

## Thermodynamics of the solvent extraction of thorium and europium nitrates by neutral phosphorylated ligands

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Solvent extraction of tetravalent thorium and trivalent europium ions from nitrate media into dichloromethane solution of triphenylphosphine oxide (TPPO) has been studied. The extractant was shown to be more efficient for europium than for thorium. A conventional log-log analysis reveals that the extraction of both metal nitrates takes place via the formation of the species with 1 : 2 metal to ligand ratio. Thermodynamic parameters i.e.,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the extraction process using 1,2-dichloroethane as diluent have been calculated based on the influence of the temperature on extraction equilibria in the range 293–313 K. While the extraction of europium is controlled by enthalpy changes, the extraction of thorium is an endothermic process and is driven by entropy changes. A comparison of these data with those obtained for the extraction of europium and thorium nitrates by two other related phosphorylated ligands, tri-*n*-octylphosphine oxide (TOPO) and diphenyl-*N,N*-dimethylcarbamoylmethylphosphine oxide (D $\Phi$ DMCMPO), indicates that D $\Phi$ DMCMPO coordinates presumably as a chelating ligand.

### Introduction

Neutral organophosphorus-based ligands are widely used in the solvent extraction processes of actinides and lanthanides.<sup>1,2</sup> For example, the unidentate extractant tributylphosphate (TBP) has industrial application in the PUREX process.<sup>3</sup> Potentially, bidentate ligands, carbamoylmethylphosphates (CMP's) and carbamoylmethylphosphine oxides (CMPO's), have been utilized to overcome the weak extractant properties of monofunctional phosphine oxide ligands.<sup>4–6</sup> In these molecules, a phosphine oxide functional group (P=O) is present together with an amide group (–C(O)NR<sub>2</sub>). The application of octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (D $\Phi$ D(iB)CMPO) which has been utilized by HORWITZ and co-workers<sup>7</sup> forms the basis of the TRUEX process.

Study of the structure of metal/CMPO and metal/CMP complexes has attracted the interest of several research groups.<sup>8–11</sup> KALINA<sup>8</sup> has used the lanthanide-induced NMR shift technique to elucidate the binding mode in potentially bidentate carbamoylphosphoryl extractants, providing evidence that, for CMP extractants, coordination occurs primarily through interaction of the phosphoryl groups with the metal ion. The carbonyl-metal interaction is significantly weaker so that the CMP ligands appear to behave much like their monofunctional analogues. A similar study by NAKAMURA and MIYAKE<sup>9</sup> on the coordination of D $\Phi$ D(iB)CMPO in lanthanide(III) complexes also provided support for the conclusion that CMPO ligands may be bound in a bidentate manner.

Recently, SCOTT et al.<sup>11</sup> have synthesized a ligand containing three preorganized CMPO molecules anchored onto a triphenoxymethane platform for

complexation and extraction of thorium and the lanthanides. The X-ray structures and NMR spectra of the complexes of this ligand show that all six oxygen donors from the three CMPO moieties coordinate to the metal ions.

Thermodynamic parameters for the extraction of U(VI) from nitrate media by dihexyl-*N,N*-diethylcarbamoylphosphonate (DHECMP) and dibutylbutylphosphonate (DB[BP]) have been determined and used by HORWITZ et al.<sup>7</sup> to elucidate the complexing manner of DHECMP. They concluded that DHECMP cannot be classified as a bidentate ligand in the experimental conditions used.

Previously, we have studied the extractive properties of diphenyl-*N,N*-dimethylcarbamoylmethylphosphine oxide (D $\Phi$ DMCMPO) (Fig. 1) in the separation of rare-earth metal ions in nitrate media.<sup>12</sup> The study of the extractive properties of D $\Phi$ DMCMPO and tri-*n*-octylphosphine oxide (TOPO) towards thorium(IV) and europium(III) ions<sup>13,14</sup> from 1M sodium nitrate shows that the extraction of thorium with both ligands takes place via the formation of an extracted species having a 1:3 metal to ligand ratio. By contrast, extraction of europium nitrate by D $\Phi$ DMCMPO produces a species with a 1:2 metal/ligand ratio.<sup>12,13</sup>

Our present objective was to evaluate the extractive properties of triphenylphosphine oxide (TPPO) towards thorium and europium nitrates and to calculate the thermodynamic parameters using the influence of the temperature on the extraction process. The results are compared with those reported previously for the extraction with TOPO and D $\Phi$ DMCMPO.<sup>13,14</sup> The extraction of europium was studied essentially to provide a model for the behavior of Ac(III) species.

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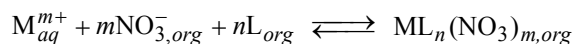
## Experimental

Triphenylphosphine oxide (Fluka) was used without further purification. Dichloromethane and 1,2-dichloroethane (Merck) were washed several times with distilled water in order to remove the solvent stabilizers and to ensure saturation with respect to their water content. The europium solutions were prepared by dissolving a weighed amount of the corresponding oxide (Fluka) in hot concentrated nitric acid and diluting to a known volume.  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  (Fluka) was used for the preparation of thorium solutions. The stock solution was standardized by complexometric titration with EDTA. All other reagents were laboratory reagent grade. The solvent extraction experiments were carried out in a stoppered glass tube immersed in a thermostated water bath ( $\pm 0.1^\circ\text{C}$ ) using equal volumes (5 ml) of the organic and the aqueous phases. The extraction equilibrium was reached after 30 minutes under continuous magnetic stirring. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was measured spectrophotometrically using Arsenazo III.<sup>15</sup> A volume of 5 ml of Arsenazo III solution ( $6 \cdot 10^{-4}\text{M}$ ) was added to 1 ml aliquot of the aqueous phase and the volume was finally adjusted to 25 ml with either a 4M nitric acid solution for the determination of thorium or with a sodium formate/formic acid buffer (pH 2.80) for the determination of europium. The absorbance was then measured at 660 nm for thorium and 655 nm for europium. The standard deviation for the lowest  $D$  values was calculated lower than  $\pm 0.01$ .

## Results and discussion

In order to characterize the extraction ability of triphenylphosphine oxide, the distribution coefficient,  $D$ , of thorium and europium cations between the 1M sodium nitrate aqueous solution and dichloromethane phases as a function of ligand concentration in the organic phase was measured at 293 K.

The extraction of a metal ion ( $\text{M}^{m+}$ ) from aqueous nitrate media to an organic solution containing a neutral ligand (L) can be described by:



where the subscripts *aq* and *org* denote the phase, aqueous or organic, in which the species is present.

The corresponding extraction equilibrium constant,  $K_{ex}$ , can be defined as:

$$K_{ex} = \frac{[\text{ML}_n(\text{NO}_3)_m]_{org}}{[\text{M}^{m+}]_{aq} [\text{NO}_3^-]_{aq}^m [\text{L}]_{org}^n} \quad (1)$$

By introducing the distribution ratio:

$$D = \frac{[\text{M}]_{org}}{[\text{M}]_{aq}} \quad (2)$$

The logarithmic expression of Eq. (1) is:

$$\log D = \log(K_{ex} [\text{NO}_3^-]_{aq}^m) + n \log [\text{L}]_{org} \quad (3)$$

Thus a plot of  $\log D$  vs.  $\log [\text{L}]$  (where the use of a large excess of L relative to the metal allows the value of  $[\text{L}]$  to be approximated as equal to the total amount added) provides the metal/ligand ratio of the extracted species. This method was applied to the extraction of an aqueous solution containing Th or Eu ions (initial concentration  $1 \cdot 10^{-4}\text{M}$ ) in the presence of 1M sodium nitrate by TPPO in dichloromethane at 293 K (Fig. 2). The slopes were in agreement with a metal/ligand ratio of 1:2 for both thorium and europium extracted species. In contrast to the results obtained for some other phosphorylated ligands,<sup>13,14,16,17</sup> it is obvious from Fig. 2 that TPPO extracts europium(III) more efficiently than thorium(IV).

Recently we have studied the extractive properties of DΦDMCMPO<sup>13</sup> and TOPO<sup>14</sup> toward thorium(IV) and europium(III) from aqueous nitrate media (1M sodium nitrate). DΦDMCMPO extracts thorium and europium via formation of the complexes having 1:3 and 1:2 metal to ligand ratios, respectively. However, the extracted species with TOPO have been found to be 1:3 (metal/ligand) for both ions. The stoichiometry of the thorium and europium species extracted by TPPO is shown together with those for TOPO and DΦDMCMPO in Table 1.

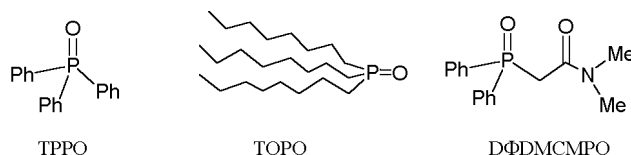


Fig. 1. Extractants mentioned in this study

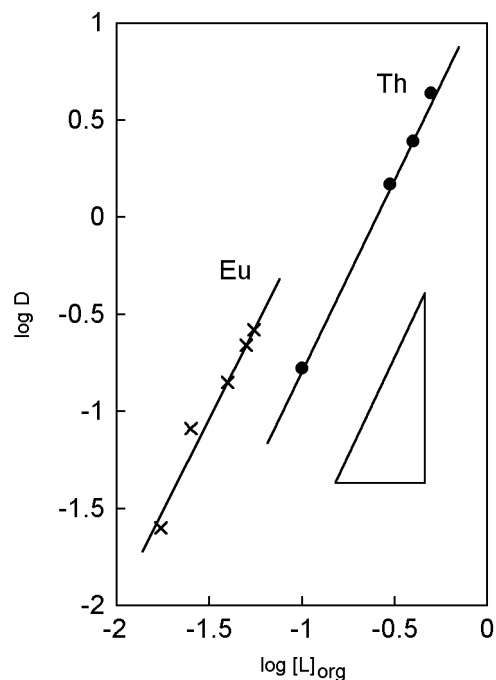


Fig. 2. Plot of  $\log D$  vs.  $\log [L]_{org}$  in solvent extraction of aqueous thorium and europium (initial concentration  $1 \cdot 10^{-4} M$ ) in the presence of  $1 M NaNO_3$  by TPPO at different ligand concentrations in dichloromethane at 293 K

In order to identify the effect of the temperature on the extraction of thorium and europium ions by TPPO, a series of extraction experiments were performed in the range of 293–313 K with 1,2-dichloroethane solution of the ligand and a  $1 M NaNO_3$  solution of the metal nitrates. 1,2-Dichloroethane was used because it has a higher boiling point than dichloromethane.

The equilibrium constants for the distribution of Eu(III) and Th(IV) between  $1 M NaNO_3$  and 1,2-dichloroethane solutions of TPPO in the range 293–313 K have been evaluated and are grouped with those obtained previously using TOPO and DΦDMCMPO in Table 2. For Eu(III), the extraction by TOPO is less efficient at higher temperature but the opposite is true for Th(IV).

Assuming  $\Delta H$  and  $\Delta S$  to be temperature independent over a narrow temperature range, the van't Hoff isochore can be simply applied to obtain values for the enthalpy and entropy changes associated with extraction. Considering

$$\log K_{ex} = \left( \frac{1}{2.303R} \right) \left( \Delta S^\circ - \frac{\Delta H^\circ}{T} \right) \quad (4)$$

a plot of  $\log K_{ex}$  vs.  $T^{-1}$  (Fig. 3) allows to calculate the enthalpy and entropy changes of the extraction process. These data and the Gibbs free energy changes calculated using the Gibbs-Helmholtz equation are presented in Table 3.

Table 1. Stoichiometry (in metal/ligand ratio) of the extracted complexes with the investigated ligands<sup>a</sup>

Ligand	Eu	Th
TPPO	1 : 2	1 : 2
TOPO <sup>b</sup>	1 : 3	1 : 3
DΦDMCMPO <sup>c</sup>	1 : 2	1 : 3

<sup>a</sup> Diluent: 1,2-dichloromethane; aqueous phase: initial metal concentration =  $0.0001 M$  and  $NaNO_3 = 1 M$ ; temperature = 298 K.

<sup>b</sup> Data are from Reference 13.

<sup>c</sup> Data are from Reference 14.

Table 2. Logarithm of the extraction equilibrium constants of Th (IV) and Eu (III) ions in the presence of  $1 M NaNO_3$  with the studied ligands in 1,2-dichloroethane as a function of temperature

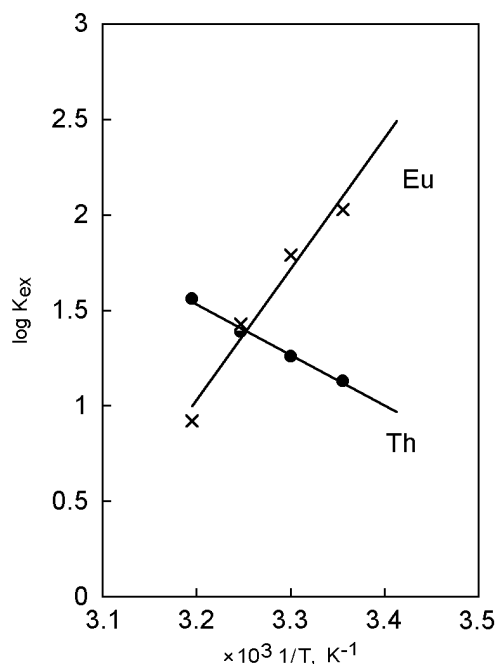
Temperature, K	TPPO		TOPO <sup>a</sup>		DΦDMCMPO <sup>b</sup>	
	$\log K_{ex}$ (Th)	$\log K_{ex}$ (Eu)	$\log K_{ex}$ (Th)	$\log K_{ex}$ (Eu)	$\log K_{ex}$ (Th)	$\log K_{ex}$ (Eu)
293	—	—	6.80	6.02	6.51	2.44
298	1.13	1.99	6.66	5.92	6.61	2.39
303	1.26	1.79	6.46	5.78	6.79	2.29
308	1.39	1.49	6.35	5.71	6.94	2.19
313	1.56	0.86	6.25	5.60	7.24	2.07

<sup>a</sup> Data are from Reference 13.

<sup>b</sup> Data are from Reference 14.

Table 3. Thermodynamic parameters associated with the extraction of Th(IV) and Eu(III) ions at 298 K<sup>a</sup>

Ligand	Eu, kJ/mol			Th, kJ/mol		
	$\Delta G^\circ$	$\Delta H^\circ$	$T\Delta S^\circ$	$\Delta G^\circ$	$\Delta H^\circ$	$T\Delta S^\circ$
TPPO	-9.1	-128.0	-118.8	-6.4	51.2	57.6
TOPO <sup>b</sup>	-33.5	-61.7	-28.3	-37.2	-46.5	-9.3
DΦDMCMPO <sup>c</sup>	-13.0	-33.2	-20.2	-38.9	62.2	101.9

<sup>a</sup> Calculating using the least-squares method  $\sigma_{N-1} \leq \pm 1.8$ .<sup>b</sup> Data are from Reference 13.<sup>c</sup> Data are from Reference 14.Fig. 3. Variation in  $\log K_{ex}$  with  $1/T$  for thorium(IV) and Eu(III) in the presence of 1M NaNO<sub>3</sub> with TPPO in 1,2-dichloroethane

The results in Table 3 show that the extraction of europium ions with all ligands and that of thorium by TOPO is exothermic and is mainly enthalpy-controlled. However, for the extraction of thorium by TPPO and DΦDMCMPO the process is endothermic and thus can be considered entropy-driven. It is noteworthy that, for all systems, the extraction enthalpy for Eu(III) species is more negative than for the Th(IV) species, a result which may correlate with the fact that the hydration enthalpy of Eu(III) is considerably less than that of Th(IV). Furthermore, in the extraction by TPPO and DΦDMCMPO the entropy is negative for Eu(III) and positive for Th(IV) ions. This may be associated with the release of a greater number of water molecules by Th(IV) than by Eu(III) in the process of complexation.

The comparison of thermodynamic values can be used to elucidate the coordination mode of potentially bidentate ligand DΦDMCMPO. It should be noted that since the stoichiometry of the extracted complexes varies, we must compare the enthalpy and entropy changes of the systems with the same ligand to metal

ratio, i.e., the extraction of europium with TPPO and DΦDMCMPO, and those of TOPO and DΦDMCMPO for the extraction of thorium ions. More negative values of enthalpy changes and lower entropy changes for the extraction of europium by TPPO than by DΦDMCMPO can be interpreted as a consequence of bidentate binding of the latter, leading to the release of a larger number of water molecules in the complexation step. The same conclusion can be drawn from the comparison of TOPO and DΦDMCMPO as extractants for Th(IV), suggesting, in support of literature observations,<sup>9</sup> that CMPO-type ligands generally function as bidentate species.

### Conclusions

The neutral phosphorylated ligand triphenylphosphine oxide is a suitable extracting agent for both Th(IV) and Eu(III), with a preference towards the latter, in nitrate media. The ligand forms 1:2 complexes with the ions studied. The entropy changes in extraction are more positive for the more strongly hydrated Th(IV) reactant, indicating an important contribution from the release of water molecules during the complexation process. Higher enthalpy changes and lower entropy changes associated with the extraction of both Eu(III) and Th(IV) by CMPO-like ligands than with their extraction by unidentate species such as TOPO and TPPO are consistent with bidentate binding of the CMPO analogues.

### References

1. B. WEAVER, Solvent Extraction in the Separation of Rare Earths and Trivalent Actinides, in Ion Exchange and Solvent Extraction, Vol. 6, J. A. MARINSKY and Y. MARCUS (Eds), Marcel Dekker, New York, 1974.
2. E. P. HORWITZ, R. CHIARIZIA, in: Separation Techniques in Nuclear Waste Management, N. A. CHIPMEN and C. M. WAI (Eds), CRC, FL, 1996.
3. W. W. SCHULZ, L. L. BURGER, J. D. NAVRATIL (Eds), Science and Technology of Tributylphosphate, Vols I-III, CRC, Boca Raton, FL., 1984-1990.
4. E. P. HORWITZ, D. G. KALINA, A. C. MUSCATELLO, Separ. Sci. Technol., 16 (1981) 403.
5. E. P. HORWITZ, D. G. KALINA, L. KAPLAN, G. W. MASON, H. DIAMOND, Separ. Sci. Technol., 17 (1982) 1261.
6. E. P. HORWITZ, K. A. MARTIN, H. DIAMOND, L. KAPLAN, Solvent Extr. Ion Exch., 4 (1986) 449.

7. E. P. HORWITZ, D. G. KALINA, H. DIAMOND, G. F. VANDEGRIFT, *Solvent Extr. Ion Exch.*, 3 (1985) 75.
8. D. G. KALINA, *Solvent Extr. Ion Exch.*, 2 (1984) 381.
9. T. NAKAMURA, C. MIYAKE, *Solvent Extr. Ion Exch.*, 12 (1994) 931.
10. T. TAKEUCHI, S. TANAKA, M. YAMAWAKI, *Solvent Extr. Ion Exch.*, 12 (1994) 987.
11. M. W. PETERS, E. J. WERNER, M. J. SCOTT, *J. Inorg. Chem.*, 41 (2002) 1707.
12. M. R. YAFTIAN, M. BURGARD, C. WIESER, C. B. DIELEMAN, *Solvent Extr. Ion Exch.*, 16 (1998) 1131.
13. M. R. YAFTIAN, L. HASSANZADEH, M. E. ESHRAGHI, D. MATT, *Separ. Pur. Tech.*, 31 (2003) 261.
14. M. R. YAFTIAN, M. E. ESHRAGHI, L. HASSANZADEH, *Iran. Chem. Chem. Eng.*, 22 (2003) 71.
15. Z. MARCZENKO, *Spectrophotometric Determination of Elements*, Wiley, New York, 1976.
16. F. ARNAUD-NEU, V. BÖHMER, J.-F. DOZOL, C. GRÜTTNER, R. A. JAKOBI, D. KRAFT, O. MAUPRIVEZ, H. ROQUETTE, M.-J. SCHWING-WEILL, N. SIMON, W. VOGT, *J. Chem. Soc., Perkin Trans. II*, (1996) 1175.
17. M. R. YAFTIAN, R. TAHERI, D. MATT, *Phosphorus, Sulfur, Silicon*, 178 (2003) 1225.