Extractive Properties of Tri-*n*-octylphosphine Oxide Towards Thorium (IV) and Europium (III) Ions in Aqueous Nitrate Media

Yaftian, Mohammad Reza*+; Eshraghi, Mohammad Ebrahim and Hassanzadeh, Leila

Department of Chemistry, Faculty of Sciences, Zanjan University, 45195-313 Zanjan, I. R. Iran.

ABSTRACT: *Phosphoryl containing ligand tri-*n*-octylphosphine oxide (TOPO) in dichloromethane has been used as an extracting agent for tetravalent thorium and trivalent europium ions from their 1 M sodium nitrates. The equilibrium data reveal that both ions are extracted as the complexes at 1:3 metal/ligand ratio. The values of conditional extraction equilibrium constant (K_{ex}) show the superior extractive properties of the ligand towards thorium than europium ions. The effects of solvent, type and concentration of the salting-out agent on the extraction abilities of the ligand are investigated. The influence of the temperature on the extraction of these ions from the sodium nitrate medium into 1,2-dichloroethane by TOPO is studied as a function of temperature in the range 20-40 ºC. The results show that the distribution ratios of thorium and europium ions decrease with the increase in temperature. Free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes associated with the extraction process are evaluated from the distribution measurements.*

KEY WORDS: *Thorium, Europium, Tri-n-octylphosphine Oxide, Extraction, Thermodynamics.*

INTRODUCTION

Inter- and intra-group separation of lanthanides and actinides are important processes for the management and storage of radioactive wastes [1]. One of the most useful processes for achieving to this goal is solvent extraction using efficient extractants [2]. Phosphorus containing ligands have been shown to exhibit interesting extractive properties towards lanthanides and actinides [3-9]. For example, the extracting ability of tributylphosphate (TBP) forms the basis of the PUREX process (plutonium / uranium separation) [10].

Tri-*n*-octylphosphine oxide (TOPO) (Fig. 1) is one of the interesting phosphorylated ligands which has been used in a great number of studies as an extractant [3, 11, 12] or as a cooperating agent [7] in solvent extraction processes.
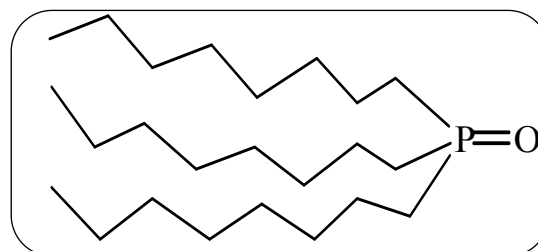

Fig. 1: Tri-n-octylphosphine Oxide (TOPO).

In this report we present some of the extractive properties of tri-*n*-octylphosphine oxide towards thorium (IV) and europium (III) ions in nitrate media. Thorium and europium ions are selected because the former can be considered as a model for tetravalent and the latter for the trivalent actinides [8]. We have also studied the influence of the temperature on the extraction of these ions from water into 1,2-dichloroethane solution of TOPO.

EXPERIMENTAL

Materials

Tri-*n*-octylphosphine oxide (TOPO) was used as received (Aldrich). Solvents used (Merck) were washed several times with distilled water in order to remove the solvent stabilizers and saturating them with water. The europium solutions were prepared from a weighed amount of the corresponding oxide (Fluka) in hot concentrated nitric acid and dilution to a known volume. The salt $Th(NO_3)_4, 6H_2O$ (Fluka) was used for the preparation of thorium solutions. The stock solutions were standardized by complexometric titration with EDTA. All other reagents were laboratory reagent grade.

Extraction Procedure

The solvent extraction experiments were carried out in a stoppered glass tube immersed in a thermostated water bath (±0.1 ℃) 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 spectrophtometrically using Arsenazo III [13]. A volume of 5 mL of Arsenazo III solution (6×10^{-4} M) was added to a 1 mL aliquot of the aqueous phase. The volume was finally adjusted to 25 mL with either a 4 M nitric acid solution for the determination of thorium or with a sodium formate/formic acid buffer (pH = 2.80) for the determination of europium. Since the Arsenazo/metal ratio is high, complete complexation of the cations can be assumed. The absorbance then measured at 660 nm for thorium and 655 nm for europium determinations.

RESULTS AND DISCUSSION

In order to characterize the extracted species, the distribution coefficient, D, of the thorium and europium

ions between nitrate aqueous solution and dichloromethane phases as a function of the ligand concentration in the organic phase has been examined at 20 ℃. The general extraction equilibrium is given as,

$$M_{aq}^{m+} + mNO_{3,org}^{-} + nL_{org} \rightleftharpoons ML_n(NO_3)_{m,org}$$

(where the subscriber "aq" and "org" denotes the presence of the species in the aqueous and organic phases, respectively).

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

$$K_{ex} = \frac{[ML_n(NO_3)_m]_{org}}{[M^{m+}]_{aq}[NO_3^-]_{aq}^m[L]_{org}^n} \qquad (1)$$

by introducing the distribution ratio,

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

the logarithmic expression of the equation 1 is:

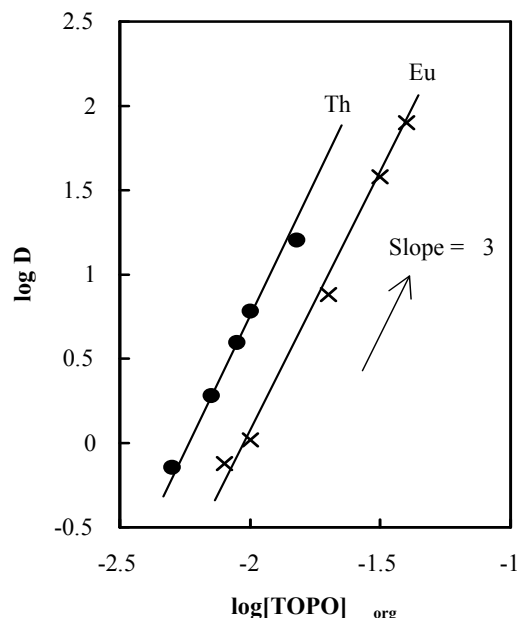$$\log D = \log(K_{ex}[NO_3^-]_{aq}^m) + n\log[L]_{org} \qquad (3)$$

Fig. 2: Plot of logD vs. log[L]$_{org}$ in solvent extraction of aqueous thorium and europium (initial concentration 1×10^{-4} M) in the presence of NaNO$_3$ (1 M) by TOPO at different ligand concentration in dichloromethane at 20 ℃.

Thus a plot of logD *vs.* log[L] provides the metal/ligand ratio of the extracted species. This method was applied to the extraction of an aqueous solution containing thorium and europium ions (initial concentration 1×10^{-4} M) in the presence of sodium nitrate (1 M) by tri-*n*-octylphosphine oxide in dichloromethane at 20 ºC (Fig. 2).

The slopes indicate a metal/ligand ratio of 1:3 for both thorium and the europium extracted complexes. The results also reveal a higher extraction by the ligand towards thorium than europium ions. Hence, some experiments were done to the study the parameters influencing the extraction ability of the ligand using it at higher concentrations.

The formation of the mono-nuclear complexes, as assumed in equation 1, was tested with saturation experiments of the organic phase by equilibration with increasing cation concentrations in the aqueous phase at the ligand concentration of 0.005 for thorium and 0.02 M for europium extractions (Fig. 3). As it is shown in figure 3 a constant M/L ratio at the values about 0.31-0.33 for both ions has been achieved, confirming the formation of mono-nuclear complexes for both systems.
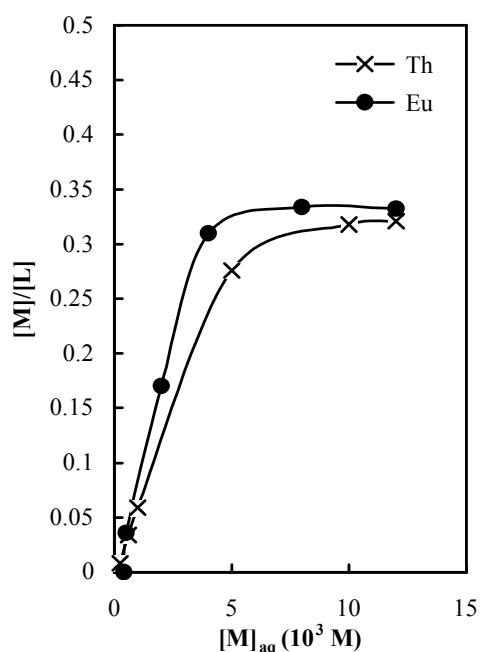
The influence of concentration of the salting-out agent was investigated by the extraction experiments of europium (initial concentration 1×10^{-4} M) in the presence of different concentration of $NaNO_3$ in aqueous phase by the ligand (0.05 M) in dichloromethane (Fig. 4). Higher extraction percentage was found with increasing nitrate ion concentration, in keeping with the participation of the nitrate anions in the extracted complexes. It is noteworthy that at the concentration above 1.5 M of sodium nitrate a nearly total extraction of europium ions has been achieved.

The nature of the counter anion can significantly alter the efficiency of the extraction with neutral extractants [14]. In order to verify this effect, the extraction experiments of thorium and europium ions in the presence of various salting-out agents $NaNO_3$, $NaClO_4$, and CH_3COONa (1M) by tri-*n*-octylphosphine oxide were carried out (Fig. 5). The results show the following order for the extraction percentages of the ions in the presence of different tested counter anions:

$$ClO_4^- > CH_3COO^- > NO_3^- \quad \text{(for thorium)} \quad \text{and}$$

$$NO_3^- > CH_3COO^- > ClO_4^- \quad \text{(for europium)}.$$

Fig. 3: The ratio metal to ligand in the organic phase as a function of Th and Eu concentrations in the aqueous phase in the presence of NaNO₃ (1 M) by TOPO (0.005 and 0.02 M for thorium and europium, respectively) in dichloromethane at 20ºC.

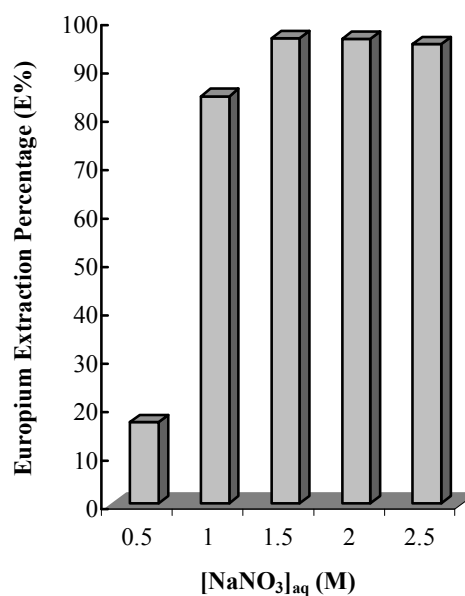**Fig. 4: Variation of the europium extraction percentages (initial concentration 1×10⁻⁴ M) as a function of NaNO₃ concentration in the aqueous phase by TOPO (0.05 M) in dichloromethane at 20 ºC.**

73

The highest extraction percentage of thorium was found when the perchlorate ions are used, which can be related to its highest lipophilic nature among the investigated anions. In contrast, the best extraction percentage of europium is found in the presence of nitrate ions. Since the lipophilic nature and hydration energy of the ions could not be successfully used for the interpretation of the all results, one should also consider the ligating ability of the anions which participate, probably, in the coordination sphere of the cations.

The separative ability of tri-*n*-octylphosphine oxide towards thorium and europium ions was tested in the presence of nitric acid in concentrations comparable to those found in nuclear wastes. Figure 6 shows the variation of the percentage of thorium extracted as a function of nitric acid concentration in aqueous phase by TOPO in dichloromethane. The percentage of thorium extracted decreases with the increase in acid concentration. This can be interpreted in terms of competition between the thorium nitrate and nitric acid. It should be noted that the extraction percentage of europium in nitric acid medium was too small for monitoring in the experimental conditions.

The effect of diluents on the extraction of thorium and europium ions was tested by performing extraction experiments with the ligand in chloroform, dichloromethane and 1,2-dichloroethane. For both ions

Table 1: Equilibrium constants of the extraction of Th(IV) and Eu (III) in the presence of $NaNO_3$ (1 M) with TOPO (0.01 M) in 1,2-dichloroethane as a function of temperature.*

Temperature (K)	$\log K_{ex}$ (Th)	$\log K_{ex}$ (Eu)
293	6.80	6.02
298	6.66	5.92
303	6.46	5.78
308	6.35	5.71
313	6.25	5.60

- *Mean value of three independent extraction experiments.*

the extraction percentage in the diluents was enhanced with increasing the diluent polarity [14], *i.e.* 1,2-dichloroethane > dichloromethane > chloroform (Fig. 7). This indicates a major contribution of the nitrate-diluent interactions to the stability of the complex ion pair in the organic phase. The lowest extraction in the case of chloroform may be related to the occurrence of hydrogen binding between the extractant and diluent.

The effect of the temperature on the solvent extraction has been frequently studied to obtain some information about the mechanism and thermodynamics of the process [9, 15, 16]. In order to determine the effect of the
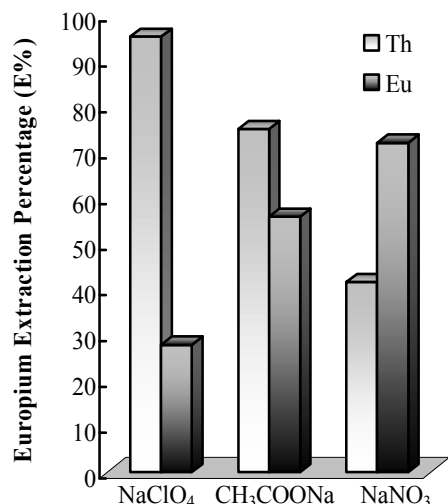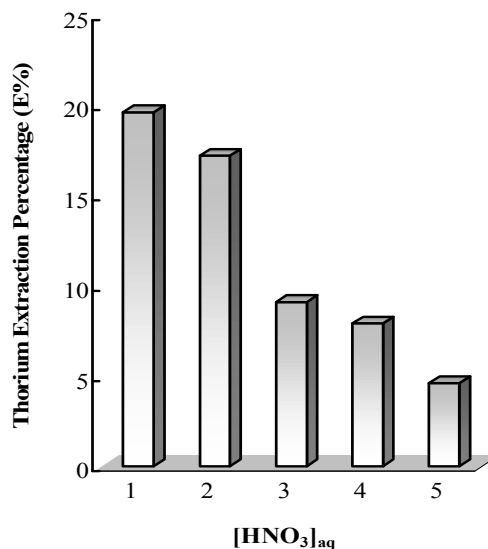

Fig. 5: Variation of the thorium and europium extraction percentages (initial concentration 1×10^{-4} M) in the presence of different salting-out agents (1 M) by TOPO (0.005 and 0.02 M for thorium and europium, respectively) in dichloromethane at 20 ºC.

Fig. 6: Variation of the thorium extraction percentage (initial concentration 1×10^{-4} M) as a function of HNO_3 concentration in aqueous phase by tri-n-octylphosphine oxide (0.01 M) in dichloromethane at 20 ºC.
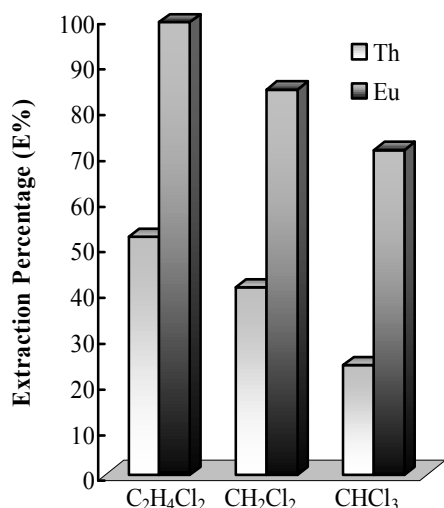
Fig. 7: Effect of diluent on the extraction of thorium and europium ions in the presence of NaNO₃ (1 M) by tri-n-octylphosphine oxide (0.005 and 0.05 M for thorium and europium, respectively) at 20 ºC.

temperature on the extraction of thorium and europium ions by tri-*n*-octylphosphine oxide, a series of extraction experiments of the ions from a sodium nitrate solution (1M) into a 1,2-dichloroethane solution of the ligand has been carried out in the range 20-40 ºC. 1,2-Dichloroethane was used because its similarity and higher boiling point with respect to dichloromethane.

The free-energy change (ΔGº) for the extraction equilibrium is calculated from the extraction constant K_{ex} (Table 1) by equation 4,

$$\Delta G° = -2.303\,RT\,logK_{ex} \tag{4}$$

$$logK_{ex} = (\frac{1}{2.303R})(\Delta S° - \frac{\Delta H°}{T}) \tag{5}$$

Figure (8) shows a Plot of the $logK_{ex}$ as a function of the inverse temperature in the selected temperature range. The calculated thermodynamic parameters are presented in Table 2. These parameters, are computed using concentrations rather than activities of the various species involved in extraction equilibria, and thus do not represent the true thermodynamic quantities. However under conditions of constant concentration of sodium nitrate, the contribution of the activity coefficients to the thermodynamic values should be fairly constant, rendering the values in Table 2 reliable for relative comparisons.
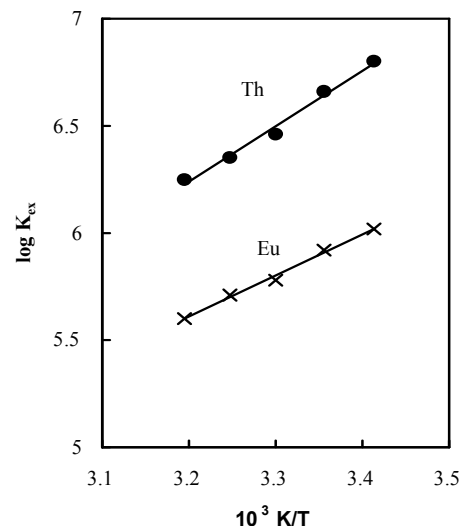

Fig. 8: Variation in log K_{ex} with T^{-1} for thorium and europium ions in the presence of NaNO₃ (1 M) with tri-n-octylphosphine oxide (0.01 M) in 1,2-dichloroethane.

It can be seen from the data that for both ions the extraction process is exothermic and associated withynegative entropy changes. The different values of the enthalpy and entropy changes can be explained considering the degree of hydration of the cations that is higher for Th (IV) than Eu (III) ions. In the case of the extraction of europium because fewer water molecules are released, the energy spent for the same procedure is less and hence the net enthalpy change (*i.e.* the energy released due to the formation of the extractable species less the energy spent in releasing the water molecules) is more negative than for thorium ions. Furthermore, the net entropy change (*i.e.* the entropy gain due to release of water molecules and the entropy loss due to bonding of TOPO and nitrate ions) is more negative for europium

Table 2: Thermodynamic parameters (ΔGº, ΔH° and TΔS) associated with the extraction of Th (IV) and Eu (III) at 298 K.*

Cation	ΔG° (kJ/mol)	ΔH° (kJ/mol)	TΔS° (kJ/mol)
Th (IV)	-37.18 (±1.21)	-46.46 (±0.24)	-9.28 (±1.23)
Eu (III)	-33.46 (±1.71)	-61.73 (±0.76)	-28.27 (±1.87)

* Calculating using the least-squares method.

75

ions with respect to that of thorium ions. However, in the case of tetrapositive thorium, the energy spent in releasing the larger number of water molecules results in a net enthalpy change which is less negative and an entropy change which is more positive.

REFERENCES

[1] Nash, K. L. *Solvent Extr. Ion Exch.*, **11**, 729 (1993).

[2] Marinsky, J. A. and Marcus Y. (Eds.) "Ion Exchange and Solvent Extraction", Marcel Dekker, New York (1974).

[3] Manning, P. G. *Can. J. Chem.*, **40**, 1984 (1962).

[4] Siddal, T. H. *J. Inorg. Nucl. Chem.*, **26**, 1991 (1964).

[5] Horwitz,E. P., Kalina, D. J., Diamond, H., Vandergift, D. G. and Schulz, W. W. *Solvent Extr. Ion Exch.*, **3**, 75 (1985).

[6] Arnaud-Neu, F., Böhmer, V., Dozol, J.-F., Grüttner, C., Jakobi, R. A., Kraft, D., Mauprivez, O., Rouquette, H., Schwing-Weill, M.-J., Simon, N. and Vogt, W. *J. Chem. Soc., Perkin Trans. 2,* 1175 (1996).

[7] Yaftian, M. R., Burgard, M., Wieser, C. and Matt, D. *Solvent Extr. Ion Exch.*, **16**, 1131 (1998).

[8] Arnaud-Neu F., Browne, J. K., Byrne, D., Marrs, D. J., McKervey, M. A., O'Hagan, P., Schwing-Weill, M.-J. and Walker, A . *Chem. Eur. J.*, **5**, 175 (1999).

[9] Yaftian, M. R. and Vahedpour M. *Phosphorus, Sulfur and Silicon*, **174**, 93 (2001).

[10] Schulz, W. W., Burger, L. L. and Navratil, J. D. (Eds.) "Science and Technology of Tributyl-phosphate", CRC Press, Boca Ratton, Fl. 1984-1990, Vols, I-III.

[11] Farah K., El-Bayoumy, S. and Kandil, A. T. *J. Radioanal. Nucl. Chem.*, **157**, 87 (1992).

[12] Hasegava, Y., Takashima, K. and Watanabe, F. *Bull. Chem. Soc. Jpn.*, **70**, 1047 (1997).

[13] Marczenko, Z. "Spectrophotometric Determination of Elements", Wiely, New York (1976).

[14] Rydberg, J., Musikas, C. and Choppin, G. R. "Principles and Practice of Solvent Extraction", Marcel Dekker, New York (1992).

[15] Inoue Y., Amano, F., Okada, N., Inada, H. Ouchi, M., Tai, A. and Hakushi, T., *J. Chem. Soc., Perkin Trans.* **2**, 1239 (1990).

[16] Mahajan, G. R., Murali, M. S., Prabhu, D. R.,Shulka, J. P., Nair, G. M. and Natarajan, P. R., *Thermochim. Acta*, **180**, 185 (1991).