EXTRACTION OF AMERICIUM WITH BENZYLDIBUTYLAMINE FROM NITRATE SOLUTIONS

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The extraction of Am(III) with benzyldibutylamine from nitrate medium was examined in dependence on the concentration of nitric acid, kind and concentration of the salting-out agent in the aqueous phase, and on the solvent. Am(III) is extracted into the organic phase in the form of $\{(R_3NH^+)\alpha, Am(NO_3)_5^{2-}\}$. The IR spectra of the organic phase are discussed and confronted with the results of the chemical analysis of the organic phase. The extraction of Am(III) and of lanthanoids was found to be considerably higher than that of some products of corrosion and nuclear fission (Cs, Sr, Zr, Fe), which is documented by the high values of the separation factors.

During the extraction separation of lanthanoids from nuclear fission products, salts of trivalent ions of transplutonium elements are extracted simultaneously too[1-4].

Tertiary trialkylyamines give very low values of distribution ratios for the separation of trivalent lanthanoids and americium[5,6] from nitric acid solutions, since the extraction of these metal salts is strongly suppressed by the competitive formation of associates of the amine nitrates with nitric acid.

Benzyldialkylamines were found[7-9] to be considerably better extracting agents for the extraction of lanthanoids, because the basicity of these amines in comparison with trialkylamines is lower, the other factors (low solubility in the aqueous phase, steric factors) being preserved. The competitive extraction of nitric acid before the extraction of the metal salts is here not so pronounced. With benzyldibutylamine, the distribution ratios were found to be two orders of magnitude higher than with trialkylamines[5,7] for the same concentration relations in the two phases. For this reason we focussed our attention also on the extraction of Am(III) with this extracting agent. Since no data on the extraction of Am(III) with benzyldibutylamine were available from the literature, we devoted the present work to the investigation of the effect of the kind and concentrations of the individual constituents of the organic as well as aqueous phase.

EXPERIMENTAL

Chemicals

All the chemicals employed — Eu_2O_3, NaOH, HNO_3, $LiNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$, C_6H_6 — were reagent grade purity. The indicators were used without prior refining.

Europium nitrate was prepared by reaction of europium oxide with the stoichiometric quantity of nitric acid, and doubly recrystallized. The isotope ^{241}Am was supplied in HNO_3 solution by the Radiochemical Centre, Amersham, England; the isotope $^{152,4}Eu$ was obtained from the USSR as the oxide and transferred into the solution by dissolving in HNO_3.

Benzyldibutylamine (BDBuN) was prepared in our laboratory by reaction of benzylamine with n-butyl bromide at the bath temperature 130—150°C for 2 h with constant stirring and alkalization with potassium hydroxide[10,11]. The chemical purity of BDBuN was tested by gas chromatography, elemental analysis, refractive index (1·48846/20°C) and boiling point (133 to 135°C/12 Torr) measurements, and measurements of its IR, NMR and mass spectra. For $C_{15}H_{26}N$ (219·4) calculated: 82·23% C, 11·52% H, 6·42% N; found: 82·13% C, 11·49% H, 6·38% N. Gas chromatograms and mass spectra did not reveal detectable impurities in the synthetized BDBuN.

Apparatus and Analytical Methods

The radioactivity of $^{152,4}Eu$ and ^{241}Am was measured by a well gamma-scintillation detector in conjunction with an automatic pulse counter NZQ 615 or measurement kit NZQ 717-T. The experiments with $^{241}Am(NO_3)_3$ were conducted in an alpha box at the Institute of Nuclear Research, Řež.

The extractions were accomplished by shaking in ground-in test tubes at the temperature 20 ± 1°C for 10 min, ratio of the aqueous to organic phase 1 : 1.

The infrared spectra were scanned on an instrument Perkin–Elmer 325 in the wavenumber region 600—4000 cm^{-1} using AgCl cells.

RESULTS AND DISCUSSION

Based on the results obtained from the extraction of europium with benzyldibutylamine[8] (BDBuN), the extractions of $Am(NO_3)_3$ were carried out in conditions approaching the concentration characteristics of the aqueous and organic phases applied to the extraction of $Eu(NO_3)_3$, for the extractabilities of Am(III) and Eu(III) to be mutually comparable.

Use was made of the conclusions[12] obtained for the extraction of $Eu(NO_3)_3$, yielding the maximum distribution ratio D_{Eu} with 0·5M-BDBuN and the starting concentration of nitric acid in the aqueous phase 0·5 mol l^{-1}. In order to suppress the formation of a third phase in the organic phase, cetyl alcohol was added to the organic phase in amount of 1 g per 100 cm^3 as a solubilizer.

For the extraction of $Am(NO_3)_3$ with BDBuN in the isomolar series of $HNO_3 + LiNO_3$, total nitrate concentration $c^0_{NO_3} = c^0_{HNO_3} + c^0_{LiNO_3} = 6 \text{ mol l}^{-1}$, $c^0_{Am(NO_3)_3} = 1 \cdot 10^{-9} \text{ mol l}^{-1}$, $c_{BDBuN,org} = 0 \cdot 5 \text{ mol l}^{-1}$ (in benzene), $c_{C_{16}H_{33}OH,org} = 0 \cdot 04 \text{ mol l}^{-1}$, the following dependence of D_{Am} on $c^0_{HNO_3}$ was found:

$c^0_{HNO_3}$, mol l^{-1}:	0·05	0·10	0·20	0·30	0·50	0·70	1·00	1·50	2·00
D :	0·06	0·21	1·24	2·12	3·49	0·54	0·12	0·03	0·01 .

Thus in the case of Am(III), too, the maximum extraction is attained with the initial 0·5M-HNO_3. If $c^0_{HNO_3}$ is lower than $c_{BDBuN,org}$, only the portion of BDBuN that is present as the nitrate adduct acts as the extracting agent, and therefore the extraction of Am(III) increases as the concentration of HNO_3 and thereby that of BDBuN.HNO_3 is raised. If $c^0_{HNO_3}$ exceeds the concentration of BDBuN in the organic phase, the extraction of Am(III) is, on the contrary, lowered owing to the competitive formation of BDBuN.$(HNO_3)_2$ preferentially to the associate $\{BDBuNH^+, Am.(NO_3)_4^-\}$, created during the extraction of $Am(NO_3)_3$ with this extractant.

The same factors operate during the examination of the Am(III) extraction in dependence on the concentration of BDBuN; for $c^0_{Am(NO_3)_3} = 1 . 10^{-9}$ mol l^{-1}, $c^0_{HNO_3} = 0{\cdot}5$ mol l^{-1}, $c^0_{LiNO_3} = 7$ mol l^{-1}, $c_{C_{16}H_{33}OH} = 0{\cdot}04$ mol l^{-1}, the following data were obtained:

c_{BDBuN}, mol l^{-1}:	0·1	0·2	0·3	0·4	0·5	0·6	0·8
D :	0·01	0·07	0·37	2·56	16·5	17·9	18·0

Obviously, additional increase of the amine concentration, if not accompanied by an increase of the initial nitric acid concentration in the aqueous phase, does not result in a pronounced increase of the distribution ratio, since again due to the deficit of nitric acid with respect to BDBuN, no additional portions of the nitrate can be formed.

Comparing the extraction of Am(III) in the two dependences we can see a marked rise of the americium nitrate extraction with the increasing concentration of the salting-out agent, the distribution ratios in the presence of 7M-NO_3 being notably higher.

TABLE I

Values of the Separation Factors (α) for the Extraction with 0·5M Benzyldibutylamine in Benzene in Dependence on the Kind and Concentration of the Salting-out Agent

Aqueous solution: 0·5M-HNO_3; 0·04M-$C_{16}H_{33}OH$ present as solubilizer.

Salting-out agent (c_{NO_3}) mol l^{-1}	$\alpha_{Am/Eu}$ for the salting-out agent			
	$LiNO_3$	$NaNO_3$	$Ca(NO_3)_2$	$Mg(NO_3)_2$
5	1·9	1·6	1·3	1·6
6	1·2	1·5	1·9	0·95
7	1·8	1·4	2·6	—

The concentration and kind of the salting-out agent affect considerably the extraction of salts of trivalent lanthanoids[2,5,7,8] and transplutonium elements[13] (Fig. 1). The effect of the kind of the salting-out agent on the extraction of Am(III) was examined using the initial concentration 0·5M-HNO_3 in the aqueous phase. The distribution ratios were found to increase in the order $NaNO_3 \ll Ca(NO_3)_2 <$ $< Mg(NO_3)_2 < LiNO_3$. The differences for the last three members of this series are not very marked. For the case that the solution after the separation of the lanthanoids and americium should be further treated as radioactive fallout, aluminium nitrate has to be taken into consideration; its salting-out properties are comparable with those of calcium nitrate, as indicated by the results of europium nitrate extractions[12]. The same conclusions are derived from the experimental data on extraction of Am(III) using lower concentration of nitric acid (Fig. 2).

Since it is Am(III) that of the actinoid series, owing to its occupation of the f-electron shells, approaches by its chemical properties most europium of the lanthanoid series, it was of interest to compare also their extraction with benzyldibutylamine using the same compositions of the organic and the aqueous phases. The Am/Eu separation factors for all the systems studied are lower than 2; this

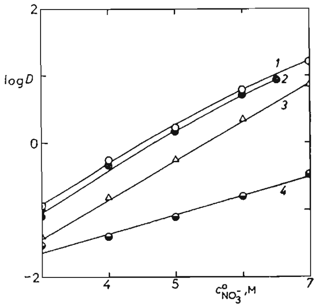

FIG. 1

Dependence of the Extraction of $Am(NO_3)_3$ with Benzyldibutylamine on the Kind and Concentration of the Salting-out Agents

$c^0_{Am(NO_3)_3} = 1 \cdot 10^{-9}$ mol l^{-1}, $c^0_{HNO_3} =$ $= 0·5$ mol l^{-1}, $c_{BDBuN,org} = 0·5$ mol l^{-1} (in benzene), $c_{C_{16}H_{33}OH,org} = 0·04$ mol l^{-1}. For $c^0_{NO_3^-} < 3$ mol l^{-1}, D is lower than 0·02. 2 $Mg(NO_3)_2$, 1 $LiNO_3$, 3 $Ca(NO_3)_2$, 4 $NaNO_3$.

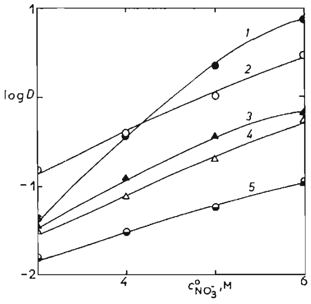

FIG. 2

Dependence of the Extraction of $Am(NO_3)_3$ with Benzyldibutylamine on the Kind and Concentration of the Salting-out Agents

$c^0_{Am(NO_3)_3} = 1 \cdot 10^{-9}$ mol l^{-1}, $c^0_{HNO_3} =$ $= 0·1$ mol l^{-1}, $c_{BDBuN,org} = 0·5$ mol l^{-1} (in benzene), $c_{C_{16}H_{33}OH,org} = 0·04$ mol l^{-1}. For $c^0_{NO_3^-} < 3$ mol l^{-1}, D is lower than 0·05. 1 $Mg(NO_3)_2$, 2 $LiNO_3$, 3 $Al(NO_3)_3$, 4 $Ba(NO_3)_2$, 5 $NaNO_3$.

indicates that the chemical similarity of Eu and Am plays here an important part. Only in the system involving calcium nitrate as the salting-out agent, the separation factor value of 2·6 was achieved (Table I).

During the technological application of the extraction separation of lanthanoids and actinoids, the extraction proceeds occasionally from aqueous solutions containing corrosion products – Fe(III) – and some other nuclear fission products – Cs, Sr, Zr. It was therefore of interest to establish to what extent the extraction of Am(III) from acidic aqueous nitrate solutions is affected by the presence of these ions.

The extraction of Fe, Cs, Sr, and Zr with benzyldibutylamine from 0·5M-HNO_3 in the presence of salting-out agents in comparison with the extraction of Eu(III) and Am(III) is negligible (Fig. 3); the separation factors are $\alpha_{Eu/Cs} = 6 \,.\, 10^2$, $\alpha_{Eu/Sr} = 6 \,.\, 10^2$, $\alpha_{Eu/Zr} = 2 \,.\, 10^2$, $\alpha_{Eu/Fe} = 5 \,.\, 10^2$; $\alpha_{Am/Cs} = 1 \,.\, 10^3$, $\alpha_{Am/Sr} = 1 \,.\, 10^3$, $\alpha_{Am/Zr} = 4 \,.\, 10^2$, $\alpha_{Am/Fe} = 8 \,.\, 10^2$.

If we compare these results with those obtained with trialkylamines (Adogen 336 (ref.[5]), trioctylamine[2], or methyldibutylamine[14]), then we find that since the extraction of europium with them is appreciably lower than with BDBuN, while that of Fe(III), Cs, and Sr is comparable in the two cases, the separation factors with trialkylamines will necessarily be essentially lower than with BDBuN.

The content of water and nitric acid and the concentration of the extracted Eu(III) (refs[8,12]) suggest that europium nitrate in the organic phase forms associates involving two nitrate molecules, $\{(BDBuNH^+)_2, Me(NO_3)_5^{2-}\}_x$. Taking into account the similarity of the atomic structure and chemical properties of Eu and Am, the formation of such associate can be assumed for Am(II) as well[15]. Unlike nitrate ions, water does not enter the structure of the associate[8,15,16].

In the infrared spectra (Table II), variations in the positions of the NH^+ absorption bands were studied for the nitrate BDBuN.HNO_3, for the nitrate of BDBuN

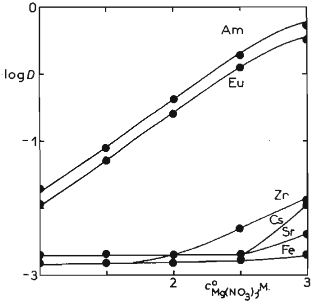

FIG. 3

Dependence of the Distribution Ratios D_{Me} on the Concentration of Magnesium Nitrate $c^0_{Eu(NO_3)_2} = 0{\cdot}02 \text{ mol l}^{-1}$, $c^0_{Am(NO_3)_3} = 1 \,.\, 10^{-9} \text{ mol l}^{-1}$, $c^0_{Fe(NO_3)_3} = 0{\cdot}008 \text{ mol l}^{-1}$, $c^0_{ZrO(NO_3)_3} = 0{\cdot}007 \text{ mol l}^{-1}$, $c^0_{CsNO_3} = 0{\cdot}005 \text{ mol l}^{-1}$, $c^0_{HNO_3} = 0{\cdot}5 \text{ mol l}^{-1}$, $c_{BDBuN,org} = 0{\cdot}5 \text{ mol l}^{-1}$ (in benzene), $c_{C_{16}H_{33}OH,org} = 0{\cdot}04 \text{ mol l}^{-1}$.

with overstoichiometric proportion of nitric acid in the associate $BDBuN.HNO_3.HNO_3$, and the associate $\{(BDBuNH^+)_2, Am(NO_3)_5^{2-}\}$. For the study of the IR spectrum of the associate of the extracted Am(III), americium nitrate was modelled by the inactive europium nitrate, since the spectrophotometer used was not installed to permit measurements of active samples.

The infrared spectra (Table II) bear out the association of nitric acid at BDBuN *via* hydrogen bonding to the nitrogen of the amine, $R^1R^2_2N.HNO_3$, exhibiting a broad N—H absorption band at 2640–2660 cm^{-1}. According to the position of the NH^+ band, the hydrogen bond in $BDBuN.HNO_3$ is stronger than in trialkylnitrates. Simultaneously with nitric acid, water is bonded in the associate too,

TABLE II

Characteristic Absorption Bands in the Infrared Spectra of BDBuN, Benzene Solutions of BDBuN, and $BDBuN.HNO_3$ in Benzene

Band positions in cm^{-1}; relative intensity: w weak, m medium, s strong; sh shoulder, b broad, v very.

Assignment		BDBuN	0·5M-BDBuN	BDBuN.HNO_3	0·5M-BDBuN + HNO_3 + Eu(Am)$(NO_3)_3$ ($c_{NO_3^-}$ = 6 mol l^{-1})	
					0·5M-HNO_3	2M-HNO_3
OH	stretch in H_2O free	—	—	—	3 660 w	—
OH, H	stretch in H_2O bonded	—	—	3 400 vs, b	3 450 m	3 450 w
OH	stretch alcohol	—	—	—	—	—
CH	asym stretch	2 960 s	2 960 vs	2 960 vs	2 950 s	2 920 s
		2 930 s	2 920 vs	2 930 s	2 880 vs	2 850 vs
CH	sym stretch	2 870 s	2 860 s	2 860 s	2 880 s	2 850 vs
CH	stretch, at C	—	2 880 m	—	—	—
NH, H	stretch bonded	—	—	2 660 m	2 640 m, b	2 610 m, b
						2 710 m, b
HOH	bend un H_2O	—	—	1 620 s	1 620 w	—
CH_3	bend	1 460 sh	1 460 m	1 450 m	—	(1 460)
CH_2	wagg	1 285 w	1 295 vw	—	—	—
N=O	stretch un HNO_3	—	—	1 630 m, b	—	1 640 m
N=O	stretch in NO_3^-	—	—	1 370 m, b	1 390 m	1 400 vs
	split					1 455 vs
N=O	stretch in NO_3^-	—	—	—	1 290 m	1 285 s
	split by H-bonding					1 310 s
CN	stretch	1 105 w	1 095 vw	—	1 095 vw	1 085 w
NO_2	bend in HNO_3	—	—	—	920 m	915 m
						940 m

as evidenced not only by the analytical data, but also by the presence of the OH stretching vibration band at 3450 cm^{-1}.

In the case of the Eu(III) or Am(III) nitrate extraction with benzyldibutylamine amine from nitric acid, we considered the possibility to identify both associate forms – the aforesaid nitrate as well as the Eu(III) associate, which will be in the organic phase in an equilibrium. In the infrared spectra, however, two different NH^+ bands were not found; the bands merge into a broad plateau centered at 2640 cm^{-1}.

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