Extraction behavior of phenyl-substituted phosphine oxides for some fission product elements

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Abstract

As potential multidentate extractants with specific high extraction behavior for metal species in aqueous acidic media, extraction behavior of 1,1,3,5,5-pentaphenyl-1,3,5-triphosphapentane trioxide (PPTPT) and 1,1,5,5,2',2'-hexaphenyl-1,3,5,2'-tetraphospha-3-ethylpentane tetraoxide (HPTEPT), one of the aprotic triphosphine trioxides and tetraphosphine tetraoxides, respectively, for fission products elements (FPs) was extensively investigated by using liquid-liquid extraction and solid-liquid adsorption in the form of a silica-supported impregnated adsorbent. It was found, from the examination up to 9 mol/dm$^3$ (=M) HNO$_3$ and HCl, that metal ions such as Fe(III), Zr(IV) and Nd(III) were in general highly extracted and adsorbed by both PPTPT and HPTEPT, and that the dependence of the extraction/adsorption behavior on the acid concentration varies depending on the metal ions. It was suggested, from the slope analysis for the extraction system of the two extractants for Nd(III) under 6 M HNO$_3$ and HCl, that they extract Nd(III) differently, i.e., three molecules of PPTPT and one or two of HPTEPT were found necessary for the extraction of one molecule of Nd(III), respectively, where some of one HPTEPT molecule binds at least two Nd(III) ions by crosslinking from the steric viewpoint.

Keywords: polyphosphine polyoxide, extractant, FP, HNO$_3$, HCl

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1. Introduction

In the treatment of radioactive liquid wastes, a lot of extractants have been developed for the extraction of actinoid (An) and lanthanoid (Ln) species from nitrate media\[1-8\]. Recently, extractants not containing phosphorus have been receiving attention because of their easy disposal after use\[1, 4, 5, 8\]. However, phosphine oxides extractants have several advantages for the application, as we mentioned earlier\[9\]:

(i) oxygen atoms of phosphoryl group have stronger affinities for An and Ln species than those of carbonyl group in amide compounds;
(ii) extraction from highly concentrated nitrate media and back-extraction with diluted HNO₃ may be expected as they have aprotic behavior;
(iii) in principle, they do not undergo acid hydrolysis unlike compounds not containing phosphorus such as diamides and ester phosphates such as tri-\textit{n}-butylphosphate.

Besides, it is reported that the ether bond decreases the stability of extractants in acid media\[4\]. Therefore, extractants like phosphine oxides and without ether bonds are expected to be chemically stable in acid media. From these viewpoints, phosphine oxides extractants have several benefits than those without phosphorus especially if they have some specific advantages on their extraction behavior and chemical stability.

It is expected that an increase in number of phosphoryl groups in extractants enhances the extraction behavior of metal ions due to a stronger chelating effect with oxygen coordination of phosphine oxides to metal ions. In addition, better extraction behavior is reported for aryl-substituted polyphosphine polyoxides than for alkyl-substituted ones\[10\]. Based on the above, we have paid attention to 1,1,3,5,5-pentaphenyl-1,3,5-triphosphapentane trioxide (PPTPT) and 1,1,5,5,2',2'-hexaphenyl-1,3,5,2'-tetraphospha-3-ethylpentane tetraoxide (HPTEPT) (Fig. 1), one of the aprotic triphosphine trioxides and tetraphosphine tetraoxides, respectively. As the result of the examination of their extraction behavior for some metal ions in the form of a silica-supported solid impregnated adsorbent in HNO₃, e.g., quite unusual adsorption behavior which is not observed for other types of extractants was found for U(VI) for PPTPT\[9\]. The silica supports have macropores and the pores are coated by polymers by the direct polymerization of the silica and monomers. This technique comes from the synthesis of an anion exchange resin for uranium enrichment system developed by Asahi Kasei Corporation ca. 30 years ago\[11\]. The use of silica support has an advantage in column operations because they can suppress swelling and shrinkage of adsorbents originated from changes in the nature of solutions passing through the column. Similar silica-supported adsorbents are studied by other research groups\[12-14\].

More data have to be obtained to evaluate the applicability of the two extractants for practical use. In the present study, therefore, extraction behavior of PPTPT and HPTEPT from HNO₃ and HCl was investigated mainly for fission products elements (FPs) more extensively by solid-liquid adsorption using the above-mentioned adsorbent and liquid-liquid extraction. The examination for plural acid media was intended to support the clarification of the interaction of the two polyphosphine polyoxides with metal ions.

Fig. 1. Chemical structures of PPTPT (left) and HPTEPT (right).
2. Experimental

2.1. Solid-liquid adsorption

The two silica-supported adsorbents for PPTPT and HPTEPT were prepared in the same manner as the earlier paper[9]. PPTPT and HPTEPT were purchased from Yashima Pure Chemicals Co., Ltd., Osaka, Japan, and Koyo Chemical Co., Ltd., Hyogo, Japan, respectively. Adsorptivities of PPTPT and HPTEPT adsorbents to metal ions at equilibrium were obtained by a batch method. Examined metal ions were Fe(III), Cu(II), Zr(IV), Mo(VI), Ru(III), Pd(II), Ag(I), and Sr(II) for HNO₃ media, where Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, ZrO(NO₃)₂·2H₂O, (NH₄)₆Mo7O24, a 1.5% solution of Ru(NO)(NO₃)x(OH)y in diluted HNO₃ (x + y = 3) from Aldrich, a 3 mol/dm³ (=M) HNO₃ solution containing 50 g/dm³ Pd(II) from Tanaka Kikinzoku Kogyo, AgNO₃, and Sr(NO₃)₂ were applied. While, Al(III), V(IV), Fe(III), Cu(II), Zr(IV), Mo(V, VI), Pd(II), Sr(II), and Nd(III) were examined for HCl media, where Al(III)Cl₃·6H₂O, VOCl₂, FeCl₃·6H₂O, CuCl₂·2H₂O, ZrOCl₂·8H₂O, MoCl₅, (NH₄)₆Mo7O24, PdCl₂, SrCl₂·6H₂O were applied, respectively. Some of the above metal ions were examined only for HPTEPT.

Samples of the adsorbent (0.1 g) and 2 cm³ of 0.1 - 9 M HNO₃ or HCl solutions containing metal ions (10 mM) were shaken at 298 K for 24 h in a thermostatic shaking bath. Samples of the supernatant were taken after contact and the concentrations of metal ions were measured using ICP-AES. Adsorptivities were evaluated by the distribution ratio, \( K_d \), defined as,

\[
K_d = \frac{C_0 - C}{C} \times \frac{V}{W} \text{ (cm}^3/\text{g)}
\]

where \( C_0 \) and \( C \) denote the concentrations of the metal ion in the solution before and after contact with the adsorbent, respectively. \( V \) and \( W \) represent the volume of the solution and the weight of the adsorbent including silica, respectively. \( C_0 \) and \( C \) for each metal ion were determined by ICP-AES.

2.2. Liquid-liquid extraction

Extraction experiments were carried out by a batch method. Dichloromethane containing 20 mM PPTPT or HPTEPT, and 0.1 - 6 M HNO₃ or HCl solutions containing metal ions (1 mM) were used as an organic phase and an aqueous phase, respectively. After the pre-equilibrium of the organic phase, both phases were mixed at an equivalent volume (6 cm³) and were shaken manually at an appropriate interval at room temperature. Samples of the aqueous phase were taken after contact for 10 min and the concentrations of metal ions were measured using ICP-AES. The contact time which is much shorter than that of the adsorption experiments was set from the preliminary experiment, where Nd(III) in 0.1 M HNO₃ attained an extraction equilibrium at ca. 1 min of contact. Extraction behavior was evaluated by the distribution ratio, \( D \), calculated as,

\[
D = \frac{C_0 - C}{C}
\]

due to the volume ratio of organic phase / aqueous phase = 1 in the present study, where \( C_0 \) and \( C \) denote the concentrations of the metal ion in the aqueous phase before and after contact with the extractant, respectively.

3. Results and discussion

3.1. Adsorptivity and extraction behavior of PPTPT

Adsorptivity of PPTPT adsorbent in HNO₃ media newly obtained in the present study is shown with the earlier results in Fig. 2. It is found that Fe(III) is adsorbed similarly to Nd(III), where the \( K_d \) values increase with increasing concentration of HNO₃. It is also found that the adsorption of Ru(III) is very weak.
Liquid-liquid extraction behavior of PPTPT in HNO₃ is shown in Fig. 3. It can be seen that Zr(IV) and Nd(III) are highly extracted. In addition, Nd(III) has a maximum $K_d$ value at around 1 to 3 M HNO₃ unlike the cases for adsorption system where $K_d$ values increase with increasing concentration of HNO₃. It should also be noted that PPTPT shows higher selectivity to Nd(III) in the extraction system compared with the adsorption one. On the contrary, extraction behavior of Mo(VI) is found low, although it is highly adsorbed to the adsorbent. The $K_d$ values for Sr(II) in the extraction system are found very low in all examined concentration range of HNO₃.

Comparing Figs. 2 and 3, the dependence of $K_d$ values on the concentration of HNO₃ is found different in Nd(III) and Sr(II). It is known that extractants consisting of diglycolamides such as TODGA are tridentate ligands with two carbonyl and an ether oxygen atoms[5]. Interestingly, the tendencies of Nd(III) and Sr(II) for the extraction system for diglycolamides with a diluent of n-dodecane are more similar to those for our adsorption system (Fig. 2) than the extraction one (Fig. 3). The reasons remain unclear. In this regard, extraction behavior of various chain ether compounds with a phosphine oxide at both ends has been investigated in HCl system with several diluents such as chloroform and toluene, where extraction behavior was found to differ depending on the kind of diluents[15]. This indicates that further investigations using other diluents would be necessary for our system.

Extraction behavior of PPTPT in HCl is shown in Fig. 4. It was revealed that Mo(V), Zr(IV), Fe(III) and Nd(III) are extracted at higher concentration range of HCl. These metal ions mainly exist as anionic species under these solution conditions, and the extraction mechanisms should be clarified in the future. It can be seen from the comparison of Figs. 3 and 4 that dependence of $K_d$ values on acid concentration is more distinguished in HCl system than in HNO₃. Extraction behavior of a number of extractants including some of the extractants described in the above Ref.[15] has been investigated both for HNO₃[16] and HCl[17] media, where extraction behavior was found to differ depending on the kind of extractants. So far, no distinguished difference is observed for the adsorption/extraction behavior between PPTPT of a triphosphine trioxide in the present study and bidentate diphosphine dioxides[18], except the unusual adsorption behavior found for U(VI) in PPTPT, as described above. The examination of other alkyl-substituted phosphine oxides would help the optimization of the combined system of the extractant and the diluent.

3.2. Adsorptivity of HPTEPT

Adsorptivity of HPTEPT adsorbent to various metal ions in HNO₃ is shown in Fig. 5 with the data for Nd(III) which had been obtained earlier[9]. As a whole, $K_d$ values are lower compared with those of PPTPT (Fig. 1). It can also seen that the selectivity to Zr(IV) is not high.

Adsorptivity in HCl is shown in Fig. 6. Nd(III), Mo(V, VI) and Fe(III) were highly adsorbed at higher concentration range of HCl. In general, Zr(IV) is widely adsorbed or extracted by various adsorbents or extractants in HCl and HNO₃ media, e.g., as shown in the literature[19]. It is, therefore, of great interest that Zr(IV) had no
adsorption. The reason still remains unclear, but it is difficult to expect the reason except a certain kind of steric hindrance.

Fig. 3 Extraction behavior of PPTPT to various metal ions in HNO₃ solutions.

Fig. 4 Extraction behavior of PPTPT to various metal ions in HCl solutions.

Fig. 5 Adsorptivity of HPTEPT adsorbent to various metal ions in HNO₃ solutions.

Fig. 6 Adsorptivity of HPTEPT adsorbent to various metal ions in HCl solutions.
3.3. Slope analysis

As a part of clarifying the adsorption/extraction mechanism of both extractants, slope analyses were carried out in 6 M HNO₃ and HCl for Nd(III). The results for PPTPT and HPTEPT are shown in Figs. 7 and 8, respectively. As can be seen in Fig. 7, the slopes for PPTPT are 2.7 and 2.4 for HNO₃ and HCl systems, respectively. This suggests that nearly three PPTPT molecules are necessary for the extraction of one Nd(III) ion in both systems. While, it is found in Fig. 8 that the slopes for HPTEPT are 1.8 and 1.3 for HNO₃ and HCl systems, respectively, which are smaller than the values for the PPTPT cases. This implies that nearly one and two HPTEPT molecules are necessary in HNO₃ and HCl systems, respectively. Namely, smaller numbers of HPTEPT molecules than the case for PPTPT participate in the extraction of one Nd(III) ion. These facts imply that, for extraction of Nd(III), plural PPTPT molecules surround only one Nd(III) ion like other bidentate extractants for instance[18]. On the other hand, it is expected that some of one HPTEPT molecule binds at least two Nd(III) ions by crosslinking, as shown in Fig. 9, because it would be impossible from the steric viewpoint that four phosphoryl oxygen atoms in one HPTEPT molecule surround and coordinate to one Nd(III) ion. Such a crosslinking may apply to the extraction of HPTEPT for other metal ions. The above facts indicate that the adsorption/extraction behavior of triphosphine trioxides and tetraphosphine tetraoxides is greatly different for some metal ions.

![Fig. 7 Dependence of PPTPT concentration on extraction of Nd(III)](image1)

![Fig. 8 Dependence of HPTEPT concentration on extraction of Nd(III)](image2)

![Fig. 9 Expected binding behavior of some of HPTEPT molecules and Nd(III)](image3)
4. Conclusions

Extraction behavior of PPTPT and HPTEPT, one of the aprotic triphosphine trioxides and tetraphosphine tetraoxides, respectively, from HNO₃ and HCl was investigated mainly for FPs more extensively by solid-liquid adsorption using the silica-supported adsorbent and liquid-liquid extraction. As the result, in general, Zr(IV), Mo(VI), Nd(III), and Fe(III) were found to be extracted by both of PPTPT and HPTEPT except no adsorption of Zr(IV) by HPTEPT adsorbent in HCl. This suggests that the dependence of acid concentrations on $K_d$ values of PPTPT for major FPs are basically similar to those of bidentate diphosphine dioxides. It was also found that selectivity to PPTPT and HPTEPT differs depending on metal ions and acidic media. In addition, it was suggested that less HPTEPT molecules are necessary for the extraction of one metal ion compared with the cases for PPTPT, which indicates that the adsorption/extraction behavior of triphosphine trioxides and tetraphosphine tetraoxides is greatly different for some metal ions.

References

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