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Solvent Extraction of Plutonium(IV), Uranium(VI), and Some Fission Products with Di-*n*-octylsulfoxide

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Abstract

Extraction behavior of plutonium(IV), uranium(VI), and some fission products from aqueous nitric acid media with di-*n*-octylsulfoxide (DOSO) has been studied over a wide range of conditions. Both the actinides are extracted essentially completely, whereas fission product contaminants like Zr, Ru, Ce, Eu, and Sr show negligible extraction. The absorption spectra of sulfoxide extracts containing either Pu^{4+} or UO_2^{2+} indicate the species extracted from nitric acid into the organic phase to be $Pu(NO_3)_4 \cdot 2DOSO$ and $UO_2(NO_3)_2 \cdot 2DOSO$, respectively. Extraction of these actinides decreases with increasing temperature, indicating the extraction to be exothermic. DOSO extracts plutonium and uranium better than di-*n*-hexylsulfoxide (DHSO) under all condition and is also more soluble in aromatic diluents than the latter. The effect of gamma radiation on the extraction properties of DOSO is found to be similar to that of DHSO.

INTRODUCTION

Long-chain sulfoxides have been gaining ever-increasing importance as extractants for many radioactive, rare, trace, and nonferrous metals as well as some inorganic and organic acids (*1–8*). Several of them can be obtained at relatively little cost from oil refineries as by-products. Furthermore, sulfoxides are known to possess good chemical and radiation stability (*8*, *9*). These considerations led us to study the extraction ability of different long-chain sulfoxides. In an earlier publication (*8*) we had reported extraction of plutonium, uranium, and some fission products from varying nitric acid concentrations using di-*n*-hexylsulfoxide (DHSO). The main drawback, however, seemed to be the rather low solubility of DHSO in kerosine-type diluents commonly used in fuel reprocessing. The present communication deals with our investigations on solvent extraction of plutonium(IV), uranium(VI) and some long-lived fission products from aqueous nitric acid media by another long-chain alkyl sulfoxide, namely di-*n*-octylsulfoxide (DOSO). The extraction of hexavalent uranium by this reagent has been demonstrated earlier (*1*). Attempts have been made to understand the nature of the metal ion as well as nitric acid species extracted into the DOSO–diluent phase from the absorption spectra of DOSO extracts containing Pu^{4+} or UO_2^{2+}. The effects of temperature and gamma radiation on extraction have also been examined. Solvesso-100, mainly consisting of a mixture of isomeric trimethylbenzenes, was selected as the diluent.

EXPERIMENTAL

Reagent. DOSO $[(C_8H_{17})_2SO]$ was synthesized by a two-step process starting from 386 g of *n*-octylbromide added dropwise to 114 g of anhydrous sodium sulfide in 1 pint of alcohol and refluxed for 20 hr as per the method described for the preparation of sulfoxides in general (*10*). The octyl sulfide was separated in a funnel, washed with water, and reacted at room temperature with stirring with 100 ml of 11 *M* HNO_3. On addition of alkali, a white flocculent precipitate of DOSO separated (~230 g), and it was washed thoroughly with water and dried. The crude product was recrystallized from petroleum ether (60 to 80%) to give white crystals (155 g): m.p. = 75°C; C = 70.1%, H = 12.3%, S = 11.8% required for $(C_8H_{17})_2SO$, C = 70.44%, H = 12.4%, S = 11.7%. All other reagents used were A.R. grade.

For comparison purposes, extraction experiments were performed under conditions similar to those employed in the case of DHSO (*8*), except where otherwise mentioned. For studying the temperature effect on extraction coefficients (*D*), equal volumes of the aqueous and organic phases containing the required tracer and DOSO, respectively, were equilibrated for 20 min in a thermostated water bath maintained at the desired temperature to within ±0.1°C. Other equilibrations were done at room temperature (~25°C).

The oxidation state of plutonium in the aqueous phase, at the end of the equilibration, was checked by the TTA extraction method, and it was ensured that it did not change during extraction. All the values were determined at least in duplicate, and the agreement of values was good (to within ±2%).

RESULTS AND DISCUSSION

Extraction of actinides into sulfoxides has been reported to be fast, attaining equilibrium within few minutes (*4, 8*). Preliminary experiments carried out on the extraction of Pu^{4+}, UO_2^{2+}, and some fission products from aqueous nitric acid solutions into DOSO/Solvesso-100 confirmed this. The extraction coefficients, observed to be virtually independent of the initial metal ion concentration employed ($\sim 10^{-4}$ to 10^{-6} M), indicated the absence of polynuclear species in the extraction system. Sulfoxides, in general, are monomeric in solutions of organic solvents (*11*). Values of D obtained by taking different metal ion activity initially in either phase remained unaltered, thereby confirming the reversibility of the extraction process (*12*).

Extraction of HNO_3 by DOSO

Figure 1 gives a plot of $\log [H^+]_{org} - 2 \log [H^+]_{aq}$ against log $[\text{extractant}]_{org}$ drawn with a unit slope, indicating the species extracted to be $HNO_3 \cdot DOSO$ (*8*). The value of K_H, derived from the equation

$$\log [\text{acid}]_{org} - \log a \pm HNO_3(aq) = n \log [DOSO]_{org} + \log K$$

where $K_H = K/$(dissociation constant of HNO_3, i.e., 23.5), for DOSO is significantly higher than that for DHSO or TBP as seen from the data given in Table 1. The order of basicity is DOSO > DHSO > TBP.

Effect of Varying HNO_3 Concentration on Metal Ion Extraction

Data on the extraction of Pu^{4+}, UO_2^{2+}, Zr^{4+}, Ru, Eu^{3+}, Ce^{4+}, and Sr^{2+} from different HNO_3 aqueous media with 0.2 M DOSO/Solvesso-100 are presented in Table 2. With an increase in HNO_3 molarity in the aqueous phase, extraction of plutonium and uranium first increases, passes through a maximum at around 2 to 5 M, and then decreases (Fig. 2). Against this, D of Zr increases and D of Ru decreases with increasing HNO_3 concentration. No detectable extraction of Eu, Ce, or Sr took place at any acidity. The decrease in the extraction coefficient at higher molarities may be attributed to the formation of less extractable acid

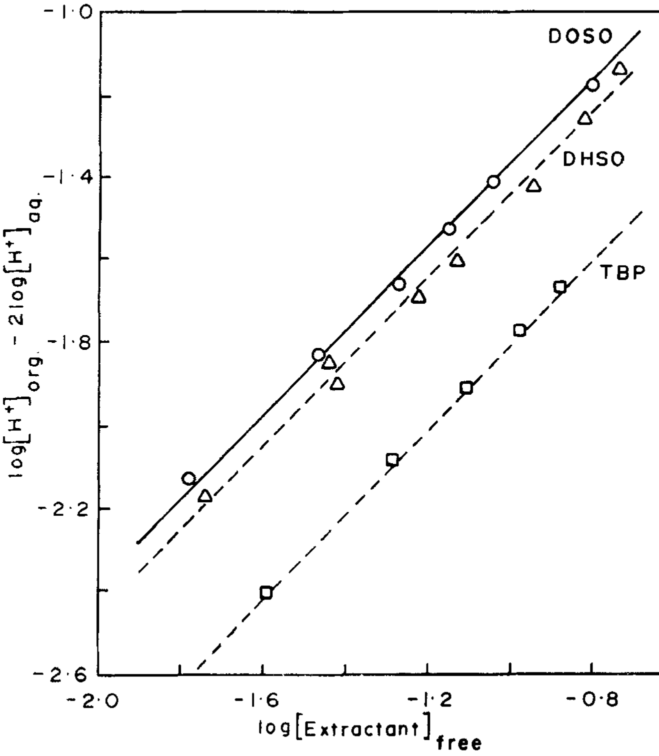

FIG. 1. Nitric acid uptake by DOSO, DHSO, and TBP (2.0 *M*): $[HNO_3] = 0.5\,M$.

TABLE 1

Equilibrium Constants (K_H) for the Uptake of HNO_3 by Different Extractants

Extractant	$H_{aq}^+ + NO_{3\,aq}^- + (\text{extractant})_{org} \xrightarrow{K_H} (HNO_3 \cdot \text{extractant})_{org}$	Refs.
TBP	0.16	*8*
DHSO	0.37	*8*
DOSO	0.42	This work

TABLE 2

Extraction of Metal Ions with 0.2 *M* DOSO/Solvesso-100 as a Function of Nitric Acid Concentration

	Extraction coefficient, D^a						
HNO_3 (*M*)	Pu	U	Zr $\times 10^2$	Ru $\times 10^2$	Eu	Ce	Sr
0.5	2.58	1.67	0.33	—	Negl.	Negl.	Negl.
1.0	3.18	3.15	0.45	8.40	Negl.	Negl.	Negl.
	(2.25)	(2.41)	(4.12)	(2.56)			
2.0	5.13	4.93	1.25	5.05			
	(4.02)	(3.43)	(4.43)	(1.96)			
3.8	7.54	4.13	3.72	1.32			
4.5	8.79	3.75	4.74	—			
5.3	9.16	3.41	—	—	Negl.	Negl.	Negl.
5.6	8.29	3.30	6.71	—			
6.0	8.25	3.08	8.36	0.48			
	(4.84)	(2.54)	(10.76)	(0.26)			
7.6	6.20	2.16	12.85	0.40			
8.0	5.77	1.91	13.55	—			
	(4.10)	(1.53)	(22.10)				
10.1	3.28	0.55	21.72	0.23			
	(1.98)	(0.78)	(83.49)	(0.46)			
13.2	2.01	—	—	—			

[a] Negl. = negligible extraction. Numbers within parentheses are *D* values obtained with 0.2 *M* DHSO/Solvesso-100 under identical experimental conditions (*8*).

complexes of the type (*13*) $HPu(NO_3)_5$ and $H_2Pu(NO_3)_6$ and also to the competition of nitric acid for the sulfoxide at higher concentrations. The pattern of acid dependence of extraction encountered here is similar to that observed in many other systems (*14–16*).

From Table 2 it is clear that extraction efficiency of DOSO for uranium and plutonium is better than that of DHSO (*8*). In contrast, extraction of zirconium is consistently lower with DOSO at all acidities as compared with DHSO, which is a disinct advantage in nuclear fuel processing. Extraction of ruthenium, however, is somewhat unpredictable, due perhaps to the complexity of the species involved. Since the decontamination of plutonium from uranium with TBP as extractant (*17*) is reported to be maximum at about 2 *M* HNO_3, this acidity was maintained in our extraction experiments.

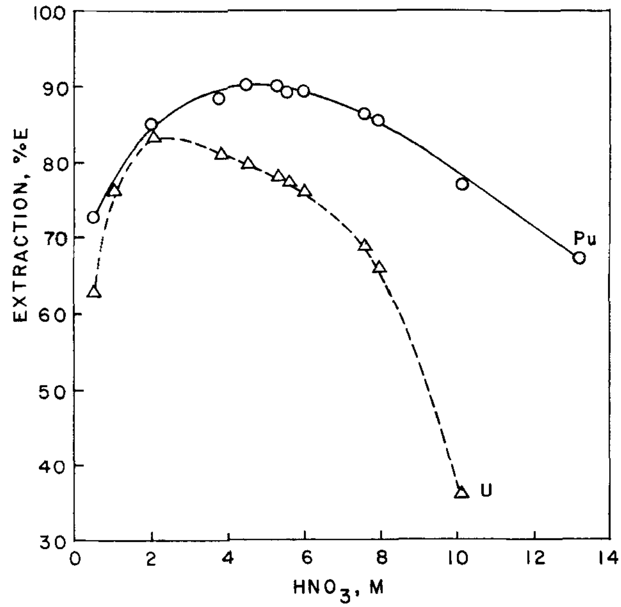

FIG. 2. Extraction as a function of acidity; org/aq = 1; [metal] = tracer (~ 10^{-4} to 10^{-6} M); [DOSO] = 0.2 M.

Dependence of Metal Ion Extraction on DOSO Concentration

The extractability of uranium and plutonium from 2 M HNO_3 by DOSO (0.08 to 0.40 M) increased with increasing reagent concentration (Fig. 3). A 0.4 M DOSO solution extracts more than 95% of either U(VI) or Pu(IV) in a single step. As expected from its basicity, DOSO extracts better than DHSO. For example, at 0.2 M extractant concentration, the values of D_{Pu} for DOSO and DHSO are 5.13 and 4.02, respectively. At constant HNO_3 molarity, the slope of the plot of log D vs log $[DOSO]_{free}$ gives the number of DOSO molecules attached to the metal ion in the organic phase (*8*). The solvation number found in the case of both uranium and plutonium is 2, indicating that the species extracted are $UO_2(NO_3)_2 \cdot 2DOSO$ and $Pu(NO_3)_4 \cdot 2DOSO$, respectively (Fig. 4), which is in accord with published results (*1*, *4*, *8*, *14*). A similar study was not possible with the fission products due to their very poor extractability. The nature of the metal ion species extracted was further confirmed spectrophotometrically (Figs. 5 and 6).

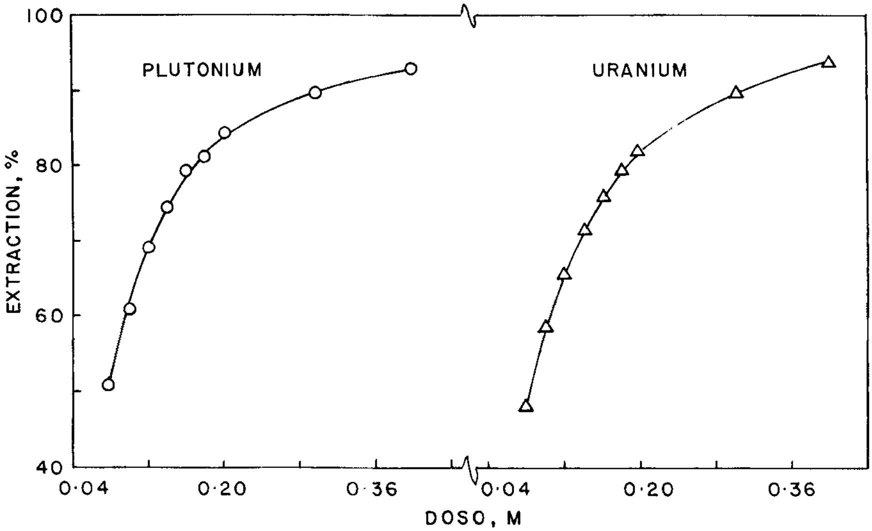

FIG. 3. Extraction as a function of DOSO concentration.

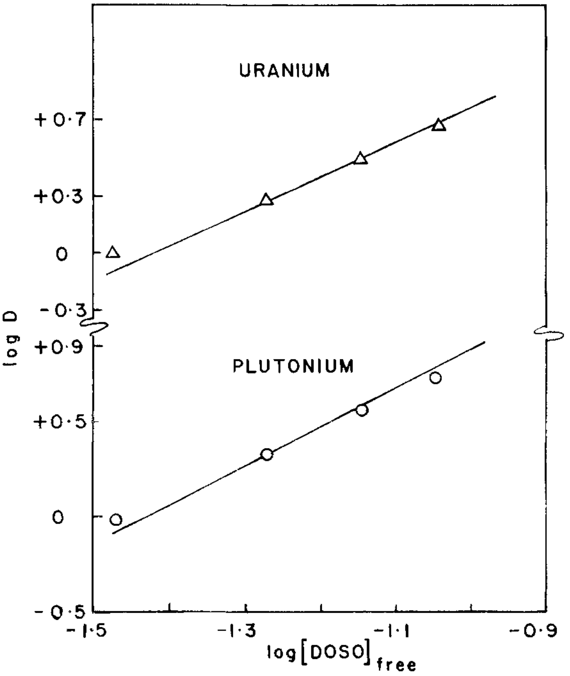

FIG. 4. Plot of log D vs log $[\text{DOSO}]_{\text{free}}$: $[\text{HNO}_3] = 2\,M$; [metal] = tracer ($\sim 10^{-4}$ to $10^{-6}\,M$). (△) UO_2^{2+}, (○) Pu^{4+}.

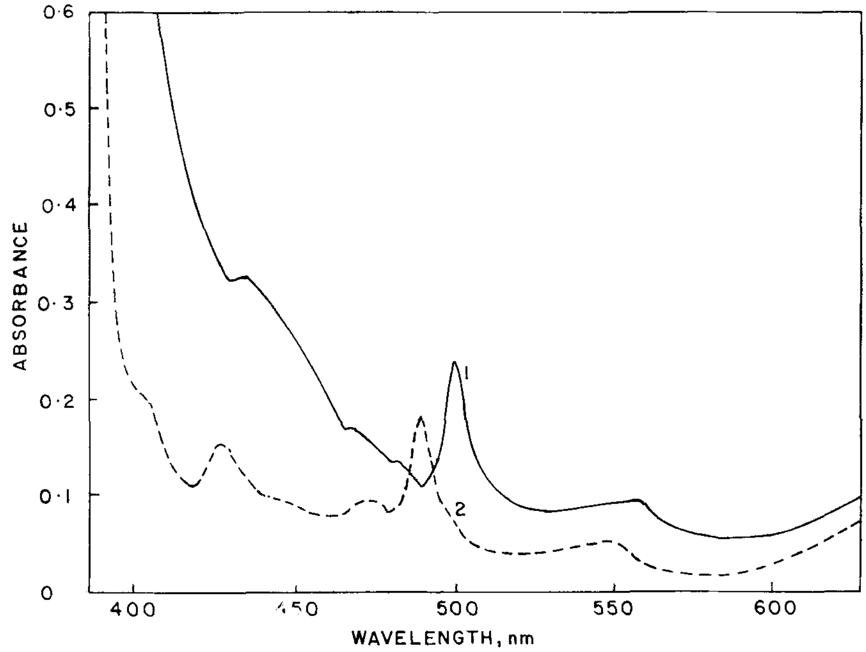

FIG. 5. Absorption spectra of plutonium(IV) species extracted with DOSO (Curve 1) and TBP (Curve 2).

The absorption spectra of the DOSO as well as of the TBP extracts of Pu^{4+} and UO$_2^{2+}$ indicate that all the spectra are similar with sharp absorption maxima, thereby proving the similarity of the species involved. However, a bathochromic shift of the peaks in the spectra of Pu(IV) and U(VI) complexes is observed both with DOSO and TBP as compared to the spectrum in aqueous acidic solutions. A similar pattern was noted on scanning absorption of DHSO extracts (*8*).

Temperature Dependence of Extraction

Extraction of Pu^{4+} and UO$_2^{2+}$ from 2 *M* HNO$_3$ aqueous medium with 0.2 *M* DOSO was investigated at different temperatures. The data given in Table 3 indicate that extraction of both plutonium and uranium decreased with increasing temperature, which is in agreement with the behavior reported for the extraction of actinides with other sulfoxides

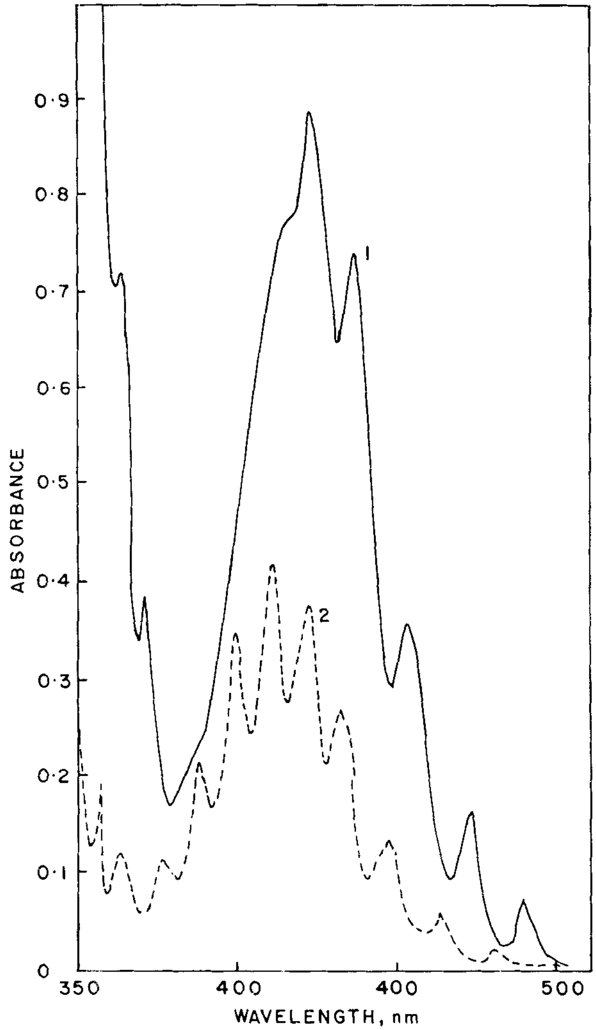

FIG. 6. Absorption spectra of uranium(VI) species extracted with DOSO (Curve 1) and TBP (Curve 2).

TABLE 3
Variation of the Extraction Coefficients of Pu(IV) and U(VI) with Temperature (aqueous medium: 2 *M* HNO_3; extractant: 0.2 *M* DOSO/Solvesso-100)

Temperature (°C)	Extraction coefficient, *D*	
	Pu(IV)	U(VI)
25	5.13	4.92
30	5.01	4.30
40	4.76	3.15
50	4.44	2.61

(*4*, *6*) and suggests that the formation of these species is exothermic. The temperature coefficient of extraction is known to be generally negative for weak solvate complexes (*18*). Evaluation of thermodynamic parameters ΔF, ΔH, and ΔS associated with actinides extractions with DOSO will be the subject matter of a future publication.

Extraction of Macro Amounts of Plutonium and Uranium and Their Stripping

Macro amounts of plutonium and uranium are present during reprocessing of spent fuel. Their extraction characteristics with DOSO were therefore investigated at such concentration levels. Extraction of plutonium (~3 mg/ml) from 2 *M* HNO_3 with 0.4 *M* DOSO in Solvesso-100 was in excess of 90% in a single contact. About 10 mg/ml of Pu(IV) was loaded into the organic phase without encountering the formation of a third phase. Plutonium could be back-extracted to the extent of 70% with ~0.4 *M* HNO_3. The use of some complexing/reducing agents (Table 4) such as acetic and formic acids (1 to 5 *M*) are preferable for stripping plutonium almost quantitatively as they can be destroyed easily, if desired, in the process.

Uranium (~10 mg/ml) in 2 *M* HNO_3 could be extracted more than 80% with 0.4 *M* DOSO and then successfully stripped from this phase with an acid solution of pH 2. Thus DOSO was found to be similar to TBP in its extraction properties of plutonium and uranium.

Effect of Radiation on the Extraction Ability of DOSO

In order to study the effect of gamma radiation on the extraction properties of DOSO, the extraction behavior of Pu and some long-lived

TABLE 4

Back-Extraction (stripping) of Plutonium(IV) from 0.4 *M* DOSO/Solvesso-100 (Pu(IV) concentration: 3 mg/ml)

Stripping agent	Molarity (*M*)	*D* of Pu(IV)	% Back-extraction
Nitric acid	0.4	0.43	69.9
Hydroxylamine hydrochloride + 0.35 *M* HNO_3	0.2	0.0007	99.9
Acetic acid	1	0.0064	99.4
	3	0.0026	99.7
	5	0.0019	99.8
Formic acid	1	0.0079	99.2
	3	0.0021	99.8
	5	0.0014	99.9

TABLE 5

Changes to Extraction Coefficient (*D*) of Pu, Zr, and Ru through Irradiation of 0.2 *M* DOSO/Solvesso-100 (aqueous medium: 2 *M* HNO_3)

Irradiation dose (Mrad)	Extraction coefficient, D^a		
	Pu	Zr	Ru
0	5.13 (4.02)	0.013 (0.037)	0.051 (0.062)
8.5	6.82 (5.09)	1.290 (0.271)	0.070 (0.083)
36.7	5.72 (3.89)	0.921 (0.556)	0.049 (0.055)

[a] Values in parentheses were obtained by using 0.2 *M* DHSO/Solvesso-100 as the extractant.

fission products employing the irradiated reagent was studied. This was accomplished by irradiating a preequilibrated 0.2 *M* DOSO solution in Solvesso-100 for different lengths of time up to a dose of around 37 Mrad. All irradiations were carried out in the presence of air at room temperature with a ^{60}Co source (~2000 Ci) at a dose rate of 1.256×10^{17} eV $g^{-}min^{-1}$ (0.1176 Mrad/hr). From Table 5, it is evident that extraction of plutonium, ruthenium, and zirconium first increased with irradiation up to 8.5 Mrad, and then it slightly decreased at a high dose level (~36.7 Mrad). The decreased metal extraction at high dose rates may be attributed to the decomposition of DOSO into sulfides and sulfones which have poor extractability for these metal ions. These are known to be the main degradation products of alkyl sulfoxides (*9*). A similar trend was also observed with 0.2 *M* DHSO, irradiated along with DOSO for comparison purposes. The effect of irradiation on the extraction properties of DOSO was thus found to be similar to that of DHSO, reported earlier by us (*8*).

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