

EXTRACTION OF AMERICIUM WITH BENZYLDIMETHYLLAURYLAMMONIUM NITRATE FROM AQUEOUS NITRATE SOLUTIONS

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The extraction of Am(III) with benzyldimethylaurylammonium nitrate from acidic nitrate solutions was studied. The effects of the kind and concentration of the salting-out agent, of the organic solvents, and of the concentrations of the other components in the extraction system on the distribution ratio values and applicability of this extracting agent to the separation of americium from lanthanoids are discussed. From the analytical data on the organic phase and from the infrared spectra, the composition of the extractable associates and their extraction mechanism were established.

Extraction of americium from effluent solutions after the processing of the burnt-up nuclear fuel is receiving considerable attention. The separation of americium and higher transplutonium elements from these solutions is so important particularly because the long-lived biotoxicity of the fallouts can thus be reduced, and also the isotopes isolated can be further utilized. However, trivalent lanthanoid ions are usually extracted together with Am(III). It would be therefore of great practical value if a method were developed making it possible to separate Am(III) from lanthanoids from acidic nitrate solutions.

At present, two technological schemes are applied to the isolation of trivalent transplutonium elements and lanthanoids and their mutual separation. The first is the Tramex method¹, which enables the separation of the elements from chloride medium. The aqueous phase is constituted by 1M-LiCl + 0.25M-HCl, and 0.6M solution of a tertiary amine (Alamine 336) in diethylbenzene serves as the extracting agent. The value of the separation factor of Am from Eu is high, about 80, a limitation, however, is the chloride medium, owing to its corrosive activity. The second is the Talspeak method², where aqueous phase is used composed of 1M lactic acid and 0.1M-DTPA (diethylenetriaminopentaacetic acid), pH 1.8—3.0. The Am/Eu separation factor up to 27 is achieved on extraction with 0.3M-D2EHPA (di-2-ethylhexylphosphoric acid). A drawback of this method is the low acidity of the aqueous phase required, calling for a considerable lowering of the acidity of the incoming solutions prior to the extraction.

During the extraction of lanthanoids with tertiary amines or quaternary ammonium salts involving the benzyl group as one of the substituents, the effect of the alkyl chain

length on the extraction selectivity and capacity was studied, and benzyldimethyl-laurylammonium nitrate (BDMLNNO₃) was found among the quaternary ammonium salts to be suitable for the extraction of europium and other lanthanoids^{3,4}.

In the present work we have therefore examined the possibility of application of BDMLNNO₃ to the separation of americium from lanthanoids⁵ and studied further the mechanism of the Am extraction with this reagent from nitrate solutions.

EXPERIMENTAL

Chemicals

All the chemicals used in this work were reagent grade purity. Europium nitrate was prepared by reaction of europium oxide with the stoichiometric amount of nitric acid and twice recrystallized. The ²⁴¹Am isotope was furnished in solution in HNO₃ by the Radiochemical Centre, Amersham, England, the ^{152,4}Eu isotope was obtained from the USSR as the oxide, and transferred into solution by dissolving in HNO₃. Benzyldimethyl-laurylammonium nitrate was prepared by conversion of benzyldimethyl-laurylammonium bromide (Slovakofarma, Hlohovec) with silver nitrate and multiple recrystallization from n-hexane. Prior to the final recrystallization, the solution was freed from Ag⁺ ion traces by sorption on the cation exchanger Ostion KS.

Apparatus and Procedures

The extraction was accomplished by agitation in ground-in stopper test tubes at 20 ± 1°C for 10 min applying the aqueous-to-organic phase ratio 1 : 1. The radioactivity of both ^{152,4}Eu and ²⁴¹Am was measured by means of a well gamma-scintillation probe in conjunction with an automatic pulse counter NZQ or a measuring kit NZQ 717-T (Tesla, Liberec).

The infrared spectra were measured in AgCl cells on a spectrophotometer Perkin-Elmer 325 in the wavenumber region 600–4000 cm⁻¹.

RESULTS AND DISCUSSION

Since no published data are available concerning the extraction of Am(III) with BDMLNNO₃, we studied first the effect of the composition of the two phases on the value of the distribution ratio of Am(III) (D_{Am}).

The effect of the initial concentration of nitric acid in the aqueous phase ($c_{HNO_3}^0$) on D_{Am} during the extraction from solutions of a constant initial concentration of the nitrate ions (6M-(H, Li)NO₃) is given in Table I. The D_{Am} value is relatively constant ($D_{Am} = 68-65$) in the region $c_{HNO_3}^0 = 0.05-0.3 \text{ mol l}^{-1}$, and only if the $c_{HNO_3}^0$ value is further raised, the distribution ratio drops rapidly. The relative constancy of D_{Am} at low nitric acid concentrations is probably due to the fact that most of the acid is extracted with the amine out of the aqueous phase, whereby its equilibrium concentration in the aqueous phase is considerably lower than $c_{HNO_3}^0$. In this region, most of the amine occurs as R₄NAm(NO₃)₄. When $c_{HNO_3}^0$ exceeds the amine concentration $c_{R_4NNO_3}^0$, most of the amine is present in the form of the associate

TABLE I

Extraction of Americium Nitrate with Benzyltrimethylammonium Nitrate in the Isomolar Series of Nitric Acid and Lithium Nitrate

$c_{\text{Am}(\text{NO}_3)_3}^0 = 1 \cdot 10^{-9} \text{ mol l}^{-1}$, $c_{\text{BDMLNNO}_3}^0 = 0.5 \text{ mol l}^{-1}$ (in benzene), $\sum c_{\text{NO}_3^-}^0 = (c_{\text{HNO}_3}^0 + c_{\text{LiNO}_3}^0) = 6 \text{ mol l}^{-1}$.

$c_{\text{HNO}_3}^0$ mol l^{-1}	D	$c_{\text{HNO}_3}^0$ mol l^{-1}	D
0.05	68.10	0.70	5.76
0.10	67.90	1.00	2.67
0.20	67.00	1.50	0.63
0.30	65.40	2.00	0.27
0.50	25.90		

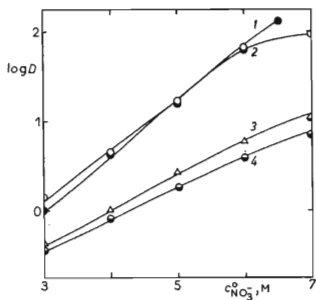


FIG. 1

Extraction of Americium Nitrate with Benzyltrimethylammonium Nitrate in Dependence on the Concentration of the Salting-Out Agents

$c_{\text{Am}(\text{NO}_3)_3}^0 = 1 \cdot 10^{-9} \text{ mol l}^{-1}$, $c_{\text{HNO}_3}^0 = 0.3 \text{ mol l}^{-1}$, $c_{\text{BDMLNNO}_3}^0 = 0.5 \text{ mol l}^{-1}$ (in benzene). For $c_{\text{NO}_3^-}^0 < 3 \text{ mol l}^{-1}$, $D \leq 0.02$. 1 $\text{Mg}(\text{NO}_3)_2$, 2 LiNO_3 , 3 $\text{Ca} \cdot (\text{NO}_3)_2$, 4 NaNO_3 .

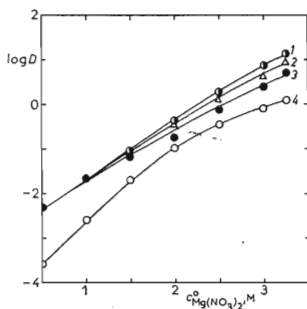


FIG. 2

Extraction of Americium Nitrate with Benzyltrimethylammonium Nitrate in Various Solvents

$c_{\text{Am}(\text{NO}_3)_3}^0 = 1 \cdot 10^{-9} \text{ mol l}^{-1}$, $c_{\text{HNO}_3}^0 = 0.3 \text{ mol l}^{-1}$, $c_{\text{BDMLNNO}_3}^0 = 0.3 \text{ mol l}^{-1}$ (in solvent naphtha 1), 0.5 mol l^{-1} (in xylene, toluene, and benzene). 1 benzene, 2 toluene, 3 xylene, 4 solvent naphtha I.

$R_4NNO_3 \cdot HNO_3$ and only a small proportion as R_4NNO_3 forming an extractable complex with $Am(NO_3)_3$, which brings about a decrease of D_{Am} .

The effects of the other parameters on the D_{Am} were examined at $c_{HNO_3}^0 = 0.3 \text{ mol} \cdot l^{-1}$, as on the one hand this is a concentration low enough for the D_{Am} to attain values suitable for the extraction, and on the other hand in comparison with the nitric acid concentrations in industrial solutions this $c_{HNO_3}^0$ value is just so high that adjustment of the acidity of these solutions will not pose a problem.

The effect of the salting-out agent on the extraction of Am(III) is similar as on the extraction of Eu(III) (ref.²). The extraction of Am(III) with comparable concentrations of the various salting-out agents and with equal concentrations of the remaining components in the aqueous and organic phases increases in the order $NaNO_3 < Ca(NO_3)_2 < LiNO_3 < Mg(NO_3)_2$ (Fig. 1). The distribution ratios are of the order of tens with the agents $LiNO_3$, $NaNO_3$ and $Ca(NO_3)_2$, the highest value ($D_{Am} = 134$) was obtained during extraction from $0.2M \cdot HNO_3 + 6.2M \cdot Mg(NO_3)_2$.

The effect of the kind of solvent was also examined by testing benzene, toluene, xylene, and solvent naphtha I. Tetrachloromethane and chloroform turned out to be unsatisfactory, as the solubility of $BDMLNNO_3$ in them is very low. The extraction of Am(III) using the agent solution $c'_{BDMLNNO_3} = 0.5 \text{ mol} l^{-1}$ (Fig. 2, Table II) decreases in the order benzene > toluene > xylene. A direct comparison of the efficacy of the extracting agent solution in solvent naphtha with the other solutions

TABLE II

Dependence of the Extraction of Americium Nitrate with Benzyldimethylaurylammonium Nitrate (in solvent naphtha I, xylene, and toluene) on the Concentration of Magnesium Nitrate $c_{Am(NO_3)_3}^0 = 1 \cdot 10^{-9} \text{ mol} l^{-1}$, $c_{HNO_3}^0 = 0.3 \text{ mol} l^{-1}$, $c'_{BDMLNNO_3} = 0.5 \text{ mol} l^{-1}$ (in xylene and toluene), $0.3 \text{ mol} l^{-1}$ (in solvent naphtha I).

$c_{NO_3^-}^0$ $\text{mol} l^{-1}$	D for the solvent		
	solvent naphtha I	xylene	toluene
0	$0.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$
1	$3.0 \cdot 10^{-3}$	0.04	0.04
2	0.03	0.19	0.23
3	0.19	0.58	0.83
4	1.09	2.55	3.63
5	3.56	7.91	12.8
6	8.45	25.0	41.6
6.5	15.2	55.1	96.3

cannot be made because in the former solvent only solutions of concentration not higher than 0.3 mol l^{-1} can be prepared. From a comparison with the results obtained with $0.3M$ solution in benzene from $0.3M\text{-HNO}_3 + 6.7M\text{-LiNO}_3$, which for $c'_{\text{BDMLNNO}_3} = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6,$ and 0.8 mol l^{-1} gave $D_{\text{Am}} = 0.96, 5.4, 13.0, 49.3, 86.5, 129,$ and $171,$ respectively, the solvent naphtha can be assessed to be in this respect comparable with benzene.

When Am(III) and Eu(III) (refs^{1,2}) are extracted from acidic nitrate solutions with benzyldimethylaurylammonium nitrate, the concentrations of the pertinent nitrates being as suggested above, the distribution ratios attain values of tens to hundreds for the highest concentrations of the salting-out agents in the aqueous phase, as against benzyldibutylamine^{1,6}, for which the distribution ratios lie in the range of units to tens, and trialkylamines, where they are as low as only tenths⁷. The separation factors $\alpha_{\text{Am/Eu}}$ (Table III) for the application of BDMLNNO₃ as the extracting agent for the separation of Am and Eu from $0.3M\text{-HNO}_3$ attain in some cases values as high as 23; thus with the application of lithium or magnesium nitrate, benzyldimethylaurylammonium nitrate can be employed as the separating agent for these ions.

The extraction of americium nitrate with quaternary tetraalkylammonium salts proceeds with the formation of $R_4N\text{Am}(\text{NO}_3)_4$ (ref.⁸). Nitric acid does not participate in the formation of the associate with Am(III), as confirmed by the infrared spectra of the systems concerned (Table IV).

A marked proportion of the complex anions $\text{Am}(\text{NO}_3)_4^-$ and $\text{Eu}(\text{NO}_3)_4^-$ is formed during the extraction of the respective ions, as indicated by the extraction data, only at high concentrations of the nitrate ions in the aqueous phase⁹, hence in the presence of high concentrations of alkaline earth nitrates and such nitrates whose cations do not form nitrate complexes and thus are not extracted^{10,11}. In solutions containing

TABLE III

Values of the Americium/Europium Separation Factor for the Extraction with $0.5M$ Benzyldimethylaurylammonium Nitrate in Benzene from Aqueous Solutions Containing $0.3M\text{-HNO}_3$ and Different Concentrations of the Salting-Out Agents

Concentration of the salting-out agent M-NO ₃	$\alpha_{\text{Am/Eu}}$			
	LiNO ₃	NaNO ₃	Ca(NO ₃) ₂	Mg(NO ₃) ₂
5	15.7	2.3	2.2	3.0
6	23.0	2.1	2.5	8.0
7	21.6	—	4.9	—

TABLE IV
 Characteristic Absorption Bands in the IR Spectra of Solid BDMLNNO₃ and Benzene Solutions of BDMLNNO₃ and BDMLNNO₃ + HNO₃ + Eu(Am)(NO₃)₃
 Band positions in cm⁻¹, relative band intensity: w weak, m medium, s strong, sh shoulder, b broad; v very.

Assignment	BDMLNNO ₃	0.5M-		0.5M-		0.5M-		0.5M-	
		-BDMLNNO ₃	-BDMLNNO ₃	-BDMLNNO ₃	-BDMLNNO ₃	-BDMLNNO ₃	-BDMLNNO ₃	-BDMLNNO ₃	-BDMLNNO ₃
				0.5M-BDMLNNO ₃ + HNO ₃	0.5M-BDMLNNO ₃ + HNO ₃	0.3M-HNO ₃	0.3M-HNO ₃	2M-HNO ₃	2M-HNO ₃
$\nu(\text{OH})$ free in water	—	—	—	3 640 sh	3 640 sh	—	—	—	—
$\nu(\text{OH}, \text{H})$ bonded	3 420 w, b	3 420 w, b	3 440 s	3 420 m	3 420 m	—	—	3 640 sh	3 640 sh
$\nu(\text{CH})_{\text{asym}}$	2 920 s	2 970 sh	2 970 sh	2 970 sh	2 970 sh	—	—	2 970 sh	2 970 sh
$\nu(\text{CH})_{\text{sym}}$	2 860 s	2 930 s	2 920 s	2 910 s	2 910 s	—	—	2 910 s	2 910 s
$\nu(\text{CH})$ on d-C	—	2 850 s	2 850 s	2 840 s	2 840 s	—	—	2 840 s	2 840 s
$\nu(\text{NH}, \text{H})$ bonded	—	—	—	—	—	—	—	—	—
$\delta(\text{HOH})$ in water	—	—	—	—	—	—	—	—	—
$\delta(\text{CH}_3)$	1 260 s	1 625 m	1 620 m	1 620 m	1 620 m	—	—	(1 620)	(1 620)
$\delta(\text{CH}_2)$ split	1 470 sh	1 460 s	1 460 s	1 450 s	1 450 s	—	—	1 450 s	1 450 s
$\omega(\text{CH}_2)$ (wagging)	—	1 470 sh	1 470 sh	1 480 sh	1 480 sh	—	—	1 480 sh	1 470 sh
$\nu(\text{N}=\text{O})$ in HNO ₃	—	—	(1 630)	—	—	—	—	—	—
$\nu(\text{N}=\text{O})$ in NO ₃	1 330 s	1 340 s	1 340 vb	—	—	—	—	1 625 w	1 640 m
$\nu(\text{N}=\text{O})$ in HNO ₃	—	—	—	—	—	—	—	1 370 s	1 370 w
(H-bonding split)	—	—	—	—	—	—	—	—	—
$\nu(\text{CN})$	1 075 w	1 075 w	1 280 w	1 290 vw, b	1 290 vw, b	—	—	1 310 s, b	1 320 s
$\delta(\text{NO}_2)$ in HNO ₃	—	—	—	—	—	—	—	1 075 w	1 075 w
	—	—	—	—	—	—	—	940 w	940 m

a higher concentration of nitric acid in the aqueous phase, the formation of the associate with the extractable nitric acid $R_4NNO_3 \cdot HNO_3$ is favoured as compared with the extraction of $Am(NO_3)_3$ and formation of $R_4NAm(NO_3)_4$, and thus the extraction of americium is suppressed.

During the scanning of the infrared spectra, americium nitrate was modelled by europium nitrate, to avoid handling active solutions. This approach is justified by the very similar behaviour of $Am(III)$ and $Eu(III)$, as found previously^{1,2,12,13} and in the present work.

In addition to the absorption band positions of the characteristic groups of the agent and of the system concerned in benzene solutions, those of the solid quaternary ammonium salt $BDMLNNO_3$ were measured as well (Table IV). The characteristic bands of the NH groups, which take part in the extraction of acids with amines, have not been found in the spectra of the quaternary ammonium salts.

Pronounced changes occur in the positions of the NO_3 bands belonging to the NO_3^- ion of the quaternary ammonium salt, which shift by up to 40 cm^{-1} on the formation of the associate with nitric acid and with the extracted metal nitrate. The NO_3^- ion of the quaternary ammonium salt is hydrogen bonded to the nitric acid, $NO_3 \cdot HNO_3$ (in the case of nitric acid extraction) or becomes part of the complex ion $Am(NO_3)_4^-$ in the associate $R_4NAm(NO_3)_4$ (in the case of americium nitrate extraction).

The infrared spectra of the organic phase were also evaluated after the extraction from americium (europium) nitrate solutions with a very low nitric acid concentration (0.05 mol l^{-1}), where high values of the distribution ratios were achieved and where the extraction of nitric acid does not compete with that of trivalent metal salts. Here the characteristic absorption bands of the $N=O$ group in nitric acid have not been found (Table IV). From this it can be concluded that, as stated above, nitric acid does not participate in the formation of the associate with the extractable americium nitrate.

At higher concentrations of nitric acid, when the extraction of $Me(NO_3)_3$ is suppressed, distinct absorption bands of NO in nitric acid bonded in the associate do appear in the infrared spectra, and their intensity increases with the increasing initial concentration of nitric acid. Pronounced intensity variations of the NO bands with the increasing nitric acid concentration are observed for the stretching vibration bands at 1625 and 1370 cm^{-1} and for the bending vibration bands at 940 cm^{-1} .

During the extraction with organic solutions of $BDMLNNO_3$, water is co-extracted; its content lowers with decreasing activity of water in the aqueous phase, hence with the increasing concentration of the salting-out agent or of nitric acid. The results of the chemical analysis of water in the organic phase¹⁰ indicate that in the case of the formation of the R_4NNO_3 associate with the examined metal nitrate, one water molecule enters the associate, $R_4NAm(NO_3)_4 \cdot H_2O$ or $R_4NEu(NO_3)_4 \cdot H_2O$ being formed.

REFERENCES

1. Luze E. E., Baybarz R. D.: Nucl. Sci. Eng. 17, 252 (1971).
2. Culler F. L.: ORNL — 3452, 1963.
3. Jedináková V., Žilková J. in the book: *Issledovaniya v Oblasti Pererabotki Obluchennogo Topлива*, Vol. 11, p. 180. Materialy IV. Simpoziuma SEV, Karlovy Vary 28. 3.—1. 4. 1977.
4. Jedináková V., Cibulková J.: This Journal, in press.
5. Jecínáková V.: Czech. 180505.
6. Baybarz R. D.: At. Energ. Rev. 8, 327 (1970).
7. Kappelmann F. A., Weaver B. S.: U. S. 3,230.036.
8. Orth D. A.: *Proc. Inter. Solvent Extraction Conf.*, Hague 1971, p. 534. London 1971.
9. Jedináková V., Čeleda J.: Sb. Vys. Šk. Chemicko-Technol. Praze B 7, 79 (1966).
10. Leuze R. E., Baybarz R. D.: ORNL — P 1577, 1965.
11. Jedináková V., Cibulková J.: Sb. Vys. Šk. Chemicko-Technol. Praze, in press.
12. Seeley F. G., Crouse D. J.: J. Chem. Eng. Data 16, 393 (1971).
13. Mezhov E. A.: *Ekstraktsiya Aminami, Solyami Aminov i Chetvertichnymi Ammonievymi Osnovaniyami*, Vol. 2, p. 190. Atomizdat, Moscow 1977.

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