

**SYNERGISTIC “An(III)/Ln(III)” SEPARATION
WITH DITHIOPHOSPHINIC EXTRACTANTS AND RELATED LMCT PHENOMENA**

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Abstract

The study of the extraction properties and the selectivity of synergistic mixtures, based on dithiophosphinic acids and oxygen atoms bearing extracting agents was conducted at Marcoule Centre. Visible spectroscopy was applied to point out the occurrence of Ligand to Metal Charge Transfer (LMCT) phenomena when using these organic solutions to extract europium (III).

In the case of “purified Cyanex 301 acid/TBP” mixtures, the separation factor between americium and europium, was maximum for 10%_{molar} TBP (S.F._{Am/Eu} > 5000, with $D_{Am} \sim 200$). This particular molar ratio was chosen for the comparison between various synergistic mixtures, based on purified Cyanex 301 acid and oxygen atoms bearing extracting agents, such as phosphates, phosphine oxides, monoamides and diamides. The extraction and separation properties were compared at pH ~ 3. Synergistic as well as antagonistic effects were observed, depending on the nature of the solvating agent. Three different behaviours could be distinguished :

Compounds such as phosphine oxides promoted ²⁴¹Am and ¹⁵²Eu extraction as compared to purified Cyanex 301 acid alone, but with a far lower S.F._{Am/Eu}.

Compounds such as sterically hindered phosphates favoured Am/Eu separation but showed poorer extracting properties than purified Cyanex 301 acid alone.

Compounds such as TBP, DOTA (monoamide) or DPSO (sulphur oxide) promoted both the extraction of ²⁴¹Am and ¹⁵²Eu and their separation. A S.F._{Am/Eu} as high as 15000 was observed for trace level ²⁴¹Am and ¹⁵²Eu in the case of DOTA, while Cyanex 301 acid alone showed a S.F._{Am/Eu} of ~ 5000, at pH ~ 3.

Purified Cyanex 301 acid was uncoloured in dodecane, whereas it became yellowish when loaded with europium(III) : the band of LMCT appeared at 434 nm. Small additions of TBP not only intensified the band of charge transfer of europium(III), but also induced a “blue-shift”. The colour of the organic solutions turned to deep orange as the concentration of TBP increased, and so up to 10%_{molar} TBP in the synergistic mixture.

Visible spectroscopy was also applied to all previously described synergistic mixtures, composed of purified Cyanex 301 acid on the one hand, and oxygen atoms bearing solvating agents on the other hand. It was rather difficult to explain the differences observed in the behaviour of monodentate ligands (phosphates or monoamides) and bidentate ligands (CMPO or diamide) or between strong and medium electron donating ligands (phosphine oxides *vs* TBP, diamide *vs* monoamide). However, it seemed that whenever a high $S.F._{Am/Eu}$ was obtained for trace level ^{241}Am and ^{152}Eu , a strong LMCT phenomenon was also observed.

Three different bis(*R*-phenyl)dithiophosphinic acids ($R = -\text{H}, -\text{Cl}$ and $-\text{F}$) were also tested in synergistic mixtures with TOPO and their extracting properties checked at medium acidity ($[\text{HNO}_3] \sim 0.5 \text{ mol/L}$). In this case, only weak Eu(III) LMCT phenomena were observed ; the loaded organic solutions were bright yellow and the maximum absorption bands could not be clearly pointed out.