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Influence of Some Organic Additives on the Extractive Separation of Americium(III) by Sulfoxides

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Influence of Some Organic Additives on the Extractive Separation of Americium(III) by Sulfoxides

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Abstract

The solvent extraction behavior of americium(III) from aqueous nitrate media by two long-chain aliphatic sulfoxides has been examined systematically in the presence of several water-miscible organic solvents to study their possible synergistic effect on metal ion extraction. Methanol, ethanol, *n*- and isopropanol, *n*-butanol, dioxane, acetone, as well as acetonitrile, were employed as the organic component of the mixed (polar) phase. These additives affected the extraction to varying degrees. Extractability of Am increased 5 to 10-fold with increasing concentration of some of these additives, with the maximum enhancement being observed in the presence of acetone or acetonitrile. However, alcohols are generally very poor in this respect. Possible reasons for such behavior are briefly discussed. The distribution of several common contaminants was also investigated at the optimum condition for americium extraction.

INTRODUCTION

Numerous applications of mixed aqueous-organic media have recently elicited much interest in extractive separations of diverse inorganic substances from aqueous solutions (*1–6*). Though such media have been in general use in ion-exchange studies and separations (*7–9*) for quite some time, nevertheless their application in extractions has been infrequent. However, several potential applications of such systems in chemical and radiochemical separations have been suggested (*10–14*). For example, separation of silver and mercury and also of silver and selenium, which did not seem feasible previously from aqueous media, could be effected from hydro-organic media (*15*). In addition, applications of mixed media for selective separation of actinides from impurity elements have been recommended owing to the simplicity and ease of removal of associated fission product contaminants after separation (*6, 16*). Recently Shabana and Ruf (*17*) have shown the possibility of the mutual separation of Am(III) and Cm(III) at low nitric acid concentrations containing 1:1 acetone with Aliquat-336 in xylene as the extractant. These considerations prompted us to study the extractability of actinides with dialkyl sulfoxides from mixed media (*18*).

As part of comprehensive studies on the extraction of actinides with long-chain aliphatic sulfoxides, we have already reported on the extraction of americium(III) from aqueous nitrate solution by sulfoxides (*19*). In this paper, results concerning the distribution of Am(III) and its extractive separation from some commonly occurring contaminants by two sulfoxides, viz., di-*n*-octylsulfoxide (DOSO) and di-isoamylsulfoxide (DISO) from mixed aqueous-organic media (polar) are presented. Different water-miscible organic solvents such as methanol, ethanol, *n*- and isopropanol, *n*-butanol, dioxane, acetone, and acetonitrile were employed as the organic component of the mixed phase (also referred to as the polar phase). The aim of this work was to ascertain the optimum conditions for the extraction as well as recovery of americium in a radiochemically pure state even from moderately concentrated acidic solutions for which no satisfactory simple methods are available.

EXPERIMENTAL

The aliphatic alcohols (methanol, ethanol, *n*- and isopropanol, *n*-butanol), dioxane, acetone, and acetonitrile were all reagent-grade solvents. The radiochemically pure isotopes ^{239}Pu, ^{233}U, ^{152,154}Eu, ^{147}Pm, ^{141}Ce, ^{137}Cs, and ^{103,106}Ru were used as tracers. ^{147}Pm, ^{233}U, and ^{239}Pu were radioassayed by liquid scintillation counting using the method given by Ihle et al (*20*). Gamma-emitters ^{103,106}Ru, ^{137}Cs, ^{141}Ce, ^{152,154}Eu, and ^{241}Am were detected by counting 1-mL aliquots in glass tubes in a well-type NaI(Tl) scintillation detector coupled with a single channel analyzer.

Details of other reagents, extraction procedure, and of ^{241}Am(III) tracer are essentially as described earlier by us (*19*) except that the aqueous phase contained the appropriate organic additive. In all extractions the polar phase was adjusted to the desired molarity of nitric acid and nitrate salt, and it contained 10–50% by volume of the water-soluble organic component. The organic phase was always preequilibrated with the suitable acidic nitrate solution. The initial americium concentration in each experiment was 10^{-6} to 10^{-4} M which gave a total of $\sim 10^5$ cpm as measured in suitable aliquots from both phases after extraction. The distribution ratios (D_{Metal}) were calculated as the ratio of the activity in the organic phase to that in the polar phase. All the values were determined at least in duplicate and the agreement in the values was good (to within ±2%). Solvesso-100 was used as the diluent for these sulfoxides throughout the investigation. Calcium nitrate was selected as the salting-out agent.

RESULTS AND DISCUSSION

Dependence of D_{Am} on Organic Additive Concentration

Preliminary experiments indicated that the organic additives generally exerted a pronounced effect on americium extraction. Figure 1 represents data on distribution of Am(III) with 0.3 M DOSO and 0.8 M DISO from [0.2 M HNO_3 + 2.5 M $Ca(NO_3)_2$] containing varying amounts of acetone, acetonitrile, dioxane, and methanol. It is clear from this plot that D_{Am} is significantly enhanced by the introduction of all the organic additives to the aqueous phase except alcohols. Methyl and ethyl alcohols only showed a marginal increase while with higher alcohols, e.g., *n*- and isopropanol, *n*-butanol, extraction of Am even decreased to some extent. The effect of alcohols is thus antagonistic, presumably due to interaction of these with sulfoxides in the organic phase and to the decrease in the partition coefficient of these extractants due to swelling of the organic phase. Maximum enhancement in extraction was accomplished in the presence of acetone or acetonitrile. Such organic liquids, being less polar than water, favor the formation of the neutral adduct, $Am(NO_3)_3 \cdot XR_2SO$. Generally, the dehydration effect (*21*) of the organic additives leads to an increase in the metal ion extraction.

At the same additive percentage, the values of distribution ratios follow the sequence acetonitrile ~ acetone > dioxane > alcohols, which is roughly in accordance with their dielectric constants. Such behavior has also been observed earlier by us while studying plutonium(IV) extraction [18], except for the reverse order between dioxane and alcohols. Shabana et al. (*12*) have also reported similar enhancement on the extractive separation of Np, U, Th, and Ce with TOPO from mixed solvents. Numerous other instances recently compiled by us (*6*) add more support. It merits mention here that these additives did not pass on to the nonpolar phase (the volume of the latter phase remained nearly constant after reaching equilibrium except when it contained about 30 vol% or more of higher alcohols) and hence their effect can be explained by interaction in the aqueous phase only.

On the basis of these data, it can be seen that the addition of acetone or

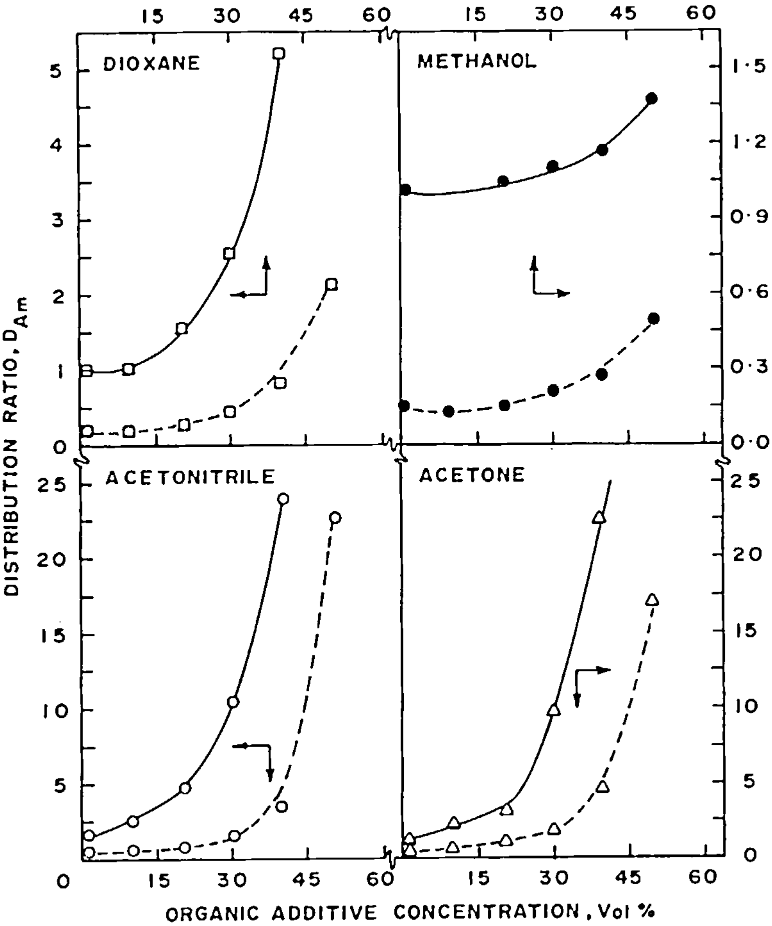

FIG. 1. Influence of organic additive content on the extraction of Am(III) from [0.2 *M* HNO_3 + 2.5 *M* $Ca(NO_3)_2$] media with 0.3 *M* DOSO (- -) or 0.8 *M* DISO (——).

acetonitrile to the acidic nitrate medium may be helpful in the recovery of americium from the organic phase. To illustrate the advantage obtained by using various additives, the D_{Am} values and the advantage factor (AF), defined as

$$AF = \frac{D_{\text{Am}} \text{ in mixed medium}}{D_{\text{Am}} \text{ in pure aqueous medium}}$$

for 50 vol% acetone as well as acetonitrile are presented in Table 1. these results indicate that for most of the nitric acid concentrations ranging from 0.2 to 1.0 M HNO_3, high D_{Am} values (AF: 10–96) could be realized for americium extraction. Values of AF are slightly higher with 0.3 M DOSO as compared to those obtained with 0.8 M DISO.

Attempts have been made to explain the effects of these additives on the basis of a number of mutually related factors such as complex formation, solvation, and ionic and molecular interaction in the aqueous solution (*22*). The decrease of electrolyte dissociation in the presence of organic solvents with low dielectric constants results in an increase in extraction.

Dependence of D_{Am} on Sulfoxide/Nitric Acid Concentration

The concentration of the organic additive in the aqueous phase significantly affects the extraction of americium (*23*). To examine this, extraction of Am(III) with 0.1–0.4 M DOSO as well as 0.3, 0.6, and 0.8 M DISO from

TABLE 1

D_{Am} Values and Calculated Advantage Factor (AF) for Extraction of Am(III) by Sulfoxides from Different Nitric Acid Media Containing Organic Additives. Salt Medium: 2.5 M $Ca(NO_3)_2$

	0.2 M HNO_3		0.4 M HNO_3		0.6 M HNO_3		0.8 M HNO_3		1.0 M HNO_3	
Additive	D_{Am}	AF	D_{Am}	AF	D_{Am}	AF	D_{Am}	AF	D_{Am}	AF
0.3 M DOSO										
	0.2	1	0.2	1	0.1	1	0.1	1	0.1	1
50% Acetonitrile	16.9	70.4	8.9	59.6	4.7	46.6	2.1	30.3	0.5	10.6
50% Acetone	22.9	95.6	10.3	68.7	5.4	53.9	3.2	45.4	1.0	20.2
0.8 M DISO										
	1.7	1	1.0	1	0.8	1	0.7	1	0.4	1
50% Acetonitrile	65.1	39.2	41.1	40.3	29.0	37.2	24.7	34.4	11.8	28.7
50% Acetone	69.5	41.9	37.2	36.5	27.7	35.5	16.0	22.3	8.0	19.5

an acidic nitrate media [0.2 *M* HNO_3 + 2.5 *M* $Ca(NO_3)_2$] with varying acetonitrile concentration was investigated. From the results summarized in Table 2, it is quite evident that D_{Am} markedly increased both with sulfoxide and acetonitrile concentrations. Essentially quantitative extraction of Am could be achieved by ~0.3 *M* sulfoxides or more from the acidic nitrate media containing more than 30% (v/v) acetonitrile. Similar behavior was also noted with acetone as the organic component.

The effect of water-miscible organic solvents on americium extraction was further studied at increasing nitric acid molarities in the aqueous phase. Representative data for only 50% acetone is shown in Fig. 2. It can be seen from this figure that D_{Am} is considerably enhanced by replacement of water with acetone. The extractability of Am both with 0.3 *M* DOSO and 0.8 *M* DISO increased 5–10 times in the presence of 50% by volume of acetone or acetonitrile as compared with that from corresponding aqueous acid solutions. The low dielectric constant values of the organic solvents enhance the association of the complex, thereby increasing the adduct stability and favoring the extraction of americium. Extraction was almost quantitative from aqueous nitrate medium [~2.5 *M* $Ca(NO_3)_2$] containing 0.1–0.4 *M* HNO_3 and then generally diminished with increasing nitric acid amounts. Negligible extraction occurred from nitric acid solutions in the absence of nitrate salts. The observed decrease was, however, not so drastic in the case of DISO (% extraction: ~90%) even up to 1 *M* HNO_3 but then decreased to about 70% at 1.75 *M* HNO_3 medium.

TABLE 2
Effect of Sulfoxide Concentration on Am(III) Extraction from Aqueous-Acetonitrile Polar Phase. Aqueous Phase:
[0.2 *M* HNO_3 + 2.5 *M* Ca $(NO_3)_2$]

	Distribution ratio, D_{Am}					
	DOSO (*M*)			DISO (*M*)		
Acetonitrile (%)	0.2	0.3	0.4	0.3	0.6	0.8
0	0.1	0.1	0.5	0.1	0.6	1.0
10	0.1	0.4	1.0	0.2	1.4	2.4
20	0.2	0.9	1.6	0.4	2.5	4.8
30	0.2	1.6	2.8	0.6	2.9	10.4
40	0.5	3.4	5.3	0.9	6.8	23.8
50	3.3	16.9	30.4	4.2	22.2	65.1

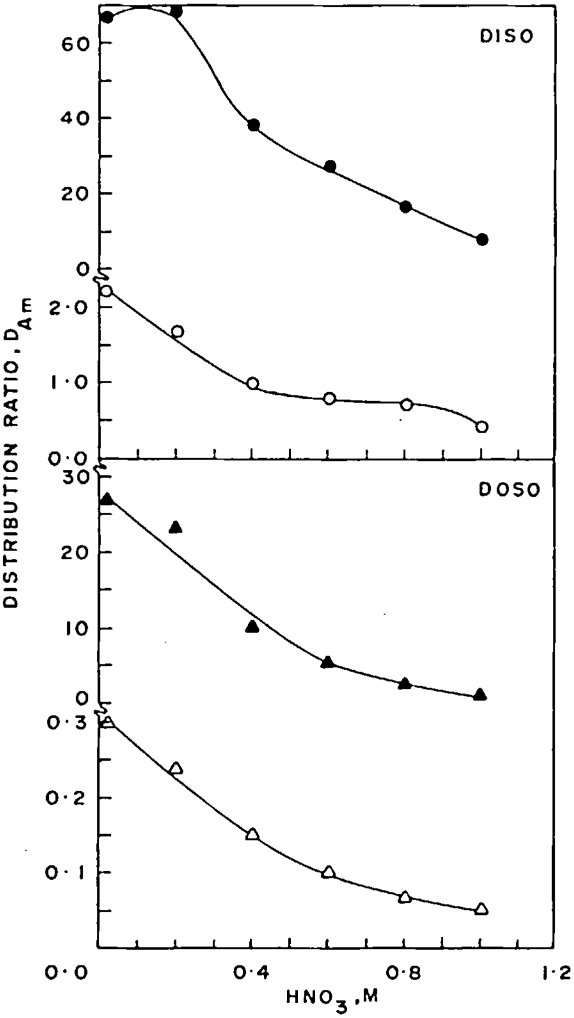

FIG. 2. Extraction of Am(III) with 0.8 *M* DISO or 0.3 *M* DOSO from (△, ○) nitric acid solutions and from (▲, ●) nitric acid solutions containing 50 vol-% acetone. Salt: 2.5 *M* $(Ca(NO_3)_2$.

Extraction of Some Contaminants

The influence of adding 50% (v/v) acetonitrile to the acidic nitrate solution on the extraction behavior of other actinides, lanthanides, and some fission product elements usually accompanying americium during its radiochemical processing was also investigated (Table 3). Extractability of Pu(IV) as well as some lanthanides like Eu, Pm, and Ce increased severalfold by the addition of this organic additive. Contrary to this, extraction of U(VI), Cs, and Ru (?) remained unaffected under such conditions. Negligble extractability is exhibited by cesium (<1%). Thus the low extractability of cesium and ruthenium, two major fission products accompanying americium, affords a relatively simple method for removing them from the actinide and fission product lanthanide elements.

Back-Extraction of Am

Value of D_{Am} at moderate nitric acid concentrations (>1 *M* HNO_3) is small enough to allow its back-extraction from the loaded organic phase. The stripping of americium from organo-aqueous media posed no problem since 1–3 *M* HNO_3 back-extracted it almost quantitatively (>98%) in a single step from the sulfoxide phase.

TABLE 3
Influence of Acetonitrile on the Extraction of Various Elements with Sulfoxides from Mixed Media. Aqueous Phase: [0.2 *M* HNO_3 + 2.5 *M* $Ca(NO_3)_2$][a]

	Distribution ratio, D_{Metal}			
	0.3 *M* DOSO		0.8 *M* DISO	
Tracer	In aq media	In 50% CH_3CN	In aq media	In 50% CH_3CN
^{241}Am	0.1	22.9	1.0	65.1
^{239}Pu	0.9	441	87.3	293
^{233}U	27.4	27.1	31.1	31.7
^{152}Eu	0.3	15.4	1.6	27.0
^{147}Pm	0.3	39	2.5	105
^{141}Ce	0.1	8.1	1.4	39.2
^{137}Cs	Neg.	Neg.	Neg.	Neg.
^{103}Ru	0.4	0.6	0.7	1.1

[a] Neg. = negligible.

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