our solubility measurement, the solubility reached a maximum within 7 h, and then it decreased. A clear decrease was observed after 1 month, and the steady state was attained after 4 months. The solubility data after 4 months of aging are shown in **Fig. 2** as a function of pH , where pH was approximated to be $-\log a_{\text{HNO}_3}$. The mean activity coefficient of HNO_3 was calculated on the basis of a semi-

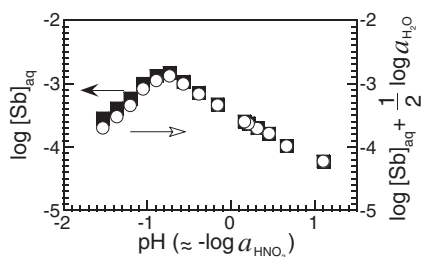
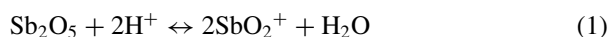


Fig. 2 Solubilities of Sb_2O_5 in HNO_3 solutions. The nitric acid concentrations were 0.1, 0.3, 0.5, 0.7, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 M

empirical theory.⁶⁾ Suppose SbO_2^+ is the major species; then the dissolution equilibrium should be



and

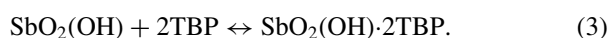
$$\log[\text{SbO}_2^+] = -\text{pH} + (1/2) \log K_{\text{sp}} - (1/2) \log a_{\text{H}_2\text{O}} - \log \gamma_{\text{SbO}_2^+}, \quad (2)$$

where K_{sp} means the solubility product. Since the $a_{\text{H}_2\text{O}}$ of HNO_3 is available,⁷⁾ $(\log[\text{SbO}_2^+] + (1/2) \log a_{\text{H}_2\text{O}})$ can be calculated, which is also shown in Fig. 2. As shown in Fig. 2, the correction brought about by $a_{\text{H}_2\text{O}}$ is quite small. Unfortunately, no data is available for $\gamma_{\text{SbO}_2^+}$. If the change in $\gamma_{\text{SbO}_2^+}$ is negligibly small, the correlation $\log[\text{Sb}]_{\text{aq}}$ vs. pH should show a slope of -1 . In the region of $\text{pH} \geq -0.74$ ($\leq 5 \text{ M HNO}_3$), the solubility decreases with increasing pH, and the slope is -1 in this region. The slope gradually deviates from -1 with increasing pH. This suggests the formation of $\text{Sb}(\text{OH})_6^-$, but the isoelectric point could not be seen. In the pioneering work,³⁾ the activity was used for HCl but the molal unit was used for Sb (the activity coefficient was treated as unity). By considering this and the possible presence of Sb(III) species in HCl, the reported isoelectric point may be shifted. In our case, we still have difficulty with the activity coefficient of Sb(V) species. However, if the activity coefficient of an Sb(V) species changes the slope, it must change logarithmically. The logarithmic change of the activity coefficient within this acidity region would be unrealistic, and hence, we conclude that SbO_2^+ is predominant in the TRUEX system, not $\text{Sb}(\text{OH})_6^-$.

In the $\text{pH} \leq -0.74$ region, the solubility decreases with the increase in acidity. This would be attributable to a drastic change of $\gamma_{\text{SbO}_2^+}$ in the concentrated HNO_3 region and/or the formation of $\text{SbO}_2(\text{NO}_3)$.

3. Extraction Behavior of Antimony under the PUREX Conditions

In a PUREX study,⁸⁾ the extraction reaction of antimony from nitric acid solutions has been reported,



This reaction can be rewritten as²⁾



or

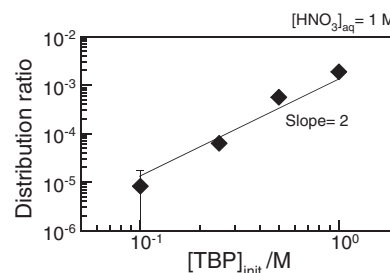


Fig. 3 Distribution ratios of antimony as a function of [TBP]

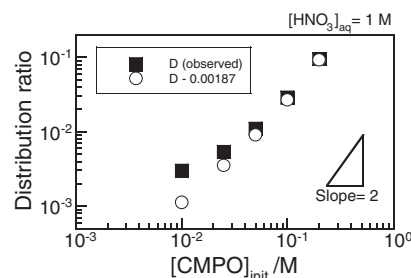
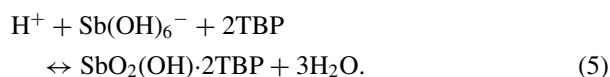
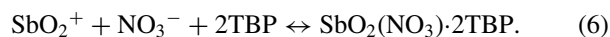


Fig. 4 Distribution ratios of antimony as a function of [CMPO]



The reported extraction reaction is based on the condition that the predominant species is the anionic species. However, from our solubility measurement and the Pourbaix diagram,⁴⁾ the predominant species should be the cationic SbO_2^+ . Hence, the extraction reaction should be



Distribution ratios of antimony under the PUREX conditions are shown in Fig. 3 as a function of $[\text{TBP}]_{\text{init}}$. The errors shown together are experimental errors of 1 standard deviation corresponding to γ -counting. The nitric acid concentrations in the equilibrated aqueous phases were 1 M. The slope of $\log D$ vs. $\log[\text{TBP}]$ is 2. This supports the reported solvation number 2 of TBP for Sb(V).⁸⁾

4. Extraction Behavior of Antimony under the TRUEX Conditions

Distribution ratios of antimony under the TRUEX conditions are shown in Fig. 4 as a function of $[\text{CMPO}]_{\text{init}}$. The errors corresponding to γ -counting are under 3%. The nitric acid concentrations in the equilibrated aqueous phases were 1 M. With the decrease in $[\text{CMPO}]_{\text{init}}$, the observed D value approaches the D of the PUREX system (see Table 1). Under a PUREX condition (1 M TBP, 1 M HNO_3), distribution ratio was obtained to be 0.00187. The difference in D between the TRUEX and PUREX systems, $D - 0.00187$, is also shown in Fig. 4. As shown in Fig. 4, the extraction of Sb(V) by TBP is considerable only at the lower [CMPO] region. At a typical [CMPO] region ($\approx 0.2 \text{ M}$), the slope of $\log D$ vs. $\log[\text{CMPO}]_{\text{init}}$ is ca. 2. This suggests the solvation number 2 of CMPO for Sb(V). Hence, the extraction reaction of antimony would be

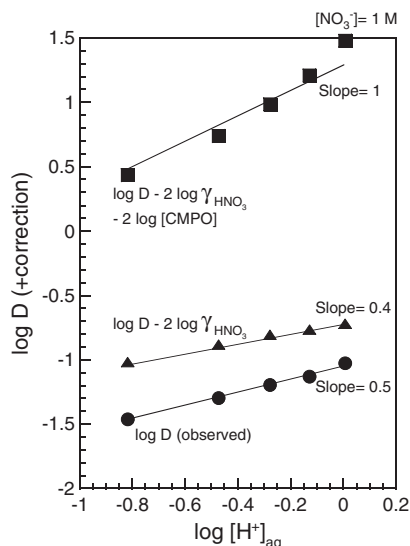
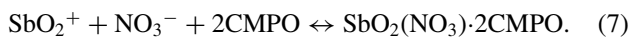


Fig. 5 Distributions ratios of antimony as a function of $[H^+]$. The γ_{HNO_3} values in the HNO_3 - $CsNO_3$ mixtures were estimated from the semiempirical equation.⁶⁾ The effective CMPO concentrations were estimated from the correlation,

$$\begin{aligned} \frac{[CMPO]}{[CMPO]_{init}} (\%) &= \exp(4.706 - 1.099[HNO_3] \\ &\quad + 0.1005[HNO_3]^2 - 0.008980[HNO_3]^3), \end{aligned}$$

reported in our previous study.⁹⁾ The slope of $(\log D - 2 \log \gamma_{HNO_3} - 2 \log [CMPO])$ vs. $\log [H^+]_{aq}$ was analyzed to be 1 with a correlation factor, $R^2 = 0.936$



Hereafter, we use activity for determining the specific extraction stoichiometry. Since the activity coefficients of Sb(V) species are not clear, we used solutions with a constant ionic strength, in which the activity coefficients of Sb(V) are approximately constants. The ionic strength was adjusted to 1 M by using HNO_3 - $CsNO_3$ mixtures, and the acidity dependence of D was studied. The obtained D values are shown in **Fig. 5**. This equilibrium constant of the reaction given by Eq. (7) is

$$K = \frac{\gamma_{SbO_2(NO_3) \cdot 2CMPO} [SbO_2(NO_3) \cdot 2CMPO]}{\gamma_{SbO_2^+} [SbO_2^+] \gamma_{NO_3^-} [NO_3^-] \gamma_{CMPO_{free}}^2 [CMPO]^2}. \quad (8)$$

Since D is equal to $[SbO_2(NO_3) \cdot 2CMPO] / [SbO_2^+]$, Eq. (8) can be written as

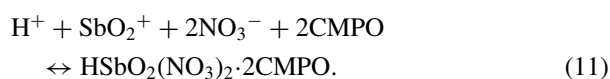
$$\begin{aligned} \log K &= \log D \\ &\quad + \log \gamma_{SbO_2(NO_3) \cdot 2CMPO} \\ &\quad - (\log \gamma_{SbO_2^+} + \log \gamma_{NO_3^-}) - \log [NO_3^-] \\ &\quad - 2 \log \gamma_{CMPO} - 2 \log [CMPO], \end{aligned} \quad (9)$$

where $\log \gamma_{SbO_2^+} + \log \gamma_{NO_3^-} = 2 \log \gamma_{SbO_2(NO_3)}$. The activity coefficients $\gamma_{SbO_2(NO_3) \cdot 2CMPO}$ and γ_{CMPO} can be treated as constants, because the conditions of the organic phases are similar. Since the ionic strength was fixed at 1 M by using the HNO_3 - $CsNO_3$ mixture, $[NO_3^-]$ is constant (1 M), and the variation of $\gamma_{SbO_2(NO_3)}$ is considered to be very small. Thus, the following equation can be obtained:

$$\log D = 2 \log [CMPO] + const. \quad (10)$$

If $[CMPO]$ is the same as the initial concentration, $\log D$ must show the same value. As shown in Fig. 5, the slope of $\log D$ vs. $\log [H^+]_{aq}$ is 0.5. This suggests a change in $[CMPO]$. Cesium is less extractable into the TRUEX solvent, while HNO_3 is extractable. The extraction of HNO_3 decreased the effective CMPO concentration (it should be noted that this extraction does not decrease $[HNO_3]$ in the aqueous phase, because the organic phase was pre-equilibrated with a fresh HNO_3 - $CsNO_3$ mixture). However, from the consumption of CMPO, the positive slope cannot be explained, because the effective CMPO concentration should decrease with increasing acidity.

CMPO is a bifunctional extractant (bidentate). Considering the extraction of HNO_3 , and the bifunctional characteristics of CMPO, the following coextraction reaction may occur:



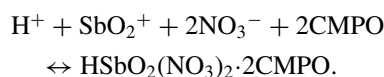
In the same manner as with Eqs. (8) and (9), from the equilibrium constant of the reaction given by Eq. (11), the following correlation can be obtained:

$$\begin{aligned} \log D - 2 \log \gamma_{HNO_3} - 2 \log [CMPO] \\ = \log [H^+] + const. \end{aligned} \quad (12)$$

$(\log D - 2 \log \gamma_{HNO_3})$ is also shown in Fig. 5. The slope of $\log D - 2 \log \gamma_{HNO_3}$ vs. $\log [H^+]$ is 0.4. This is smaller than 1 and requires the correction of the consumption of CMPO. In our previous study,⁹⁾ we have reported the correlation between the effective CMPO concentration and $[HNO_3]$. We introduce the effective CMPO concentration into Eq. (12). As shown in Fig. 5, the correlation between $(\log D - 2 \log \gamma_{HNO_3} - 2 \log [CMPO])$ and $\log [H^+]$ shows a slope of 1. This is consistent with the extraction reaction given by Eq. (11). The slope analysis suggests that the extraction of antimony from HNO_3 by the TRUEX solvent has the stoichiometry of $[HNO_3]:[SbO_2(NO_3)]:[CMPO] = 1:1:2$.

IV. Conclusion

The distributions of antimony(V) under TRUEX and PUREX conditions were studied with nitric acid solutions. The D values in the TRUEX system could be reduced to about 1/4 by adding oxalic acid. The solvation number of TBP for Sb in the PUREX system was 2, and that of CMPO for Sb in the TRUEX system was also 2. The extraction reaction of antimony in the TRUEX system was analyzed to be



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