Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction Separation of Some Actinides and Lanthanides with 2-Thenoyltifluoroacetone

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To cite this Article Reddy, A. Sambasiva and Reddy, L. Krishna(1980) 'Solvent Extraction Separation of Some Actinides and Lanthanides with 2-Thenoyltifluoroacetone', Separation Science and Technology, 15: 5, 1263 — 1269

To link to this Article: DOI: 10.1080/01496398008066971

URL: http://dx.doi.org/10.1080/01496398008066971

SEPARATION SCIENCE AND TECHNOLOGY, 15(5), pp. 1263–1269, 1980

NOTE

Solvent Extraction Separation of Some Actinides and Lanthanides with 2-Thenoyltrifluoroacetone

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Abstract

Solvent extraction behavior of Th(IV) and U(VI) and some lanthanides [Ce(III), Nd(III), Eu(III), Tb(III), and Yb(III)] from thiocyanate medium into sulfoxides and/or 2-thenoyltrifluoroacetone has been studied. The actinides are found to be favorably extracted by both the extractants. The alkyl sulfoxides extract Th(IV) and U(VI) as $Th(SCN)_4 \cdot 3DPSO$, $Th(SCN)_4 \cdot 3DOSO$, $UO_2(SCN)_2 \cdot 2DPSO$, and $UO_2(SCN)_2 \cdot 3DOSO$. The chelate extracts the metals in the following order: U(VI) > Th(IV) > Eu(III) > Tb(III) > Yb(III) > Ce(III) or Nd(III).

INTRODUCTION

The extraction of Th(IV) and U(VI) by alkyl and aryl sulfoxides from mineral acid solutions has been studied in detail by several workers (*1–4*). However, no data have been reported on the extraction of these metals from thiocyanate medium. Furthermore, it is important to note that both the trivalent lanthanides and the actinides are extracted favorably from a pseudohalide medium (*5–8*) which is also noncorrosive. The deposits of Th(IV) and U(VI) are generally associated with rare earths. It is therefore of technological importance to make a comparative study of the solvent extraction behavior of lanthanides and actinides so as to develop an efficient separation and purification procedure. The present communication includes data on Th(IV) and U(VI) extracted from thiocyanate medium by di-*n*-pentyl sulfoxide (DPSO), di-*n*-octyl sulfoxide (DOSO), and 2-thenoyltrifluoroacetone (TTA) in $CHCl_3$. The β-diketone has been suggested for the individual separation of Th(IV), U(VI), Ce(III), Nd(III), Eu(III), Tb(III), and Yb(III).

EXPERIMENTAL

Sulfoxides were synthesized according to procedures already described (*4*). All chemicals and reagents used were of analytical grade or chemically pure. The tracers ^{141}Ce, ^{147}Nd, $^{152+154}$Eu, ^{160}Tb, and ^{169}Yb were obtained from Isotope Group, Bhabha Atomic Research Centre, India.

Solvent Extraction Procedure

The aqueous phase was 1.0 *M* in ammonium thiocyanate; the pH was adjusted to $\sim$3. In the case of Th(IV), pH $\sim$ 1 was maintained to avoid third-phase formation. An aliquot of the metal stock solution was introduced into a given aqueous phase (preequilibrated with appropriate organic phase) and was equilibrated with an equal volume of an appropriate organic phase in a glass-stoppered vial for about 30 min in a thermostat at 30 ± 1°C. At the end of equilibration the phases were allowed to settle, and suitable aliquots of each phase were withdrawn for radioassay of lanthanides by gamma counting using a well-type NaI(Tl) scintillation detector. Th(IV) was estimated as the oxalate (*9*, *10*). U(VI) was estimated spectrophotometrically using 1-(2-pyridylazo)-2 naphthol (PAN) indicator; the metal content can be more conveniently determined in the organic phase than in the aqueous phase (*11*).

RESULTS AND DISCUSSION

The mechanism of extraction of Th(IV) and U(VI) from thiocyanate medium by sulfoxides may be represented by

$$M_{aq}^{m+} + y\mathrm{SCN}_{aq}^{-} + z\mathrm{S}_{org} = \mathrm{M(SCN)}_y \cdot z\mathrm{S}_{org} \qquad (1)$$

where M^{m+} is the metal ion and S is the extractant. The equilibrium constant $K_x{}^1$ for the extraction process may be written as (*6*)

$$K_x{}^1 = D/[\mathrm{SCN}^-]^y[\mathrm{S}]^z \qquad (2)$$

Taking logarithms and rearranging, Eq. (2) yields

$$\log D = \log K_x{}^1 + y \log [\mathrm{SCN}^-] + z \log [\mathrm{S}] \qquad (3)$$

By studying the distribution of the metal as a function of [SCN$^-$] and [S], the compositions of the extracted species have been determined.

The extraction of Th(IV) and U(VI) increases with increases in thiocyanate and extractant concentrations. The slope analysis method indicates the association of four thiocyanate ions with Th(IV) and two thiocyanate ions with U(VI). At constant thiocyanate concentration the slopes of the

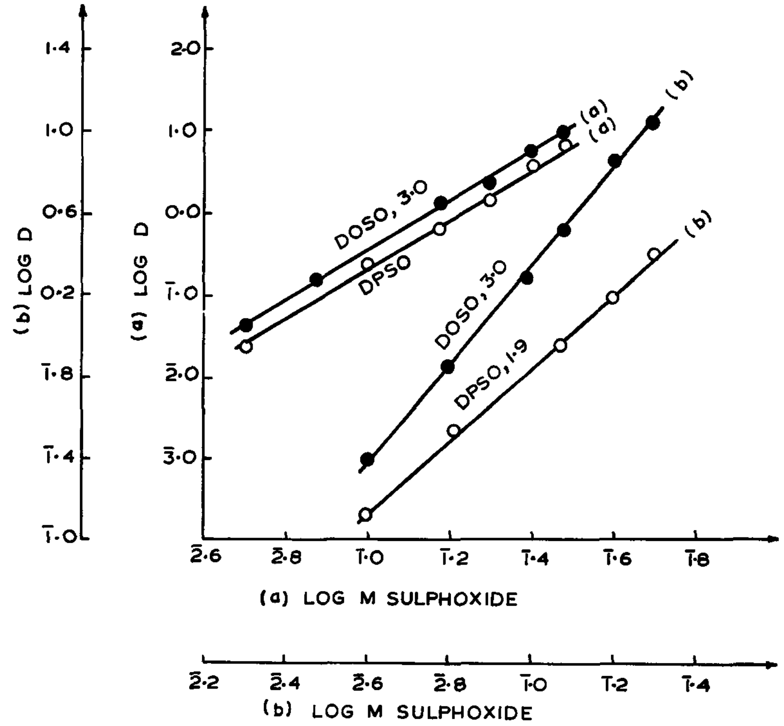

FIG. 1. Log-log plots of the variation of the extraction of Th(IV) and U(VI) with the concentration of di-*n*-pentyl sulfoxide (DPSO) and di-*n*-octyl sulfoxide (DOSO). Slopes of the lines are given.

plots of log *D* against log [S] (Fig. 1) show that the species $Th(SCN)_4 \cdot 3DPSO$, $Th(SCN)_4 \cdot 3DOSO$, $UO_2(SCN)_2 \cdot 2DPSO$, and $UO_2(SCN)_2 \cdot 3DOSO$ are extracted into the organic phase. It is interesting to note that the composition of the metal species identified both in the halide (*4*) and in the pseudohalide media are identical.

Figure 2, a plot of log equilibrium organic-phase metal concentration against log equilibrium aqueous-phase metal concentration, shows that the actinides are extracted as mononuclear species.

Th(IV) and U(VI) can be quantitatively extracted into the sulfoxide (CCl_4 as diluent), leaving behind the lanthanides in the aqueous phase. The clean separation can be achieved by employing a low concentration of the sulfoxide (Table 1).

The individual separation of Th(IV) and U(VI) can be achieved by changing the diluent.

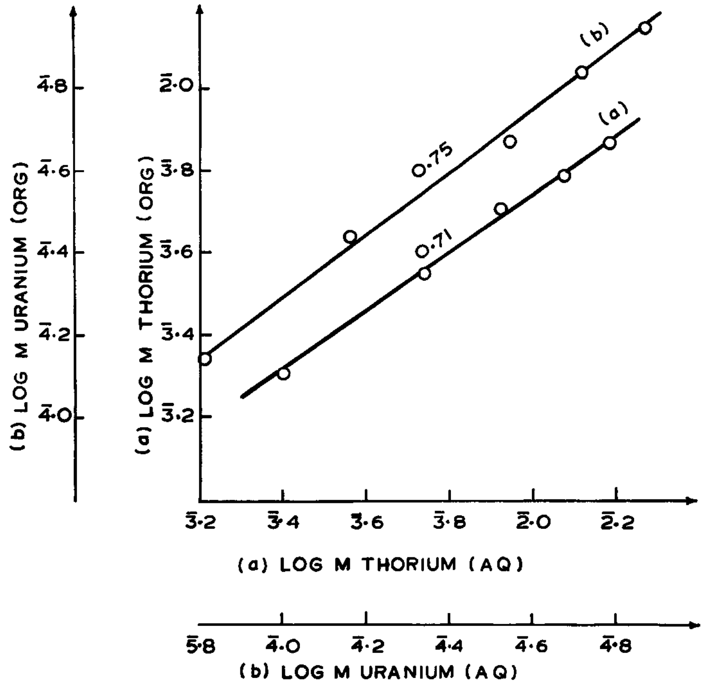

FIG. 2. Effect of metal concentration on the extraction of Th(IV) and U(VI) by di-*n*-pentyl sulfoxide (DPSO). Slopes of the lines are given.

TABLE 1

	%*E*	
M DPSO in CCl_4	Actinides	Lanthanides
0.01	100	0
0.1	100	1–6

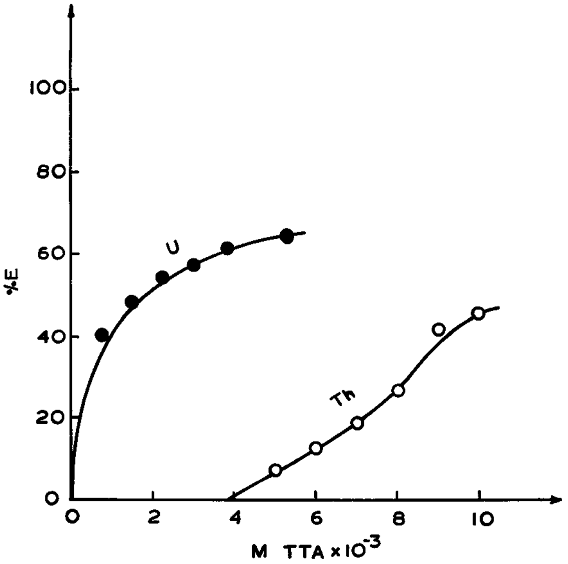

Fig. 3. Extraction as a function of 2-thenoyltrifluoroacetone (TTA) concentration.

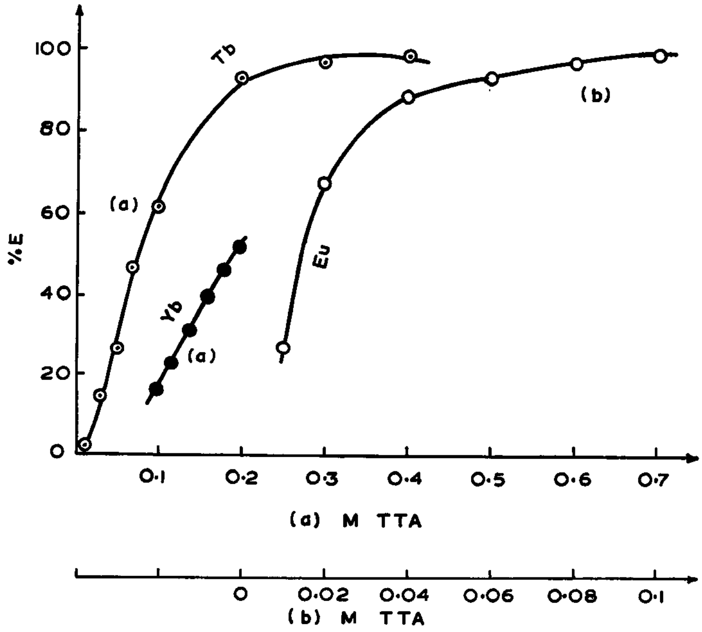

Fig. 4. Extraction as a function of 2-thenoyltrifluoroacetone (TTA) concentration.

TABLE 2

Aqueous phase	Organic phase
1.0 *M* thiocyanate solution containing Th(IV), U(VI), Ce(III), Nd(III), Eu (III), Tb(III), and Yb(III)	(7.5×10^{-4} *M* TTA in $CHCl_3$)
Quantitative extraction of U(VI)	~10 runs
Quantitative extraction of Th(IV)	(7×10^{-3} *M* TTA in $CHCl_3$) ~10 runs
Quantitative extraction of Eu(III)	(1×10^{-2} *M* TTA in CCl_4) ~10 runs
Quantitative extraction of Tb(III)	(7×10^{-2} *M* TTA in CCl_4) ~10 runs
Quantitative extraction of Yb(III)	(2×10^{-1} *M* TTA in CCl_4) ~10 runs
Ce(III) and Nb(III) remain in the aqueous phase	

Effect of TTA Concentration

Distribution as a function of TTA concentration (0 to 0.5 *M*) with diluent $CHCl_3$ for Th(IV) and U(VI) and CCl_4 for lanthanides was examined. Although Th(IV) and U(VI) are extracted quantitatively at low concentrations of TTA in CCl_4, the diluent $CHCl_3$ is preferred to achieve individual separation of the actinides. On the other hand, the latter is not suitable for the extraction of lanthanides because of their poor extraction. The efficiency of extraction of the chelate for the metals is found to decrease in the order U(VI) > Th(IV) > Eu(III) > Tb(III) > Yb(III) > Nd(III)/Ce(III) (Figs. 3 and 4); Ce(III) and Nd(III) are not extracted even into 0.5 *M* TTA in CCl_4. A careful observation of the data reveals a method for the clean separation of these actinides and lanthanides. The conditions for separation are represented schematically in Table 2.

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Received by editor October 5, 1979