研究論文

271. *Inorganic Extraction Studies on the System
Alkylamine-nitric Acid**Amberlite LA-1 and tri-iso-octylamine*

アルキルアミン-硝酸系における諸元素の行動

アンバーライト LA-1 およびトリイソオクチルアミン

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The solvent extraction behavior of about sixty chemical elements was extensively surveyed in the alkylamine-nitric acid system, clarifying radiochemically the acid dependence of distribution ratios. The organic phases used were 10% (V/V) Amberlite LA-1 and 5% (V/V) tri-iso-octylamine xylene solution.

The highly extractable chemical species were not so many in number through two extraction systems. In most cases the acid dependence curves of a given element were not only similar each other between the two systems, but also resembled to that in 100% TBP-HNO₃ system. The exceptional high K_d value of technetium at 1 N HNO₃ suggested an application to separating ^{99m}Tc from neutron irradiated ammonium molybdate.

The alkylamines as the solvent extraction agent had been widely studied by many investigators from various point of view and in fact a few hundreds papers had been published before. However, these published results were given each in their own way.

So the extraction behavior of about sixty chemical elements, ranging from sodium to uranium, in Amberlite LA-1 (10% xylene solution)-and tri-iso-octylamine (5% xylene solution)-nitric acid system was comprehensively surveyed following solvent extraction study on the same alkylamines-hydrochloric acid system reported in the previous paper⁽¹⁾.

EXPERIMENTAL

1. Reagents

Tri-iso-octylamine received from the Union Carbide and Chemicals Corp., N. Y., and

Amberlite LA-1, high molecular weight secondary amine, were used as 5% and 10% (V/V) xylene solution without further purification respectively.

Nitric acid solutions were prepared by diluting commercial concentrated nitric acid, analytical grade. The acidity was adjusted to desired concentrations with aids of volumetric analysis.

2. Radioisotopes used

Table 1 includes a list of the radioisotopes used together with their target materials and purification methods whenever necessary. The imported radioisotopes were received from the ORNL, USA, or the Radiochemical Centre, Amersham, UK. Irradiation of targets and subsequent chemical treatments,

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method of checking radiochemical purity, specific activities of tracers, and special cautions for measurement of radioactivities for ^{212}Pb , $^{95}\text{Zr-Nb}$, ^{210}Bi , ^{99}Mo and ^{113}Sn were the same as the previous work⁽²⁾.

The radioactivities of ^{88}Y , ^{231}Th and ^{237}U were obtained as products of (γ, n) reaction caused by γ -rays from the linear accelerator of JAERI.

All of tracers were converted to nitrate before use. The definite oxidation states of

Table 1 Radioactive tracers used

Tracer	Target (irradiated in) and chemical treatment
^{24}Na	Na_2CO_3 (JRR-1)†
^{27}Mg	Mg-metal (JRR-1)
^{28}Al	Al-metal (JRR-1)
^{32}P	JAERI, interim facilities for radio-isotope production
^{35}S	JAERI, interim facilities for radio-isotope production
^{38}Cl	NH_4Cl (JRR-1)
^{42}K	KNO_3 (JRR-1)
^{45}Ca	imported
^{48}Sc	Sc_2O_3 (JRR-2)††
^{51}Ti	Ti hydroxide (JRR-1)
^{52}V	NH_4VO_3 (JRR-1)
^{51}Cr	JAERI, interim facilities for radio-isotope production
^{56}Mn	MnO_2 (JRR-1)
$^{55, 59}\text{Fe}$	imported
^{60}Co	imported
^{65}Ni	Ni sponge (JRR-1), separated from Co.
^{64}Cu	Cu metal (JRR-1)
^{65}Zn	imported
^{72}Ga	Ga_2O_3 (JRR-1)
^{71}Ge	GeO_2 (JRR-2)
^{76}As	As_2O_3 (JRR-1)
^{76}Se	imported
$^{80, 80\text{m}}\text{Br}$	NH_4Br (JRR-1)
^{86}Rb	imported
^{90}Sr	milking from ^{90}Sr
^{85}Sr	imported
^{91}Y	imported
^{88}Y	Y_2O_3 (LINIAC)
^{95}Zr	imported
^{95}Nb	imported
^{99}Mo	ammonium molybdate (JRR-1)
^{99}Tc	imported
^{106}Ru	imported
^{109}Pd	Pd metal (JRR-1), purified from ^{111}Ag
$^{110\text{m}}\text{Ag}$	AgNO_3 (JRR-1)
$^{115\text{m}}\text{Cd}$	imported
$^{114\text{m}}\text{In}$	imported
^{113}Sn	imported
^{124}Sb	imported

Tracer	Target (irradiated in) and chemical treatment
$^{127, 129}\text{Te}$	TeO_2 (JRR-2)
^{131}I	JAERI, interim facilities for radio-isotope production
^{137}Cs	imported
^{139}Ba	$\text{Ba}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (JRR-1)
^{140}La	La_2O_3 (JRR-1)
^{144}Ce	imported
^{147}Pm	imported
$^{152, 154}\text{Eu}$	imported
^{160}Tb	Tb_4O_7 (JRR-2)
^{177}Lu	Lu_2O_3 (JRR-1, 2)
^{181}Hf	imported
^{182}Ta	imported
^{185}W	imported
$^{186, 188}\text{Re}$	Re metal (JRR-1)
^{191}Os	imported
^{194}Ir	Ir sponge (JRR-1)
^{199}Pt	Pt sponge (JRR-1), separated from Au
^{198}Au	Au metal (JRR-1)
^{208}Hg	imported
^{204}Tl	imported
^{212}Pb	radioactive deposit of Th
^{210}Bi	milking from RaDEF by TBP extraction
^{231}Th	ThO_2 (LINIAC), separated by TBP extraction ⁽³⁾
^{233}Pa	$\text{Th}(\text{NO}_3)_4$ (JRR-1), separated by TBP extraction ⁽⁴⁾
^{237}U	UO_2 (LINIAC), separated by TBP extraction ⁽⁵⁾
^{239}Np	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (JRR-1), separated by TBP extraction ⁽⁶⁾

† neutron flux = 10^{11} n/cm²/sec

†† neutron flux = 10^{13} n/cm²/sec

Table 2 Chemical treatment of tracers

Element	Treatment
^{3+}As	reduced with ascorbic acid The aqueous solution was scrubbed with the organic solution.
^{5+}As	oxydized with KClO_4 in 6 N HCl
^{4+}Se	heated in 4 N HCl with ascorbic acid
^{3+}Ce	reduced with $\text{NH}_2\text{OH} \cdot \text{HCl}$
^{4+}Ce	oxydized with ceric ammonium nitrate The organic solution was scrubbed 3 times.
^{2+}Hg	heated in conc. HNO_3
^{1+}Tl	reduced with $\text{NH}_2\text{OH} \cdot \text{HCl}$
^{3+}Tl	oxydized with ceric ammonium nitrate
^{4+}Np	reduced with ferrous sulfamate The organic layer was scrubbed 4 times with the fresh aqueous solution.
^{5+}Np	^{4+}Np and ^{6+}Np was removed after heating in 1 N HClO_4 solution.
^{6+}Np	oxydized with ceric ammonium nitrate The scrubbing was the same above.

† Ichikawa and Uruno, 5% kerosene soln.

Fig. 1 10% Amberlite LA-1 xylene-HNO₃ acid dependence

Fig. 2 5% tri-iso-octylamine xylene- HNO_3 acid dependence

Fig. 3 Decay curve of ^{99m}Tc

some tracers were attained by the suitable chemical treatment appearing in Table 2.

3. Determination of distribution ratios

Distribution ratios were determined radio-metrically as was stated in the previous paper⁽¹⁾. In the present work, the organic phase was pre-equilibrated with the corresponding nitric acid.

RESULTS AND DISCUSSION

The results obtained are summarized in Figs. 1 and 2 as a series of graphs of $\log K_d$ vs. normality of nitric acid, where K_d is the distribution ratio. Because of insufficient amount of radioactivities obtained or too low K_d value, some distribution ratios could not be determined very accurately.

It is seen in Figs. 1 and 2 that K_d values are generally low in the surveyed solvent

Fig. 4 Preparation of ^{99m}Tc

Fig. 5 K_d values in 10% LA-1-HNO₃ system

extraction systems. The extractable species with 5% TIOA* xylene solution are bromine, iodine, gold, thallium, and neptunium(VI); technetium, paradium, rhenium and cerium(IV) in low acidity region. On the other hand, 10% Amberlite LA-1 xylene solution extracts bromine, iodine, zirconium, niobium, technetium, hafnium, tungsten, rhenium, gold and protactinium.

Generally speaking, acid dependence curves of a given element are very similar each other between the two extraction systems concerning K_d values and the shape of curve. The distribution ratios for technetium, tung-

sten, rhenium, and bismuth decrease with increasing acidity, while those for chlorine, bromine, niobium and silver increase with increasing acidity in both solvent extraction systems.

The extraction curves of cerium(IV), thorium and uranium have peaks at about 7 N acid.

The distribution ratios for arsenic(III), zirconium, niobium, molybdenum, technetium, iodine, tin(IV), hafnium and protactinium in Amberlite LA-1 system are remarkably higher than those in TIOA system. Contrary to

* tri-*iso*-octylamine

Fig. 6 K_d values in 5% TIOA- HNO_3 system

these elements, cerium(IV) and thorium are more extractable in TIOA- HNO_3 system than Amberlite LA-1.

Most acid dependence curves of a given element in the present extraction systems are very close to that in 100% TBP- HNO_3 system⁽⁷⁾. Especially the similarity between 10% Amberlite LA-1 and 100% TBP- HNO_3

systems is proved except for scandium, yttrium, lanthanum and lanthanide elements which indicate higher K_d values in the TBP extraction system.

Figs. 1 and 2 also contain other investigators' results for thorium⁽⁸⁾⁽⁹⁾, protactinium⁽⁸⁾, uranium⁽⁸⁾ and plutonium⁽⁸⁾. Although slight differences are found between these known

acid dependence curves and the present, this could be attributed to the different conditions in the organic diluent or in the concentration of alkylamines chosen.

Technetium-99m is available as a radioactive tracer after isolating from neutron irradiated molybdenum compound. Figs. 1 and 2 give an isolation method basing on fairly high K_d values of technetium and low values of molybdenum at 1N HNO_3 in the amine extraction. Starting from 2.5 mg ammonium molybdate irradiated in JRR-1 for 5 hr and cooled for 6 days, about 1 mc of technetium-99m was extracted with 5% Amberlite LA-1 xylene solution from 1N HNO_3 . The radiochemical purity was shown to be 99.8% from the decay curve measurement (Fig. 3). The separation process used is represented in Fig. 4.

Figs. 5 and 6 give the exact K_d values for each element. These figures serve an advantage to see easily the difference of K_d values of two elements.

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研究論文

272. A Study of Plutonium Recycle in a Gas-cooled, Graphite-moderated Reactor, (II)

黒鉛減速ガス冷却炉におけるプルトニウムリサイクルの研究, (II)

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The modified bidirectional fuel management method on plutonium recycle in a gas-cooled and graphite-moderated reactor was investigated. The modified bidirectional fuel management was so designed that the fresher fuel and the more burned fuel existed at the outer and inner regions of the reactor, respectively, to reduce the peak to average ratio of power density.

This fueling method was effective to reduce the peak to average ratio of power density without sacrificing much burn-up of the fuel. The optimum irradiation control factors, A 's, were at around 0.5 and 0.3 for natural uranium feed and 1.0% enriched uranium feed, respectively.

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