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Extraction of Trivalent Actinides and Lanthanides from Nitric Acid Solutions by Ion Flotation

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Abstract

To determine whether the deep extraction of trivalent actinides from liquid active waste is feasible, we made a detailed investigation into the ion flotation of europium (as a simulator of americium) and americium from nitric acid solutions by using as an SAS precipitant either lauril phosphoric acid (LPA) to reprocess 0.1–0.7 *M* HNO_3 or diphosphine dioxides (PO) for 1–5 *M* HNO_3. In all instances the extent of metal removal increases with floto-reagent expenditure. When the floto-reagent excess required for full precipitation is reached, the extraction of the metals under study is high, viz., 97–98% from 0.1 *M* HNO_3 with LPA and ~75% from 3–3.5 *M* HNO_3 with PO per one flotation operation.

INTRODUCTION

Present-day processes of liquid active waste reprocessing comprise extraction and separation by evaporation, ion exchange, coagulation, and precipitation (*1*). To remove microconcentrations of different metals from effluents, the method of flotation has recently been developed. Previously we proposed ion flotation for extraction of tetravalent actinides from nitric acid solutions by using lauril phosphoric acid (LPA) as an SAS precipitant (*2–4*). It was demonstrated that in principle it is feasible to remove plutonium and thorium to 97–100% independent of the nitric acid concentration of solutions reprocessed (1–5 *M* HNO_3). It is no less interesting to ensure the extraction of americium (possibly together with plutonium) from nitric acid solutions. This paper deals with the investigation of the feasibility of such an extraction by ion flotation.

EXPERIMENTAL

Reagents

The experiments were performed by using an americium simulator—a stable isotope of europium tagged with ^{152}Eu and plutonium containing 0.3

mass % americium-241. Aqueous solutions of $Eu(NO_3)_3$ and $Pu(NO_3)_4$ in 0.1–5 *M* HNO_3 containing up to 50 mg/L metal were subjected to flotation. We have already tested LPA as well as diphoshine dioxide (PO) derivatives—tetraphenyl methylene diphosphine dioxide (PPO) and diphenyl di-*p*-tolylmethylenediphosphine dioxide (TPO)—as SAS precipitants.

Experimental Techniques and Instruments

LPA as a 0.3% solution in 2 *M* NH_4OH and PO as a ~0.02 *M* solution in ethanol were added to the solutions under study while stirring intensively for 15 min prior to flotation. The flotation of aqueous nitric acid solutions of metals was performed at room temperature in an acrylic plastic column 500 mm high and 25 mm in diameter, the bottom of which was made of stainless steel. The air flow rate was 2 L/h. The volume of the aqueous solution filling the column was 60 mL. The aqueous solutions were analyzed for europium, plutonium, and americium by radiometric and alpha-spectrometric methods. The efficiency of the process was judged from the final metal concentration of the solution (x_{Me}) and the extent of the metal removal $\alpha = (x^0_{Me} - x_{Me})/x^0_{Me}$ (x^0 is the initial concentration). The SAS precipitant expenditure was taken into account as the mole ratio $\gamma = x^0_{SAS}/x^0_{Me}$.

RESULTS AND DISCUSSION

Europium Extraction with LPA

Ion flotation can be depicted as two sequential processes: 1) formation of a barely soluble hydrophobic precipitate resulting from chemical interaction between metal ions and an SAS precipitant, and 2) forcing it to the surface of the solution by passing air that concentrates it in a thin layer of unstable foam.

Based on these concepts, we first studied the *precipitation of europium laurylphosphate*. Figures 1–4 present our experimental data in the form of curves which show "the extent of removal (α) of the Eu-LPA complex vs the precipitation time (τ_0), concentrations of nitric acid and europium in initial solutions ($x^0_{HNO_3}$ and x^0_{Eu}, respectively), and LPA expenditure (γ)." It can be seen that with an increase of τ_0, α is sharply increased for 15–20 min, while the subsequent growth of τ_0 up to 2 h has an insignificant effect: α increases by only ~10%. Therefore, precipitation was conducted for $\tau_0 = 30$ min in all experiments. α is observed to decrease sharply to 3% with the growth of the acidity of the aqueous solution, even at $x^0_{HNO_3} = 0.68M$. With the growth of γ, a linear increase of α up to $\gamma = 3$ is observed, but then the growth of α slows down.

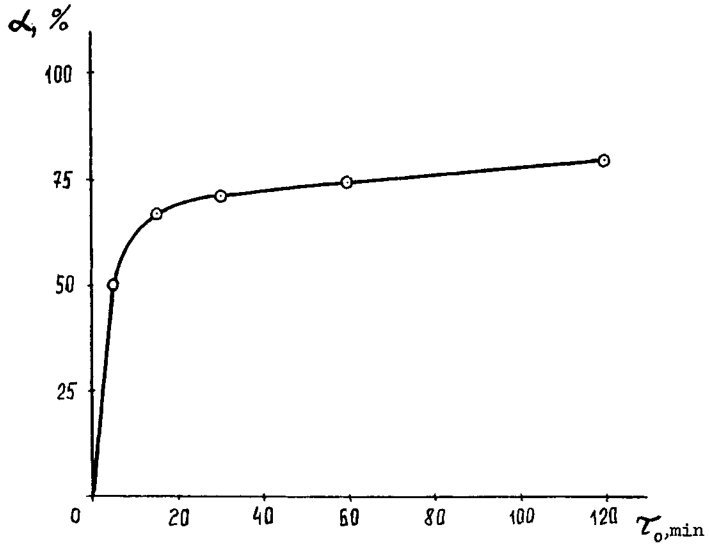

FIG. 1. Precipitation of europium for different process times (τ_0). $x^0_{HNO_3} = 0.1\ M$, $x^0_{Eu} = 1.6 \times 10^{-5}\ M$ or 2.4 mg/L. $x^0_{LPA} = 8.0 \times 10^{-5}\ M$ ($\gamma = 5$).

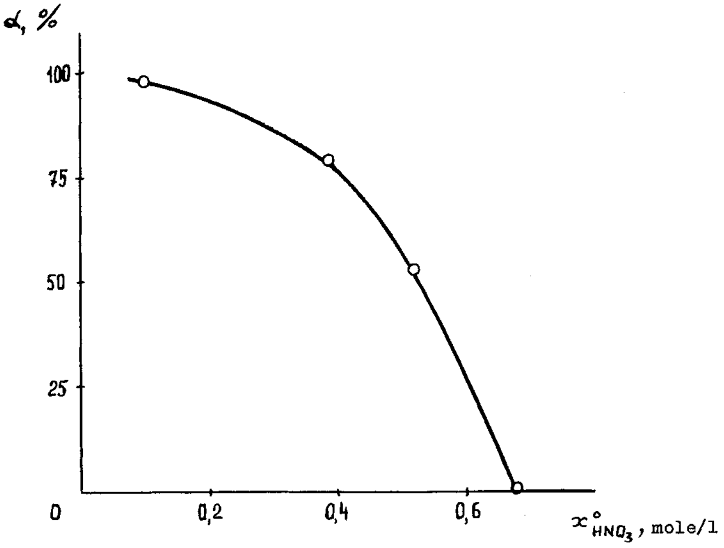

FIG. 2. Precipitation of europium at different HNO_3 concentrations. $x^0_{Eu} = 32.0 \times 10^{-5}\ M$ or 49 mg/L. $x^0_{LPA} = 1.0 \times 10^{-3}\ M$ ($\gamma = 3.1$).

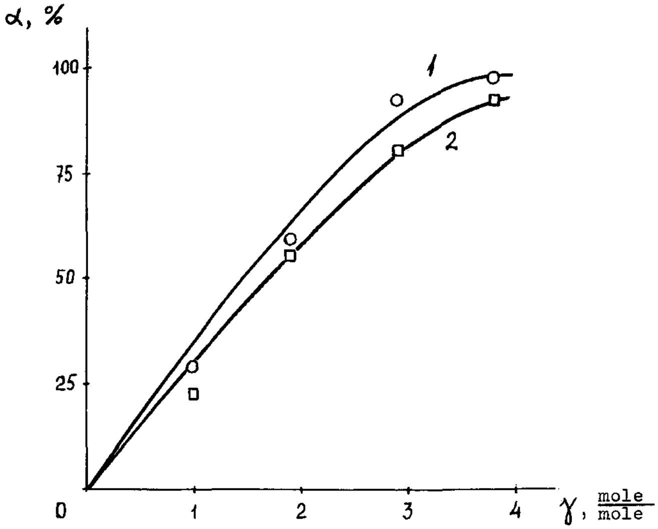

FIG. 3. Precipitation of europium at different LPA expenditures. $x^0_{HNO_3}$ = 0.1 *M*. x^0_{Eu}: (1) 17.0 × 10^{-5} *M* or 26 mg/L; (2) 7.0 × 10^{-5} *M* or 10.6 mg/L.

The precipitation of europium was studied in more detail at an initial solution concentration of nitric acid equal to 0.1 *M*, i.e., under conditions of maximum precipitate formation. All other things being equal ($x^0_{HNO_3}$ and γ), the α value is higher the higher the concentration of europium in a reprocessed solution, and at $x^0_{Eu} \simeq 50$ mg/L it reaches 98% ($\gamma \simeq 3$). At $x^0_{Eu} \simeq 2$ mg/L the α value is rather low, viz., ~30% under the same conditions (see the top of Fig. 4). Even a considerable increase of γ weakly affects the extent of removal; at $\gamma = 70$, α increases only to ~50% (the bottom of Fig. 4). A decrease of α with decreasing x^0_{Eu} matches the solubility of the resultant europium lauryl phosphate precipitate that in a crude approximation becomes comparable to the initial concentration of europium. In these instances it would be more credible to use the equilibrium concentration x_{Eu} instead of α.

Flotation of europium lauryl phosphate has been studied at different concentrations of nitric acid, LPA, and metal. The results are given in Tables 1 and 2. It follows from the data that as in the case of europium lauryl phosphate, europium extraction to 95–98% takes place at $x^0_{HNO_3}$ = 0.1–0.2 *M*, and α is lowered with a further growth of the aqueous solution acidity. With an increase of γ within the 1 to 3 range, a linear increase of α is observed for all x^0_{Eu}. A longer period of foaming Eu (τ') is due to

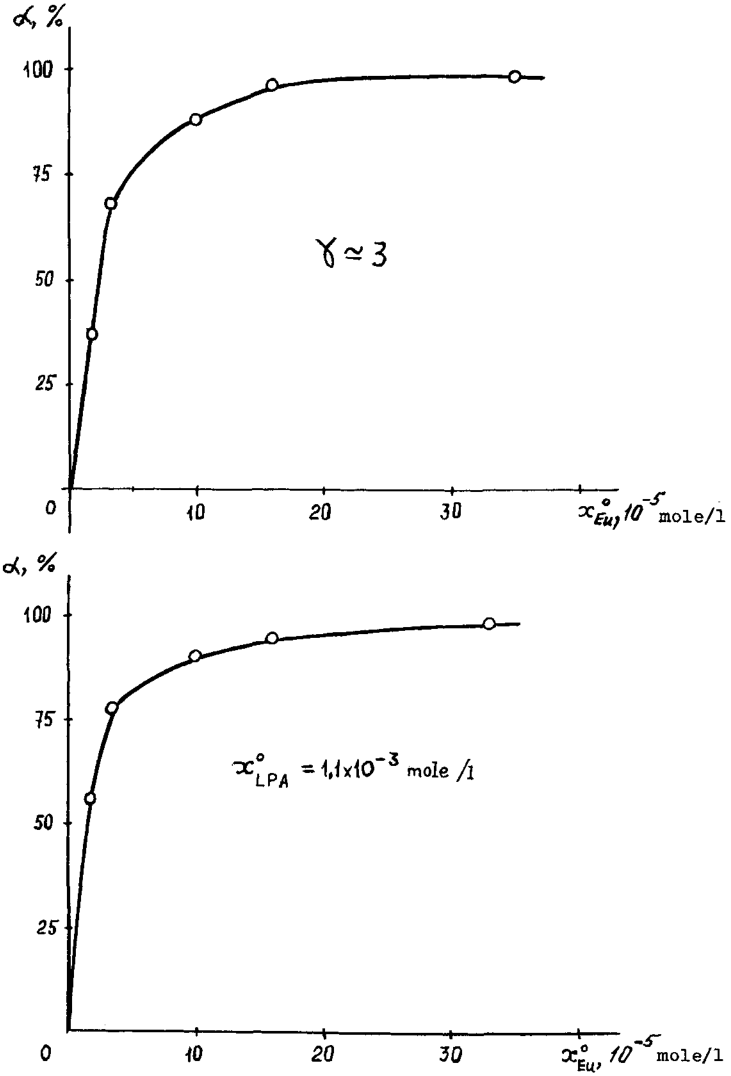

FIG. 4. Precipitation of europium at different initial concentrations. $x^0_{HNO_3} = 0.1$ M.

growth in the concentration of nitric acid, which can be explained by the increased fraction of free LPA in the system.

Adequate agreement between data on the precipitation and flotation of europium lauryl phospate indicates that the determining stage of the process is most likely to be precipitate formation, while the method of its

TABLE 1

Extent of Europium Removal (α) by Ion Flotation and Time of Foaming (τ') at Different HNO_3 Concentrations in Initial Aqueous Solutions. $x^0_{Eu} = 32 \times 10^{-5}\,M$, $x^0_{LPA} = 96 \times 10^{-5}\,M$ ($\gamma = 3$)

$x^0_{HNO_3}$ (M)	x_{Eu} ($10^{-5}\,M$)	α (%)	x_{LPA} ($10^{-5}\,M$)[a]	τ' (min)
0.1	0.9	97	2	1
0.2	2.0	94	6	3
0.3	4.3	87	13	5
0.4	8.5	73	25	10
0.5	18.0	44	55	20
0.6	28.0	13	84	45

[a] $x_{LPA} = x^0_{LPA} - 3(x^0_{Eu} - x_{Eu})$.

removal (filtration or flotation) plays a secondary role. One of the significant differences between the removal of a precipitate by filtration or flotation is the stability of mother liquors. Thus, the europium concentration of the mother liquors after filtration drops practically to zero in 3 days (at $\gamma \gtrsim 3$) while after flotation it remains practically unchanged, which is likely related to partial or full removal of excess LPA.

TABLE 2

Extent of Europium Removal by Ion Flotation at Different Concentrations of Europium and LPA. $x^0_{HNO_3} = 0.1\,M$

			x_{Eu} ($10^{-5}\,M$)		
x^0_{Eu} ($10^{-5}\,M$)	x^0_{LPA} ($10^{-5}\,M$)	γ	Experimental	Calculated by Eq. (7)	α (%)
32.0	33.0	1.0	21.0	21.6	34
	66.0	2.1	11.0	10.7	68
	98.0	3.1	0.9	0.8	97
17.0	16.0	0.9	12.0	12.4	29
	33.0	1.9	6.9	6.8	59
	50.0	2.9	1.4	1.6	92
	66.0	3.9	0.5	0.2	97
7.0	6.5	0.9	5.7	5.7	19
	13.0	1.9	3.3	3.6	53
	20.0	2.9	1.5	1.6	79
	26.0	3.7	0.6	0.4	91
1.6	1.5	0.9	1.3	1.6	19
	4.0	2.5	1.1	1.5	31
	8.0	5.0	0.4	0.6	75
	16.0	10.0	0.4	0.2	75
	34.0	21.0	0.2	0.2	87

It follows from the above that the extent of europium extraction is limited by *the solubility of europium lauryl phosphate* in reprocessed nitric acid solutions. The relationship between the residual concentration of europium and SAS precipitant expenditure is shown in Fig. 5 where the lines cross at a point corresponding to $\gamma \simeq 3$. Based on the Yoe–Jones approach (5), a complex formation with the mole empirical composition Eu:LPA = 1:3 is assumed from the stoichiometric equation of the reaction:

$$Eu^{3+} + 3H_2R \rightleftarrows Eu\,(HR)_3\downarrow + 3H^+ \qquad (1)$$

The cation-exchange mechanism is also evidenced by the drastic α–$x^0_{HNO_3}$ dependence (see Fig. 2 and Table 1).

At a fixed acidity, Equilibrium (1) can be described by equations of the mass action law

$$x_{Eu^{3+}} x^3_{LPA} = SP \text{ (solubility product)} \qquad (2)$$

and material balance

$$x^0_{Eu} = x_{Eu^{3+}} + (Y + S) \qquad (3)$$

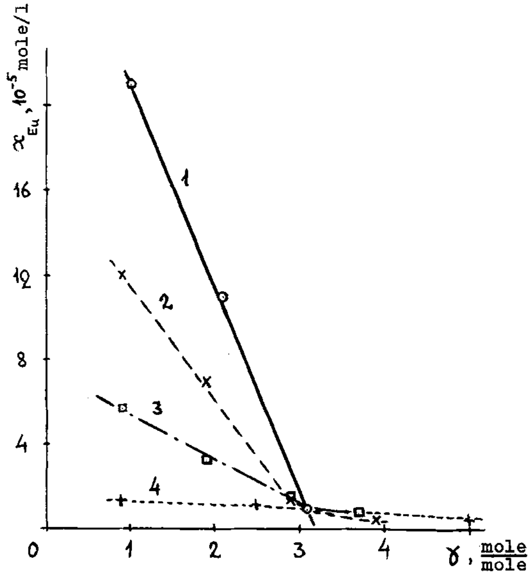

FIG. 5. Flotation of europium at different LPA expenditures. $x^0_{HNO_3}$ = 0.1 M. x^0_{Eu}, 10^{-5} M: (1) 32; (2) 17; (3) 7; (4) 1.6.

$$x^0_{\mathrm{LPA}} = x_{\mathrm{LPA}} + 3\,(Y + S) \qquad (4)$$

where Y is the mass of a precipitate in a solution volume and S is the solubility of the Eu-LPA complex precipitate. It follows from Eqs. (2)–(4):

$$x_{\mathrm{Eu^{3+}}}(x^0_{\mathrm{LPA}} - 3x^0_{\mathrm{Eu}} + 3x^0_{\mathrm{Eu^{3+}}})^3 = SP \qquad (5)$$

Since the europium concentration was found radiometrically, the measured values will be higher than the true ones by the amount of the (S) complex solubility

$$x_{\mathrm{Eu}} = x_{\mathrm{Eu^{3+}}} + \mathrm{S} \qquad (6)$$

and Eq. (5) will assume the form

$$(x_{\mathrm{Eu}} - S)(x^0_{\mathrm{LPA}} - 3x^0_{\mathrm{Eu}} + 3(x_{\mathrm{Eu}} - S))^3 = SP \qquad (7)$$

Figure 6 is a graphic illustration of Eq. (7).

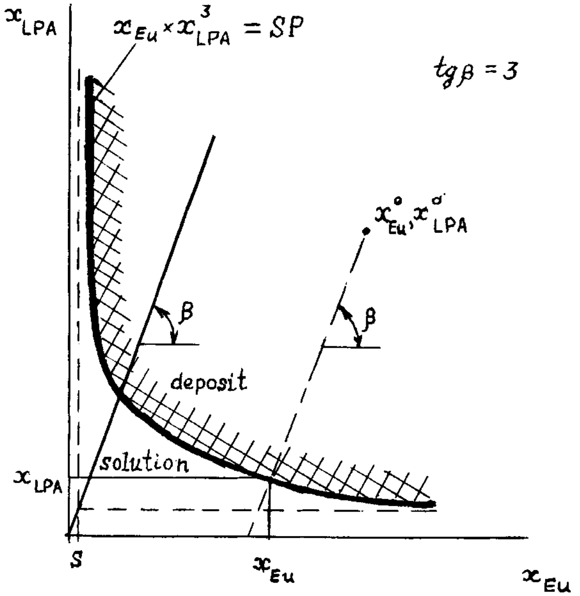

FIG. 6. Graphic illustration of model (2)–(4).

Assuming the data of Table 2 to be at equilibrium, one can approximately estimate the parameters S and SP for the nitric acid concentration in a 0.1 M system. Thus, at γ ($= x^0_{\mathrm{LPA}}/x^0_{\mathrm{Eu}}$) $= 21$, one can assume $S \approx x_{\mathrm{Eu}} = 2 \times 10^{-6}$ M, while at $\gamma = 3$ it follows from Eq. (7) that

$$27(x_{\mathrm{Eu}} - S)^4 = SP \tag{8}$$

Using the values for x_{Eu} for $\gamma = 3.1$ and 2.9 (Table 2), one obtains $SP \approx 4 \times 10^{-19}$.

Based on the parameters S and SP determined by using Eq. (7) or a graph similar to that of Fig. 6, one can predict the final analytical concentration of europium (x_{Eu}) for any values of x^0_{Eu} and x^0_{LPA} in the range of the experimental conditions described in Table 2. To check the suitability of such an approach, x_{Eu} was calculated by using Eq. (7); the results are listed in Column 5 of Table 2. From a comparison of the data presented, it follows that the predicted values of x_{Eu} adequately agree with the experimental ones.

Despite the fact that the suggested model is approximate and does not take into account the kinetic and diffusion processes occurring in such a complex system, the simplicity of the model allows it to be the starting point for a more detailed analysis. In particular, the effect of acidity on the precipitation of the europium-LPA complex according to Eq. (1) can be taken into account by the LPA dissociation reaction

$$\mathrm{H_2R} \rightleftarrows \mathrm{H^+} + \mathrm{HR^-} \tag{9}$$

by supplementing model (2)–(4) with the respective balance equations.

Europium, Plutonium, and Americium Extraction with PO

Despite the good properties of LPA required for SAS precipitants for flotation to be a success, viz., the ability to form hydrophobic precipitates with ions of the metals to be extracted, selectivity, and foaming ability, the use of LPA for trivalent metal extraction is limited to low-acidity solutions. Therefore, we continued our search for floto-agents that would permit extraction of trivalent lanthanides and actinides from moderately acid solutions. Through the estimation of the complex-forming ability of different classes of organic substances based on extraction data, we gave priority to bidentatic neutral organophosphorus compounds—diphosphine dioxides (PO)—that are widely used in the extraction of transplutonium elements from nitric acid solutions (*6–10*), in particular, phenyl and tolyl derivatives.

TABLE 3

Extent of Europium Removal (α) with PPO at Different Initial Concentrations of Nitric Acid and Precipitant with and without 0.42 *M* Aluminum Nitrate (numbers in parentheses). $x^0_{\mathrm{Eu}} = 33 \times 10^{-5}$ *M*

$x^0_{\mathrm{HNO_3}}$ (*M*)	x^0_{PPO} (10^{-5} *M*)	γ	x_{Eu} (10^{-5} *M*)	α (%)
1.0	33	1	30.0	9
	66	2	26.0	21
	99	3	20.0 (17.0)	39 (48)
	130	4	13.0	61
	160	5	7.9	76
	200	6	4.5	86
3.0	33	1	32.0	3
	66	2	27.0	18
	99	3	20.0 (19.0)	39 (42)
	130	4	13.0	61
	160	5	7.8	76
	200	6	4.4	87
5.0	33	1	32.0	3
	66	2	28.0	15
	99	3	19.0	42
	130	4	14.0	58
	160	5	11.0	67
	200	6	4.9	85

Experimental data on *europium extraction* as dependent on concentrations of nitric acid and europium in initial solutions as well as PO expenditures with and without aluminum nitrate impurities are listed in Tables 3 and 4. It follows from an analysis of the experimental data for an increasing PO expenditure, α increases independent of the acidity of the solutions and becomes constant at $\gamma \approx 10$. Following the Yoe–Jones approach (*5*),

TABLE 4

Extent of Europium Removal (α) with TPO at Different Concentrations of Nitric Acid with and without 0.42 *M* Aluminum Nitrate. $x^0_{\mathrm{Eu}} = 33 \times 10^{-5}$ *M*, $x^0_{\mathrm{TPO}} = 99 \times 10^{-5}$ *M* ($\gamma = 3$)

	Without Al		With Al	
$x^0_{\mathrm{HNO_3}}$ (*M*)	x_{Eu} (10^{-5} *M*)	α (%)	x_{Eu} (10^{-5} *M*)	α (%)
1.0	9.4	72	9.0	73
2.0	9.1	73	10.0	70
3.0	11.0	67	14.0	58

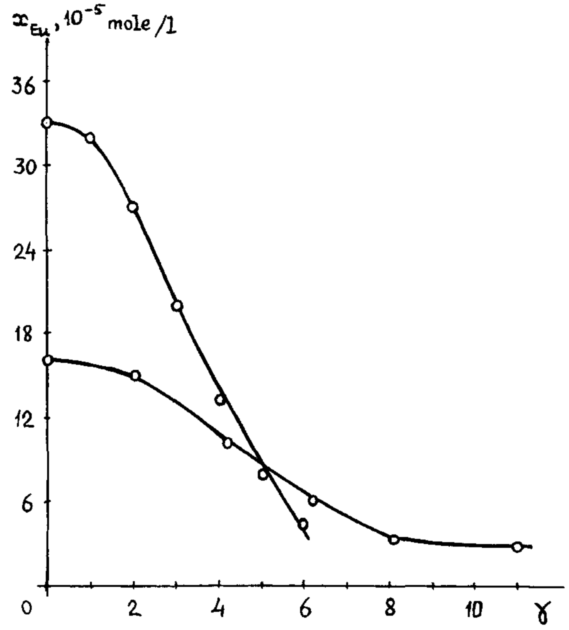

FIG. 7. Final concentration of europium in solutions after flotation with PPO. $x^0_{HNO_3}$ = 3.0 *M*. x^0_{Eu}, 10^{-4} *M*: (top) 3.3; (bottom) 1.6.

one can assume that the extracted complex has the empirical composition Eu:PO = 1:5 (Fig. 7). At fixed γ the concentration of nitric acid does not significantly affect the extent of Eu extraction. The influence of aluminum additives on this paramenter is insignificant. Under comparable conditions,

TABLE 5
Extent of Plutonium (IV) and Americium Removal with PPO at Different Concentrations of Precipitant and Nitric Acid. $x^0_{Pu} = 6.4 \times 10^{-5}$ *M*, $x^0_{Am} = 21 \times 10^{-8}$ *M*

$x^0_{HNO_3}$ (*M*)	$\gamma \left(\frac{\text{mol PPO}}{\text{mol Pu}}\right)$	x_{Pu} (10^{-5} *M*)	x_{Am} (10^{-8} *M*)	α_{Pu} (%)	α_{Am} (%)
3.6	0.9	5.6	21	13	0
	1.7	3.4	16	47	24
	2.6	2.7	14	58	33
	3.5	2.0	14	69	33
	4.3	1.9	15	70	29
	5.2	1.8	15	72	29
1.2	2.6	4.4	17	31	19
2.2	2.6	3.4	14	47	33
4.2	2.6	2.2	13	66	38
5.2	2.6	1.7	15	73	29

TABLE 6

Extent of Plutonium (IV) and Americium Removal with TPO at Different Concentrations of Precipitant and Nitric Acid. $x^0_{Pu} = 6.4 \times 10^{-5}\ M$, $x^0_{Am} = 21 \times 10^{-8}\ M$

$x^0_{HNO_3}$ (M)	$\gamma \left(\frac{\text{mol TPO}}{\text{mol Pu}}\right)$	x_{Pu} (10^{-5} M)	x_{Am} (10^{-8} M)	α_{Pu} (%)	α_{Am} (%)
3.1	0.9	4.9	18	23	14
	1.7	3.3	16	48	24
	2.6	1.9	13	70	38
	3.5	1.5	10	77	52
	4.3	1.0	8	84	62
	5.2	0.6	5	91	76
1.2	2.6	2.8	14	56	33
2.2	2.6	2.5	13	61	38
4.2	2.6	1.6	11	75	48
5.2	2.6	1.1	12	83	43

the extraction of europium with TPO proceeds more fully than with PPO at ~70 and ~40% at $\gamma = 3$. However, even with the use of PPO, $\alpha = 85\%$ at $\gamma = 6$ was obtained per flotational operation.

Experimental data on the *extraction of plutonium (IV) and americium* as related to the acidity of the solutions and the PO expenditure are listed in Tables 5 and 6. It can be seen that with the needed excess of an SAS precipitant, one can observe an appreciable co-extraction of plutonium (IV) and americium from moderately acid solutions. Thus, at $\gamma \simeq 5$, $\alpha_{Pu} \simeq 70\%$, and $\alpha_{Am} \simeq 30\%$ for PPO, $\alpha_{Pu} \simeq 90\%$ and $\alpha_{Am} \simeq 75\%$ for TPO were obtained per flotation operation from 3–3.5 M HNO_3. The higher flotation properties of TPO as compared to PPO agree with the extraction abilities of those reagents (*10*).

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