研究論文

317. *Inorganic Extraction Studies on the System
of Some Diphosphonates-nitric Acid**Tetrabutyl methylene-diphosphonate and
tetrabutyl ethylene-diphosphonate*

10 % TBEDP, TBMDP キシレン溶液-硝酸系における諸元素の分配

By Tomitaro ISHIMORI*, Kan KIMURA*,
Eiko NAKAMURA*, Johkun AKATSU* and Toshiko KOBUNE*

A radiochemical study on the solvent extraction behavior of about sixty chemical elements performed in 10%TBEDP- and 10%TBMDP-nitric acid systems, respectively. The acidity of the aqueous phase was changed from 1 to 15 N.

The acid dependence curves obtained for each element were very similar between the two systems studied. Considerable regularities were found with respect to the extraction behavior of the corresponding congeners. It was also found that the present results for both systems are fairly similar to those of 100 %TBP-HNO₃ system.

INTRODUCTION

Many organic phosphate esters and phosphine oxides are now known to extract some chemical elements, including tri-*n*-butyl phosphate (TBP) which has been proved to be extractant. The extraction properties of TBP, and some phosphine oxides were systematically surveyed before⁽¹⁾⁻⁽⁴⁾. Following these surveys, organic diphosphonate esters were studied as the extracting agent for inorganic ions.

In the present work, two of the diphosphonates, tetrabutyl methylene-diphosphonate (TBMDP)** and tetrabutyl ethylene-diphosphonate (TBEDP)** were chosen as the extractant, and the systematic extraction study was carried out radiometrically for about sixty chemical elements, from sodium to neptunium, in 10 % (v/v) TBMDP- and 10 % (v/v) TBEDP-nitric acid systems, respectively. These agents have been a little studied by the other investigators already⁽⁵⁾⁽⁶⁾.

EXPERIMENTAL

1. Reagents

TBEDP and TBMDP received from the Tama Chem. Co., Tokyo, was used without further purification and diluted to 10 % with xylene, c.p. grade. Nitric acid solutions were prepared by diluting commercial concentrated nitric acid. The acidity was adjusted volumetrically whenever necessary.

2. Radioisotopes

The radioactive isotopes used in this experiment were mainly prepared by irradiation of high purity targets in JRR-1**, or JRR-2**

* 石森富太郎, 木村 幹, 中村永子, 吾勝常勲, 小船敏子. Chem. Div., Japan Atomic Energy Res. Inst. (日本原子力研究所 化学部)

** Tetrabutyl ethylene diphosphonate and tetrabutyl methylene diphosphonate are abbreviated as TBEDP and TBMDP respectively.

** neutron flux: $5 \times 10^{11} \text{ n/sec} \cdot \text{cm}^2$

** neutron flux: $\sim 10^{13} \text{ n/sec} \cdot \text{cm}^2$

or a linear electron accelerator, JAERI, whereas some of the isotopes were imported from the Oak Ridge National Laboratory, USA and from the Radiochemical Centre, Amersham, UK, or obtained from Radioisotope Production Facilities, JAERI. The checking methods of the radiochemical purity and the specific activity were the same as those reported in the previous papers⁽¹⁾⁽⁷⁾. Table 1 shows the radioisotopes used together with their target materials and remarks. In most cases, familiar chemical forms were chosen as far as possible, and in some cases, the oxidation states and the chemical forms of the tracers were clearly defined, as shown in Table 2. In the case of gold, the ionic species might be chlorocomplex because gold target was dissolved with aqua regia.

Table 1 Sources of radioactive tracers used

Element	Tracer	Target	Remarks
Na	²⁴ Na	Na ₂ CO ₃	
Mg	²⁷ Mg	Mg-metal	
Al	²⁶ Al	Al-metal	
P	³² P		Production Group, JAERI
S	³⁵ S		Production Group, JAERI
Cl	³⁶ Cl	NH ₄ Cl	
K	⁴² K	KNO ₃	
Ca	⁴⁵ Ca		imported
Sc	⁴⁶ Sc		imported
Ti	⁵¹ Ti	Ti hydroxide	
V	⁵² V	NH ₄ VO ₃	
Cr	⁵¹ Cr		imported
Mn	⁵⁶ Mn	MnO ₂	
Fe	^{55, 59} Fe		imported
Co	⁶⁰ Co		imported
Ni	⁶⁵ Ni	Ni sponge	
Cu	⁶⁴ Cu	Cu metal	
Zn	⁶⁵ Zn		imported
Ga	⁷² Ga	Ga ₂ O ₃	
Ge	⁷¹ Ge	GeO ₂	
As	⁷⁶ As	As ₂ O ₃	
Se	⁷⁵ Se		imported
Br	^{80, 80m} Br	NH ₄ Br	
Rb	⁸⁶ Rb		imported
Sr	⁸⁵ Sr		imported
Y	⁸⁸ Y	Y ₂ O ₃	(LINIAC)
Zr	⁹⁵ Zr		imported
Nb	⁹⁵ Nb		imported
Mo	⁹⁹ Mo	molybdate	
Tc	⁹⁹ Tc		imported

Element	Tracer	Target	Remarks
Ru	¹⁰⁶ Ru		imported
Pd	¹⁰⁹ Pd	Pd metal	¹¹¹ Ag was removed by pptn. of AgCl after addition of Ag carrier.
Ag	^{110m} Ag	AgNO ₃	
Cd	^{115m} Cd		imported
In	^{114m} In		imported
Sn	¹¹³ Sn		imported
Sb	¹²⁴ Sb		imported
Te	^{127, 129} Te	TeO ₂	
I	¹³¹ I		Production Group, JAERI
Cs	¹³⁷ Cs		imported
Ba	¹³⁹ Ba	Ba(OH) ₂ ·2H ₂ O	
La	¹⁴⁰ La	La ₂ O ₃	
Ce	¹⁴⁴ Ce		imported
Pm	¹⁴⁷ Pm		imported
Eu	^{152, 154} Eu		imported
Tb	¹⁶⁰ Tb	Tb ₄ O ₇	
Lu	¹⁷⁷ Lu	Lu ₂ O ₃	
Hf	¹⁸¹ Hf		imported
Ta	¹⁸² Ta		imported
W	¹⁸⁵ W		imported
Re	^{186, 188} Re	Re metal	
Os	¹⁹¹ Os		imported
Pt	^{193m, 197} Pt	Pt metal	¹⁹⁹ Au was removed ⁽³⁾ .
Ir	¹⁹⁴ Ir	Ir sponge	
Au	¹⁹⁸ Au	Au metal	
Hg	²⁰³ Hg		imported
Tl	²⁰⁴ Tl		imported
Pb	²¹² Pb		collected from ²³² ThO ₂
Bi	²¹⁰ Bi		separated from RaD ⁽¹⁾
Th	²³¹ Th	ThO ₂	(LINIAC) processed by TBP-extraction ⁽⁹⁾
Pa	²³³ Pa	Th(NO ₃) ₄	Processed by TBP-extraction
U	²³⁷ U	UO ₂	(LINIAC) processed by TBP-extraction ⁽¹¹⁾
Np	²³⁹ Np	UO ₂ (NO ₃) ₂	Processed by TBP-extraction

Table 2 Chemical treatment of tracers

Element	Treatment	Oxidation state obtained
As	Reduced with ascorbic acid	3
	Oxidized with KClO ₃	5
Se	Warming in 4 N hydrochloric acid	4
Sn	Oxidized with KClO ₃	4
Sb	Reduced with ascorbic acid	3
	Oxidized with KBrO ₃	5
Hg	Heated in concentrated nitric acid	2
Tl	Oxidized with 0.1 M ceric ammonium nitrate	3

Fig. 1 10% TBEDP- HNO_3 acid dependence

Fig. 2 10 % TBMDP- HNO_3 acid dependence

Element	Treatment	Oxidation state obtained
Ce	Reduced with hydroxylamine	3
	Oxidized with 0.1 M ceric ammonium nitrate	4
Np	Reduced with hydroquinone and KI	4
	Eliminating Np^{+4} and Np^{+6} with 100 % TBP	5

The distribution ratios were determined

radiometrically changing nitric acid concentration⁽⁸⁾⁽⁹⁾.

A portion of organic solution was contacted with the equal volume of acid solution containing the radioisotopes, after being pre-equilibrated with barren acid solution. The resultant organic or aqueous solution was sometimes scrubbed with fresh acid or organic solution, respectively, in order to obtain the exact distribution ratios.

Fig. 4 K_d values in 10% TBMDP- HNO_3

RESULTS AND DISCUSSION

Figs. 1 and 2 represent the acid dependence curves of distribution ratios in the systems of TBEDP- and TBMDP- HNO_3 , respectively, as a series of graphs of $\log K_d$ vs. $N \text{HNO}_3$, where K_d is the distribution ratio and N the normality.

As are seen in Figs. 1 and 2, K_d values

for many elements are generally low, and the acid dependence curve for each element in the system of TBMDP- HNO_3 is very similar to that of TBEDP- HNO_3 system.

None of alkali and alkaline earth metal ions are extractable at all in the whole acidity range studied.

Acid dependence curves for lanthanide elements are generally low, however, as are seen in Figs. 1 and 2, K_d values increase gra-

dually with increasing atomic number.

K_d values for scandium, yttrium and lanthanum decrease with increasing atomic number, so scandium has very high K_d values ($\sim 10^3$) in $\sim 3N$ HNO_3 media.

On the contrary to these elements, K_d values increase remarkably or little by little with increasing atomic number in some other series, like titanium, zirconium and hafnium; vanadium, niobium and tantalum; or halogen ions. This tendency is also seen in the series of copper, silver and gold, or of zinc, cadmium and mercury. For example, titanium, zirconium and hafnium give K_d values of 2×10^{-1} , 7 and 9×10 at $3.5N$ nitric acid respectively, in TBEDP- HNO_3 system. This results show also that hafnium is one of the most extractable element in both systems studied.

Both thorium and uranium are extracted well from $\sim 11N$ nitric acid solution. $Np(IV)$ and (V) is also extractable, however, the K_d values are somewhat small comparing with those of the above two elements.

The distribution ratios for protactinium are remarkably low in TBMDP- HNO_3 system compared to those for other actinide elements studied. In the system of TBEDP- HNO_3 , actinide elements including protactinium gives always high K_d values.

The K_d values for many elements change little with varying the acidity in the systems studied. Those values of tantalum give typical examples as are given in Figs. 1 and 2.

The strong similarity was observed between the two systems studied and 100%TBP- HNO_3 system⁽²⁾. For example scandium, zirconium, hafnium, niobium, gold and actinide elements

are extractable in both systems. Especially, uranium shows almost the same behavior in 100%TBP and 10%TBEDP- HNO_3 systems.

Appreciable difference between the extraction behavior in the two systems and 100% TBP- HNO_3 system are observed in the acid dependence curves of several elements, above all, scandium and hafnium, which show high K_d values in the low acidity region in TBEDP- and TBMDP- HNO_3 system, and in high acidity region in TBP- HNO_3 system.

Figs. 3 and 4 show precise K_d values in 10%TBEDP- and 10%TBMDP- HNO_3 systems.

(Received February 11, 1963)

—REFERENCE—

- (1) T. ISHIMORI, K. WATANABE, E. NAKAMURA: *Bull. Chem. Soc. Japan*, **33**, 636 (1960).
- (2) T. ISHIMORI, K. WATANABE: *ibid.*, **33**, 1443 (1960).
- (3) T. ISHIMORI, K. WATANABE, T. FUJINO: *This Journal*, **3**, No. 1, 19 (1961).
- (4) T. ISHIMORI, K. KIMURA, T. FUJINO, H. MURAKAMI: *ibid.*, **4**, No. 2, 117 (1962).
- (5) T. V. HEARLY, J. KENNEDY: *J. Inorg. Nucl. Chem.*, **10**, 128 (1959).
- (6) H. SAISHO: *Bull. Chem. Soc. Japan*, **34**, No. 6, 859 (1961); **34**, No. 9, 1254 (1961).
- (7) T. ISHIMORI, K. WATANABE, K. KIMURA: *This Journal*, **2**, No. 12, 750~757 (1960).
- (8) K. KIMURA: *Bull. Chem. Soc. Japan*, **33**, 1038 (1960).
- (9) T. ISHIMORI, E. NAKAMURA: *ibid.*, **32**, 713 (1959).
- (10) E. NAKAMURA: *Radiochimica Acta*, **2**, 66 (1963).
- (11) E. AKATSU, T. KUROYANAGI, T. ISHIMORI: To be published.