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Extraction of americium and lanthanides with tributylphosphate from water-deficient nitrate media

T. Mitsugashira[a], M. Kamoshida[b], Y. Suzuki[a] and I. Satoh[a]

[a]*The Oari Branch, Institute for Materials Research, Tohoku University, Oarai-machi, Higashiibaraki-gun, Ibaraki-ken 311-13 (Japan)*
[b]*Energy Research Laboratory, Hitachi Ltd., 1168 Moriyama-cho, Hitachi-shi, Ibaraki-ken 316 (Japan)*

Abstract

The extraction of Am and lanthanides (La, Ce, Nd, Pm, Eu, Gd, Tb, Tm, Yb) from water-deficient nitrate medium was studied using tributylphosphate–dodecane solution. Am and lanthanides were highly extractable from salt melt made of $Ca(NO_3)_24H_2O$ and its mixture with $Mg(NO_3)_26H_2O$ at 50–80 °C. The distribution ratio decreased with the increase in the content of water. The decrease was explained by increasing hydration. Extractions for the recovery of Am and lanthanides were carried out successfully using a salt melt made from a simulated waste solution which contained nitric acid.

1. Introduction

The extraction of trivalent transuranium elements (TRUs) must be attained for the development of advanced reprocessing to obtain α-decontaminated liquid waste. Widely used extractants such as tributylphosphate (TBP) and acidic organophosphorus extractants are not suitable for the extraction of trivalent TRUs from nitric acid solution. Advanced extractants have been intensively studied to achieve the extraction. These approaches implicitly assume extraction from a feed solution generated at the U–Pu coextraction stage of the PUREX process.

In contrast, Kubota *et al.* proposed the use of diisodecyl phosphoric acid as an extractant [1]. According to their flow sheet, it is necessary to decompose nitric acid previously. If similar simple pretreatment on a feed solution is feasible, we can claim the possibility of TBP as an extractant for the recovery of trivalent TRUs. Akatsu and coworkers studied the liquid–liquid extraction system of the hydrate melt *vs.* TBP at a little above room temperature and found that TRUs are highly extractable [2–4]. Nitrates of trivalent lanthanides are known to form a stable melt of the hexahydrate below 100 °C. The supercooled lanthanide nitrate hydrate melt is stable at room temperature without forming any solid salts. Thus, it was supposed that a nitric acid solution of trivalent TRUs and lanthanides could be transformed into an inorganic salt melt by neutralization and dehydration. This work was designed to examine the possibility of the inorganic salt melt *vs.* the TBP extraction system as a method for the recovery of trivalent TRUs. As a first step, this report is mainly concerned with the basic behaviour of Am and lanthanides in such water-deficient extraction systems.

2. Experimental details

^{140}La, ^{139}Ce, ^{141}Ce, ^{147}Nd, ^{153}Gd, and ^{177}Lu were produced by neutron irradiation using the Japan Materials Testing Reactor. ^{147}Nd, ^{149}Pm, ^{157}Dy, ^{161}Er, ^{168}Tm and ^{175}Yb were produced from a mixture of the oxides of Nd, Dy, Er, Tm, and Yb through (γ, n) reactions using the bremsstrahlung generated from a Pt converter 2 mm in thickness irradiated by 30 MeV electrons from the Electron Linear Accelerator of Tohoku University. ^{152}Eu and ^{241}Am were supplied from Amersham Japan Ltd. The γ rays of energies 1596 keV of ^{140}La, 166 keV of ^{139}Ce, 145 keV of ^{141}Ce, 91 keV of ^{147}Nd, 286 keV of ^{149}Pm, 97 keV of ^{153}Gd, 326 keV of ^{157}Dy, 827 keV of ^{161}Er, 198 keV of ^{168}Tm, 396 keV of ^{175}Yb, 208 keV of ^{177}Lu, 122 keV of ^{152}Eu, and 59.5 keV of ^{241}Am were used to measure the distribution ratio D.

A nitric acid solution of a mixture of radioactive tracers was evaporated to dryness and the residue was dissolved into a hydrated salt melt made of calcium nitrate tetrahydrate or its 3:1 mixture with magnesium nitrate hexahydrate at 80–90 °C. The latter salt mixture

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was used to observe the extraction behaviour at a water activity A_{aq} lower than 0.25. TBP (99.9% purity) was used as an extractant and reagent grade *n*-dodecane was used as a diluent.

A 1–5 ml aliquot of salt melt was shaken for 60–90 min with a TBP–dodecane solution in a glass vial at a constant temperature. A 1–2 g aliquot of each phase was taken for γ ray spectrometry. The γ ray spectra were accumulated by a Ge detector coupled with an 8 K pulse height analyser. *D* values were calculated as the counting rate ratio of each γ ray peak in 1 cm^3 of each phase taking into account the correction for self-absorption and the change in counting geometry. The correction factors for the self-absorption and counting geometry were calibrated preliminarily as a function of density and the weight of counting sample respectively. The accuracy of the estimated *D* values depends mainly on the counting statistics. The spectrum accumulation time and the quantity of a counting sample were adjusted so as to obtain the net peak counts of each γ ray peak larger than 3000. The standard deviation ratios for estimated *D* values were about 30% at $D=100$ and less than 10% at $D=1$–10.

In order to elucidate the basic partition behaviour, *D* values were measured as a function of temperature in the range 50–80 °C and A_{aq} in the salt phase. The activity of water was evaluated from humidity measured by a thermohygrometer (TRH-3A, Shinei Co.).

3. Results and discussion

It was found that the extractability of Am and lanthanides in the melt of $Ca(NO_3)_2 4H_2O$ is very large even for the extraction with diluted TBP. The TBP solvation number was found to be 3 as was consistent with the normal aqueous extraction system. *D* values were very sensitive to the water content in the salt phase. It was found that the increase of 0.2 in molar fraction X_{aq} of water from an ideal hydrate melt composition caused a decrease of about 3 orders of magnitude in *D*. Figure 1 shows log *D* *vs.* log A_{aq} plots in the extraction system $Ca(NO_3)_2 \cdot Mg(NO_3)_2 \cdot xH_2O$–0.073 M TBP–dodecane at 60 °C. The data points for Eu and Gd in the low A_{aq} region were reproduced from the *D* values obtained by using 0.036 M TBP–dodecane solution taking into account the TBP–solvation number of 3. The value $A_{aq}=0.27$ corresponds to $X_{aq}=0.62$. As is obvious in Fig. 1, $\partial \log D/\partial \log A_{aq}$ decreases with increasing A_{aq}. This indicates the increase in hydration number. The value of the slope is about -6 at $A_{aq} \leq 0.27$, suggesting a hydration number of 6, *i.e.* equal to the number of water molecules in the hydrate melt of lanthanide nitrate. The slope becomes -10 to -12 at $A_{aq} \approx 0.4$ ($X_{aq} \approx 0.72$). This implies that the hydration number becomes larger than the number of water molecules in the inner sphere of trivalent lanthanides but smaller than the total hydration number observed in an aqueous system [5].

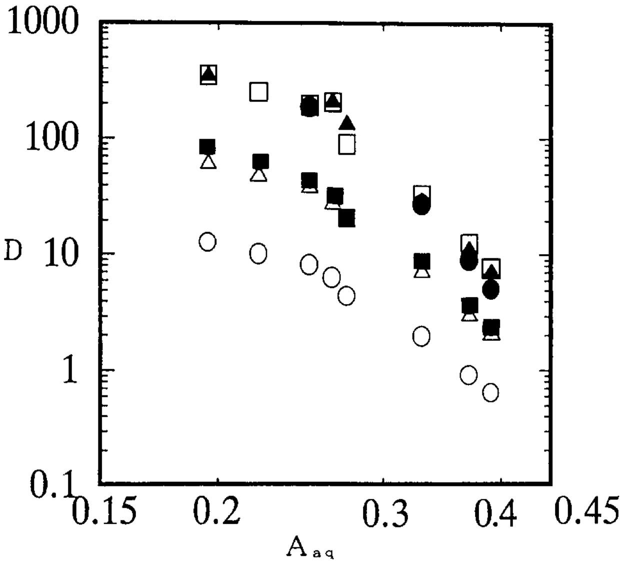

Fig. 1. Change in distribution ratio with the increase in water activity (salt phase, $Ca(NO_3)_2 \cdot Mg(NO_3)_2 \cdot xH_2O$; organic phase, 2 vol.% TBP–dodecane; $T=60$ °C): ○, Ce; △, Nd; □, Eu; ▲, Gd; ●, Lu; ■, Am.

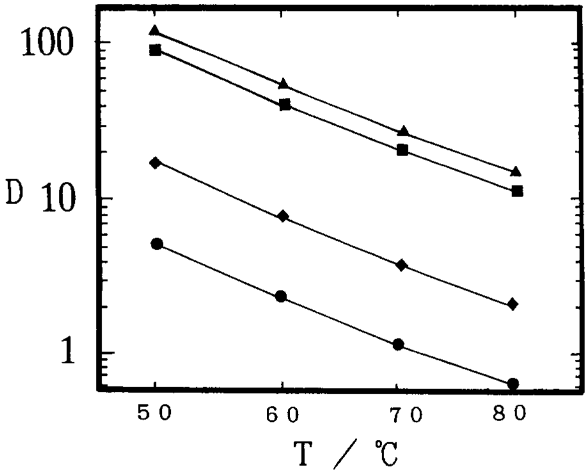

Fig. 2. Effect of temperature on distribution ratios (salt phase, $Ca(NO_3)_2 \cdot 6H_2O$; organic phase, 1 vol.% TBP–dodecane): ●, Ce; ◆, Nd; ▲, Eu; ■, Tm.

D values decrease with the increase in temperature. In Fig. 2, almost parallel curves are shown in the log *D* *vs.* *T* relation. The mutual separation factor α_{Ce} relative to Ce is written as

$$\ln \alpha_{Ce} = \ln(D_{Ln}/D_{Ce}) = -(\Delta H_{Ln} - \Delta H_{Ce})/RT + (\Delta S_{Ln} - \Delta S_{Ce})/R$$

where ΔH_{Ln} and ΔS_{Ln} are the changes in enthalpy and entropy of the extraction reaction. The accuracy of α_{Ce}

was not enough to estimate ΔH_{Ln}-ΔH_{Ce} values, but the finding in Fig. 2, *i.e.* α_{Ce} is independent of T, indicates that $(\Delta H_{Ln}-\Delta H_{Ce})/T<\Delta S_{Ln}-\Delta S_{Ce}$. Then, we assume $\Delta S_{Ln}-\Delta S_{Ce}\approx R\ \ln\ \alpha_{Ce}$. $R\ \ln\ \alpha_{Ce}$ values found in the $Ca(NO_3)_2\cdot 6H_2O$–0.037 M TBP–dodecane system are comparable with the relative values calculated from the corrected entropy of hydrated lanthanide ions evaluated by David *et al.* [6] in Fig. 3. α_{Ce} increases with atomic number and $R\ \ln\ \alpha_{Ce}$ values are nearly equal to the difference in entropy values in light lanthanides. This seems to indicate that the selectivity in this extraction system is affected by the structural change of hydrated ions of lanthanides. However, for Tm and Lu, the increase in α_{Ce} is saturated at much lower values than the corresponding relative entropy values. The reason is not known but is probably related to the too simplified assumption that implicitly expects the same structure of the TBP complex for all lanthanides and Am.

A decrease in D was observed in the extraction system when nitric acid was contained in the initial salt phase. However, the decrease could be explained by the decrease in free TBP concentration in the organic phase caused by the formation of a TBP–HNO_3 adduct whose content was determined by titration when the content of nitric acid was lower than 1 M. This finding seems to suggest that the hydration sphere is not affected by the addition of a small quantity of nitric acid into hydrated melt. The fraction of TBP–HNO_3 adduct in the organic phase is not as large when the concentration of nitric acid is lower than 0.5 M. Thus, we can say that the extraction was not affected greatly by the addition of nitric acid until the concentration exceeded about 0.5 M. A 2.6 M nitric acid solution of ^{241}Am and fission products was prepared as a simulated waste (SLW) in which Cs, Sr, Zr, Ce and Nd were added to concentrations of 0.033 M, 0.017 M, 0.067 M, 0.035 M and 0.089 M respectively. The acidity of the SLW was reduced by the addition of freshly prepared aluminium hydroxide precipitate and it was evaporated nearly to dryness at 80 °C. Then, $Ca(NO_3)_2\cdot 4H_2O$ was added to the salt mixture to adjust $[H_2O]/[Ca]\approx 5$–6 and acidity lower than 0.5 M. The mixture was shaken with 0.67 M TBP–dodecane solution at 60 °C. The D values thus observed are summarized in Table 1. Although the conditions used to prepare the salt melt were not optimized, the high extractability for Am and lanthanides is quite valid. Runs 3 and 4 were carried out using TBP nearly saturated with calcium nitrate. This pretreatment was very effective. This effect indicates that the extraction proceeded through a substitution reaction which suppressed the increase in water content in the salt melt. The results shown in Table 1 suggest clearly the possibility of the application of TBP to the recovery of trivalent TRUs and lanthanides.

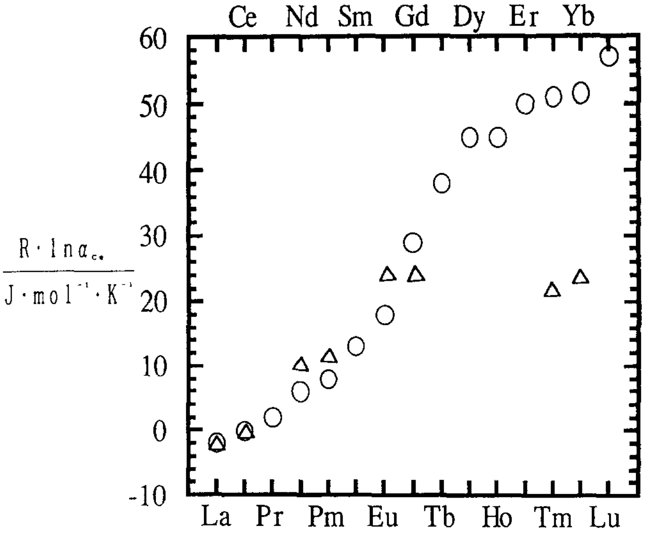

Fig. 3. $R\ \ln\ \alpha_{Ce}$ values compared with relative values of the entropy of trivalent lanthanide ions in aqueous solution: ○, relative entropy calculated from David's entropy values; △, $R\ \ln\ \alpha_{Ce}$ values.

TABLE 1. Extraction from the water-deficient salt mixture made from simulated liquid waste by 10 vol.% TBP–dodecane solution

		Run 1	Run 2	Run 3[a]	Run 4[a]
Salt phase composition	$[H_2O]/[Ca]$	4.9	5.8	6.2	5.6
	$[H^+]$ (M)	1.0	0.5	0.6	0.5
	[Al] (M)	0.23	0.23	0.5	0.5
Distribution ratios	Am	2.2	11	>30	>30
	Ce	0.48	2.2	9.8	7.6
	Zr	<0.07	<0.1	0.23	0.18
	Ru	<0.1	<0.1	0.35	0.21
	Sn	<0.1	<0.1	<0.1	<0.1
	Sb	<0.1	<0.1	<0.1	<0.1

[a] Undiluted TBP was contacted with an equal volume of the melt of $Ca(NO_3)_2\cdot 4H_2O$ before dilution with dodecane.

4. Conclusion

TBP can be used for the recovery of trivalent TRUs and lanthanides from water-deficient nitrate media. Nitric acid solution containing trivalent TRUs and lanthanides can be easily transformed to such water-deficient nitrate media.

D values for the extraction of Am and trivalent lanthanides were very sensitive to the water content in nitrate media. It was found that the increase in hydration number suppresses the extraction of these trivalent cations.

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