

## Synergic extraction of uranium(VI) by combination of tri-iso-octylamine and neutral donors

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Synergistic effect of neutral donors like tri-butyl phosphate (TBP), triphenyl phosphine oxide (TPPO), trioctyl phosphine oxide (TOPO), and dimethyl sulphoxide (DMSO) on the extraction of uranium(VI) by tri-iso-octyl amine into  $\text{CCl}_4$  is reported. Synergistic coefficients and adduct formation constants are calculated from distribution data and correlated with relative donor abilities of added bases.

### Introduction

High molecular weight amines have been used for the preconcentration and separation of actinide elements.<sup>1</sup> Among these materials, tertiary amines are the most widely used. They have been applied for the extraction of uranium(VI) from aqueous chloride,<sup>2,3</sup> sulphate<sup>4</sup> or nitrate<sup>5</sup> media. Such extraction processes involve the formation of anionic complex of metal and because of that, they are also described as liquid anion exchangers. Mixture of the liquid anion exchangers with a neutral donor was found to produce considerable synergism in actinide extraction from aqueous acidic media.<sup>6,7</sup> Synergism has also been reported for the extraction of uranium(VI) by the combination of a chelating agent and neutral donor, organophosphorus reagents in particular.<sup>8,9</sup> In the present investigation, we report the use of tri-iso-octyl amine (TIOA) and the effect of neutral donors on such extraction process. Extent of synergism is correlated with relative donor abilities of several bases and from the measured values of distribution coefficients, formation constants of the complex-adducts are also calculated.

### Experimental

The extractant tri-iso-octyl amine (TIOA, Aldrich Chemical Co.), tri-*n*-butyl phosphate (AR, BDH), tri-phenyl phosphine oxide (Aldrich Chemical Co.), tri-octyl phosphine oxide (Aldrich Chemical Co.), and dimethyl sulphoxide (S. D.) were used as received. Uranyl nitrate (BDH) were AR quality. All solvents were of AR grade.

For the extraction, an aqueous solution containing ~ 100  $\mu\text{g}$  uranium(VI) in 1-2M  $\text{HNO}_3$  was equilibrated with equal volume of organic phase containing TIOA in  $\text{CCl}_4$ . For synergistic extraction, organic phase was mixed with appropriate reagent of desired concentration. After equilibration and phase separation, aqueous solution was mixed with oxine reagent following the usual procedure<sup>10</sup> and absorbance was measured with a Shimadzu UV-vis

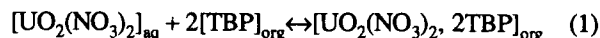
spectrophotometer. The concentration of metal ion in organic phase was calculated by mass balance. The distribution coefficient was calculated from

$$D = \frac{\text{Concentration of metal in organic phase}}{\text{Concentration of metal in aqueous phase}}$$

IR spectra of organic extract was recorded with a Shimadzu model 408 spectrophotometer.

### Result and discussion

Extraction of  $\text{UO}_2(\text{NO}_3)_2$  from 1.5M  $\text{HNO}_3$  by TIOA into  $\text{CCl}_4$  is shown in Fig. 1. The log-log plot of distribution coefficient ( $D$ ) against amine concentration results in a straight line of slope 1.0 indicating the extraction of species of composition  $[(\text{R}_3\text{NH})\text{UO}_2(\text{NO}_3)_3]$  where R = Iso-octyl group. The formation of tri-nitrato complex of uranium(VI) under these conditions has been reported in an earlier work.<sup>11</sup> However, the extent of extraction is not very high under the present conditions and the amine is poorer extracting agent than organo-phosphorous bases or DMSO. They form uranyl adduct even under nearly neutral condition and the extraction is more efficient than with pure amine. The log-log plot of distribution coefficient against the donor concentration results straight lines of slope ~ 2, which can be exemplified by the reaction



The efficiency of extraction of pure donors follows the order



In the synergistic extraction, it is found that for each donor reagent, the extraction increases with the increase in donor concentration at a given amine concentration. This

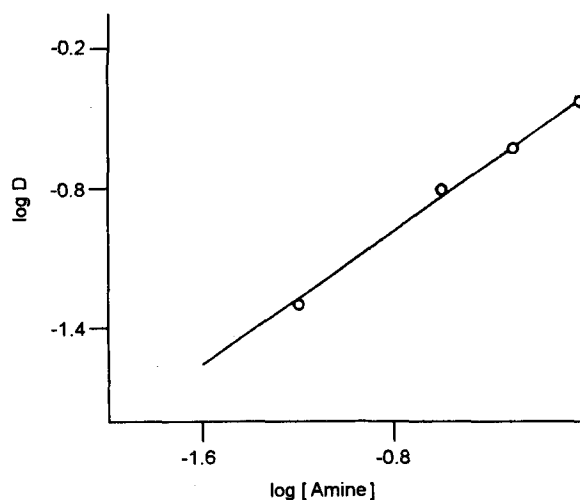
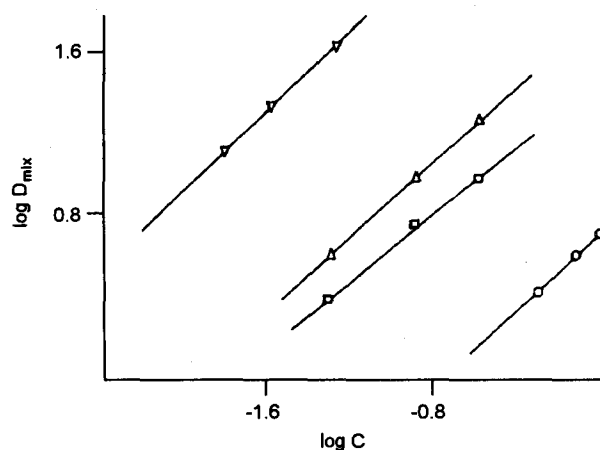


Fig. 1. Extraction of U(VI) against amine

leads to a corresponding rise in synergistic coefficient given by

$$S.C. = \log \frac{D_{mix}}{D_A + D_B} \quad (3)$$

where  $D_A$ ,  $D_B$  are  $D$  values for pure amine and pure donor only, respectively. Again the trend in  $S.C.$  follows the same order of donor as with the pure base. This is also the order of their basic character and their relative abilities to co-ordinate to central uranyl group. The plot of  $\log D_{mix}$  against  $\log$  [Donor] at a fixed

Fig. 2. Variation of distribution coefficient of U(VI) with donor concentration;  $\circ$  TBP,  $\square$  DMSO,  $\Delta$  TPPO,  $\nabla$  TOPO

amine concentration results in straight lines of slope 1 (Fig. 2) and corresponding slope for amine variation is also  $\sim 1$ . Hence the nature of extracted adduct in presence of combined extractant is  $[R_3NH UO_2(NO_3)_3, B]$  where  $B$  represents neutral donors used in this study. Thus, the effect of donor may be described in terms of the replacement of water molecules from  $[R_3NH UO_2(NO_3)_3, xH_2O]$ . Such a replacement reaction, leading to adduct formation, is responsible for the enhanced extraction into carbon tetrachloride. The formation-constant ( $\beta$ ) of metal-aminedonor adduct<sup>12</sup> may be calculated from

Table 1. Synergistic effect and adduct formation constant in presence of different donors; [TIOA] = 0.50%,  $D_A = 0.218$

Donor	Donor concentration, %	$D_B$	$D_{mix}$	$S.C.*$	$\beta,** \text{ mol}^{-1}$
TBP	0.50	0.177	0.92	0.8687	$6.86 \cdot 10^2$
	0.75	0.342	4.46	1.9009	$7.19 \cdot 10^2$
	1.00	0.656	5.7	0.8492	$6.98 \cdot 10^2$
DMSO	0.05	0.100	2.55	0.9013	$1.671 \cdot 10^2$
	0.125	0.2818	6.066	1.0838	$1.674 \cdot 10^3$
	0.250	1.650	11.9	0.8200	$1.674 \cdot 10^3$
TPPO	0.05	0.100	4.233	1.1268	$1.078 \cdot 10^4$
	0.125	0.316	10.028	1.2734	$1.0 \cdot 10^4$
	0.250	0.710	20.2	1.3370	$1.078 \cdot 10^4$
TOPO	0.015	0.020	13.3	1.7445	$1.54 \cdot 10^4$
	0.025	0.050	22.3	1.9201	$1.53 \cdot 10^4$
	0.05	0.160	45.0	2.0755	$1.57 \cdot 10^4$

\*Synergistic coefficient ( $S.C.$ ) =  $\log \frac{D_{mix}}{D_A + D_B}$

\*\*Adduct formation constant  $\beta = \frac{\Delta D}{D_A \cdot [\text{Donor}]}$

$$\beta = \frac{\Delta D}{D_A [\text{Donor}]}$$

where  $\Delta D$  is the difference of  $D$ -values in presence and in absence of donor, and  $[\text{Donor}]$  = molar concentration of donor.

The calculated values of  $\beta$  (Table 1) shows a strong complex formation in organic phase and again the strength of the complex follows the same trend of relative donor ability of the base used, i.e., TBP < DMSO < TPPO < TOPO.

The formation of strong adduct has been also confirmed by the study of IR data of extracted complex. Characteristic absorption of  $\sqrt{\text{P-O}}$  in TOPO is shifted from  $1150 \text{ cm}^{-1}$  to  $1120 \text{ cm}^{-1}$  and  $\sqrt{\text{NH}}$  absorption takes place at  $2900 \text{ cm}^{-1}$  instead at  $3000\text{--}3500 \text{ cm}^{-1}$ . Thus, it may be concluded from the experimental data that amine extraction is definitely enhanced by the addition of donors and the synergism is attributed to the higher donating power of the ligands than pure amine itself.

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