EXTRACTION OF Am(III) BY BENZYLDIBUTYLAMINE FROM NITRATE SOLUTIONS OF LANTHANIDES

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Benzyldibutylamine is a suitable extractant for the separation of Am(III) and Ln(III) from the acidic nitrate solutions. The effect of lanthanides and yttrium on the extraction of Am(III) has been followed under the conditions modelling the content of these components in the spent nuclear fuel. The separation factors $\alpha_{\mathrm{Am/Ln}}$ were evaluated for the optimum conditions found for the separation of Am(III) from the lanthanides. The coextraction of nitric acid and water into the organic phase is discussed.

In our previous papers[1-4] we have dealt with the use of benzyldibutylamine (BDBuA) for the extraction separation of certain lanthanides and for the separation of Am(III) from nuclides[5,6] present in the solutions of nuclear fission products[7,8]. Very similar chemical properties of trivalent lanthanides and actinides reveal themselves also in the extraction by this extractant[4-6]. It can be expected that the presence of lanthanides in concentrations higher than that of americium can affect the extraction of americium from the solutions under study.

For these reasons we turned our attention in this study to the effect of lanthanides on the extraction of americium from the nitric acid medium at the concentration conditions modelling the solutions of high-level wastes from fuel reprocessing[7,8].

EXPERIMENTAL

Reagents

All reagents used were of the analytical grade. Europium(III)- and yttrium(III) nitrates were prepared by dissolving the respective oxides in the stoichiometric amount of nitric acid and they were purified by double recrystallization.

The solutions of $Eu(NO_3)_3$ were labelled by $^{152+154}Eu$ (initially in the form of Eu_2O_3, Poland). ^{241}Am (in the form of $Am(NO_3)_3$, Amersham, England) was used in tracer concentrations.

The extractant BDBuA was prepared in this laboratory[9].

Apparatus and Procedures

The concentration of water in the organic phase was determined by the Karl Fischer method using the apparatus DST-1 (Znak, Brno).

All experiments with americium were carried out in the glove box in the Nuclear Research Institute, Řež. Radiometric measurements were done with the well-type NaI(Tl) scintillation detector and NZQ 717-T counter. The solutions were extracted in test tubes equipped with glass joints at 20 ± 1°C for 20 min, which is enough for the equilibrium establishment. The volume ratio of the organic and aqueous phases was 1 : 1. The concentration of lanthanides was determined either by the complexometric titration using xylenol orange as an indicator[10] or radiometrically in both phases. The nitric acid concentration in the organic phase was determined by titration with the ethanol solution of NaOH, $c(\text{NaOH}) = 0{\cdot}1 \text{ mol l}^{-1}$.

RESULTS AND DISCUSSION

The extraction of individual lanthanides and yttrium in the absence of americium was done for comparison (Figs 1 and 2). The lanthanide concentration was chosen so that it corresponded to their concentrations in the spent nuclear fuel[7,8]. The effect of individual lanthanides on the extraction of Am(III) was studied at constant con-

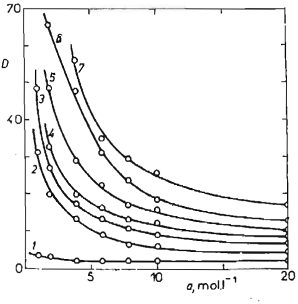

FIG. 1

Distribution Ratios of Trivalent Lanthanides in BDBuA Extraction as a Function of the Initial Concentration of the Metal

$c^0_{\text{LiNO}_3} = 6{\cdot}0 \text{ mol l}^{-1}$, $c^0_{\text{HNO}_3} = 0{\cdot}5 \text{ mol}\,.\,\text{l}^{-1}$, $c_{\text{BDBuA}} = 0{\cdot}5 \text{ mol l}^{-1}$ (in benzene), $c_{\text{C}_{16}\text{H}_{33}\text{OH}} = 0{\cdot}04 \text{ mol l}^{-1}$. *1* $\text{Y(NO}_3)_3$, *2*, $\text{Eu(NO}_3)_3$, *3* $\text{Sm(NO}_3)_3$, *4* $\text{Nd(NO}_3)_3$ *5* $\text{Pr(NO}_3)_3$, *6* $\text{Ce(NO}_3)_3$, *7* $\text{La(NO}_3)_3$. *a* $c^0_{\text{Ln(NO}_3)_3} \cdot 10^3$, mol l^{-1}.

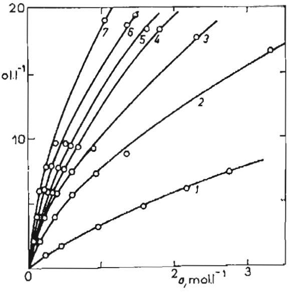

FIG. 2

Extraction Isotherms of Trivalent Lanthanides for BDBuA Extraction at 20 ± 1°C

$c^0_{\text{LiNO}_3} = 6{\cdot}0 \text{ mol l}^{-1}$, $c^0_{\text{HNO}_3} = 0{\cdot}5 \text{ mol}\,.\,\text{l}^{-1}$, $c_{\text{BDBuA}} = 0{\cdot}5 \text{ mol l}^{-1}$ (in benzene), $c_{\text{C}_{16}\text{H}_{33}\text{OH}} = 0{\cdot}04 \text{ mol l}^{-1}$. *1* $\text{Y(NO}_3)_3$, *2* $\text{Eu(NO}_3)_3$, *3* $\text{Sm(NO}_3)_3$, *4* $\text{Nd(NO}_3)_3$, *5* $\text{Pr(NO}_3)_3$, *6* $\text{Ce(NO}_3)_3$, *7* $\text{La(NO}_3)_3$. *a* $c_{\text{Ln(NO}_3)_3} \cdot 10^3$, mol l^{-1}, *a'* $c'_{\text{Ln(NO}_3)_3} \cdot 10^3$.

centrations of both americium and the respective lanthanide in dependence on the concentration of the salting-out agent (Fig. 3). At the same time the effect of the initial concentration of the lanthanide or yttrium on the extraction of Am(III) was followed (Fig. 4).

From the dependence of Ln(III) extraction on the metal concentration in the absence of Am(III) (Fig. 1) it is evident that the distribution ratios D_{Ln} and D_Y decrease exponentially with the increasing concentration of the metal. Y(III), the distribution ratios of which lie in the range of units, is extracted in the lowest extent though not with so conspicuous difference. The values of the lanthanide distribution ratios D_{Ln} decrease with the increasing relative atomic mass of the respective lanthanide.

In the extraction at the highest initial concentrations of the metal the values of the distribution ratio do not decrease under the value of 10 for most lanthanides. Only for the heaviest lanthanides, Sm(III) and Eu(III), these values reach the order of units already at rather low initial concentrations of Ln(III).

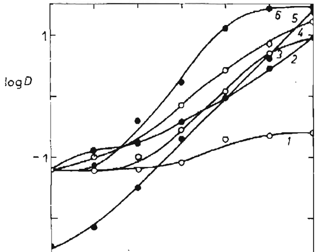

Fig. 3

Dependence of log D on $LiNO_3$ Concentration in the Extraction of Lanthanides and Americium by BDBuA

$c^0_{Am(NO_3)_3} = 1 \cdot 10^{-7}$ mol l^{-1}, $c^0_{Ln(NO_3)_3} = 0{\cdot}01$ mol l^{-1} = const, $c^0_{HNO_3} = 0{\cdot}5$ mol . . l^{-1}, $c_{BDBuA} = 0{\cdot}5$ mol l^{-1} (in benzene), $c_{C_{16}H_{33}OH} = 0{\cdot}04$ mol l^{-1}. *1* $Y(NO_3)_3$, *2* $Sm(NO_3)_3$, *3* $Nd(NO_3)_3$, *4* $Pr(NO_3)_3$, *5* $Am(NO_3)_3$, *6* $Ce(NO_3)_3$. *a* $c^0_{LiNO_3}$, mol l^{-1}.

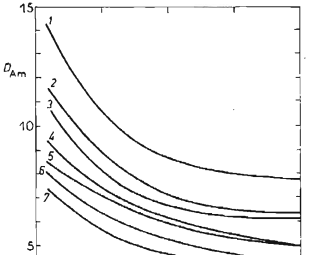

Fig. 4

Extraction of Am(III) by BDBuA in the Presence of Trivalent Lanthanides and Yttrium

$c^0_{Am(NO_3)_3} = 1 \cdot 10^{-7}$ mol l^{-1} = const, $c^0_{LiNO_3} = 6{\cdot}0$ mol l^{-1}, $c^0_{HNO_3} = 0{\cdot}5$ mol l^{-1}, $c_{BDBuA} = 0{\cdot}5$ mol l^{-1} (in benzene), $c_{C_{16}H_{33}OH} = 0{\cdot}04$ mol l^{-1}. *1* $Y(NO_3)_3$, *2* $Eu(NO_3)_3$, *3* $Sm(NO_3)_3$, *4* $Nd(NO_3)_3$, *5* $Pr(NO_3)_3$, *6* $Ce(NO_3)_3$, *7* $La(NO_3)_3$. *a* $c^0_{Ln(NO_3)_3} \cdot 10^3$, mol l^{-1}.

In such an extraction system it would be possible to separate with high separation factors the lighter lanthanides, particularly La(III), Ce(III), and Pr(III), from the group of medium heavy lanthanides (Table I). The separation of lanthanides from yttrium will proceed quite well as the separation factor $\alpha_{\mathrm{Ln/Y}}$ ranges from 5 to 25.

Together with the extraction of lanthanides we have studied also the effect of the extraction of lanthanide nitrates at various concentrations on the nitric acid coextraction and on the extraction of water. It has been found that at low concentrations of the metal as well as in the absence of the metal nitric acid is practically completely extracted into the organic phase with the formation of the amine nitrate $\mathrm{BDBuA\,.\,HNO_3(H_2O)_x}$, which acts as the proper extractant. From the coextraction of water into the organic phase it is evident that the concentration of water in the organic phase decreases with the increasing concentration of the metal; this is obviously caused by its displacement from the organic phase due to the formation of non-hydrated associates of ammonium nitrate with nitrates of the metals under study[11]. The equilibrium concentrations of the metal in the organic phase as a function of the equilibrium concentration of the metal in the aqueous phase are given in Fig. 2.

The effect of the concentration of $\mathrm{LiNO_3}$ as a salting-out agent was studied in the extraction of Am(III), Y(III), and lighter lanthanides (Ce, Pr, Nd, Sm) (Fig. 3). The shape of the extraction curve and the values of the distribution ratios reveal the analogy between the extraction of Am and that of lighter lanthanides (namely Sm, Nd, Pr) which can be observed also in other extraction systems with amines and which points out that the separation of Am from this group of elements, to which also Eu can be added, is most difficult. Relatively low values of the separation factors $\alpha_{\mathrm{Am/Eu}}$

TABLE I

Separation Factors (α) of the Light and Medium Heavy Lanthanides and Yttrium
$c^0_{\mathrm{Am(NO_3)_3}} = 1\,.\,10^{-7}\ \mathrm{mol\,l^{-1}}$, $c^0_{\mathrm{LiNO_3}} = 6{\cdot}0\ \mathrm{mol\,l^{-1}}$, $c^0_{\mathrm{HNO_3}} = 0{\cdot}5\ \mathrm{mol\,l^{-1}}$, $c_{\mathrm{BDBuA}} = 0{\cdot}5\ \mathrm{mol\,l^{-1}}$ (in benzene), $c_{\mathrm{C_{16}H_{33}OH}} = 0{\cdot}04\ \mathrm{mol\,l^{-1}}$.

$c^0_{\mathrm{Ln(NO_3)_3}}\cdot 10^3$. $\mathrm{mol\,l^{-1}}$	$\alpha_{\mathrm{La/Eu}}$	$\alpha_{\mathrm{Ce/Eu}}$	$\alpha_{\mathrm{Pr/Eu}}$	$\alpha_{\mathrm{Ce/Y}}$	$\alpha_{\mathrm{Eu/Y}}$
2	4·72	3·55	2·31	20·0	6·52
4	4·06	3·07	2·16	17·1	4·83
6	3·60	2·79	1·91	11·7	3·46
8	3·23	2·51	1·46	10·0	2·85
10	3·47	2·17	1·70	7·63	2·40
20	3·03	1·76	1·31	5·71	2·06

obtained when nitrates are used as the salting-out agents in this extraction system were already reported in our previous paper[12].

The extraction of Am(III) from aqueous solutions containing macroconcentrations of the ions of the above-mentioned lanthanides is suppressed due to the competitive extraction of lanthanides resulting in the decrease of the free benzyldibutylamine nitrate concentration. This dependence is shown on Fig. 4 for the initial lanthanide concentrations in the aqueous phase ranging from 10^{-3} to $2 . 10^{-2}$ mol l^{-1}. The effect of the competitive extraction is more evident from the comparison with Fig. 1 which presents the extraction of lanthanides in the same concentration range. Because Am(III) is present in the system in trace concentrations, it has no effect on the extraction equilibrium of lanthanides so that the data on the initial concentrations of lanthanides in Figs 1 and 4 are comparable. The results show that the distribution ratio of Am(III) (Fig. 4) decreases in the presence of lanthanides in the sequence Y > Eu > Sm > Nd > Pr > Ce > La, *i.e.* in the reverse sequence of the distribution ratios of individual lanthanides (Fig. 1). In comparison with the extraction in the absence of lanthanides the value of D_{Am} decreases as much as by one order of magnitude (in the presence of Ce, Pr, and Nd) due to the competitive extraction. The given sequence of the effect of individual lanthanides is in agreement with the results obtained in the extraction of Am(III) by quarternary ammonium salts[5,12,13].

In the practical use of the extraction system under study for the separation of Am(III) from the lanthanides in solutions containing macroconcentrations of lanthanides and trace concentrations of Am(III) two simultaneous effects should be taken into consideration, namely the decrease of D_{Am} with the increase of c^0_{Ln} and the decrease of D_{Ln} with the increase of c^0_{Ln}. Though both effects are qualitatively similar, their magnitude is different so that they cannot compensate each other and they give a net change of the separation factor with the increase of c^0_{Ln} as it is demonstrated by the following data:

$c^0_{\mathrm{Eu(NO_3)_3}} . 10^3$, mol l^{-1}:	1	2	4	6	8	10	20
$\alpha_{\mathrm{Am/Eu}}$:	0·37	0·52	0·70	0·92	1·05	1·22	1·35

These data correspond to the following conditions: $c^0_{\mathrm{Am(NO_3)_3}} = 1 . 10^{-7}$ mol l^{-1} = = const; $c^0_{\mathrm{HNO_3}} = 0{\cdot}5$ mol l^{-1}; $c^0_{\mathrm{LiNO_3}} = 6{\cdot}0$ mol l^{-1}; $c_{\mathrm{BDBuA}} = 0{\cdot}5$ mol l^{-1} (in benzene); $c_{\mathrm{C_{16}H_{33}OH}} = 0{\cdot}04$ mol l^{-1}.

The situation is more complicated if americium is extracted from solutions containing more elements of the lanthanide group and if a multistage extraction is used. The separation factors $\alpha_{\mathrm{Am/Eu}}$ gradually increase (Table II). However, one should take into consideration that in higher extraction stages there are present only low concentrations of the nitrates of lanthanides, Y(III), and Am(III), because their greatest part is extracted already in the first stage. The respective values of the separation factors for individual lanthanides in the first extraction stage are given in Table I.

In the multistage extraction of Am(III) the value of D_{Am} decreases in higher extraction stages (Table III). For the determination of the extraction of individual lanthanides in different stages of the extraction cycle their extraction isotherms were measured for the concentrations that are expected in high-level wastes from the nuclear fuel reprocessing (Fig. 2).

The values of $\alpha_{Am/Ln}$ indicate that the multistage extraction can be used for the separation of Am(III) from other trivalent metal cations in the solutions of nuclear fission products but the method of extraction chromatography[14] seems to be more perspective and selective.

TABLE II

Separation Factors $\alpha_{Am/Ln}$ in 3-Stage Extraction

Extraction stage	$\alpha_{Am/Ce}$		$\alpha_{Am/Eu}$	
	A[a]	B[b]	A	B
1	0·86	0·97	2·79	2·88
2	2·85	2·22	8·57	84
3	2·42	3·44	9·67	155

[a] In the presence of lanthanides, $c^0_{Ln(NO_3)_3} = 2{\cdot}8 \,.\, 10^{-2}$ mol l^{-1}. [b] In the presence of both lanthanides and yttrium, $c^0_{Ln(NO_3)_3} + c^0_{Y(NO_3)_3} = 2{\cdot}8 \,.\, 10^{-2}$ mol l^{-1}. $c^0_{Am(NO_3)_3} = 1 \,.\, 10^{-7}$ . . mol l^{-1}, $c^0_{HNO_3} = 0{\cdot}5$ mol l^{-1}, $c^0_{LiNo_3} = 6{\cdot}0$ mol l^{-1}, $c_{BDBuA} = 0{\cdot}5$ mol l^{-1} (in benzene), $c_{C_{16}H_{33}OH} = 0{\cdot}04$ mol l^{-1}.

TABLE III

Three-Stage Extraction of Am(III) in the Presence of Lanthanides and Yttrium Using BDBuA For the extraction conditions, see Table II.

Extraction stage	D_{Am}	
	$Ln(NO_3)_3$	$Ln(NO_3)_3 + Y(NO_3)_3$
1	6·78	6·31
2	0·60	0·84
3	0·29	0·31

LIST OF SYMBOLS

$c^0_{\mathrm{Am(NO_3)_3}}$	initial concentration of $\mathrm{Am(NO_3)_3}$ in the aqueous phase
$c^0_{\mathrm{Ln(NO_3)_3}}$	initial concentration of $\mathrm{Ln(NO_3)_3}$ in the aqueous phase
$c^0_{\mathrm{LiNO_3}}$	initial concentration of $\mathrm{LiNO_3}$ in the aqueous phase
$c^0_{\mathrm{HNO_3}}$	initial concentration of $\mathrm{HNO_3}$ in the aqueous phase
c_{BDBuA}	initial concentration of BDBuA in the organic phase
$c_{\mathrm{C_{16}H_{33}OH}}$	initial concentration of $\mathrm{C_{16}H_{33}OH}$ in the organic phase
$c_{\mathrm{Ln(NO_3)_3}}$	equilibrium concentration of $\mathrm{Ln(NO_3)_3}$ in the aqueous phase
$c'_{\mathrm{Ln(NO_3)_3}}$	equilibrium concentration of $\mathrm{Ln(NO_3)_3}$ in the organic phase
D	distribution ratio
α	separation factor

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