

6 Solvent extraction chemistry

Solvent extraction is a widely-used technique for separating and purifying ionic species. Solvent extraction is applied on an industrial level e.g. in the reprocessing of spent nuclear fuels by the PUREX process and in the large-scale copper production by the solvent extraction/electro-winning technique.

We develop and study solvent extraction systems both in the nuclear and the non-nuclear context. Within the nuclear context, we have been focusing on solvent extraction systems for actinide separations, most notably for separating trivalent actinides, An(III), from the chemically similar lanthanides, Ln(III). From the early 1990's with Z. Kolarik's contribution to an FP3 EURATOM project [1], these studies have continuously been performed in the framework of EURATOM research programs, the most recent being SACSESS [2]. A common denominator throughout these projects is the use of heterocyclic nitrogen donor complexing agents. Such compounds exhibit high selectivity for An(III) over Ln(III), with molecules based on the BT(B)P (bis-triazinyl-(bi)-pyridine) core being among the most efficient.

Non-nuclear applications are related to the recycling of critical metals such as rare earth elements (REE) and refractory metals. With this topic being a comparatively recent addition to our portfolio, we have started work on REE separations using commercial extracting agents. Currently we are contributing to the ERA-MIN project, ENVIREE (environmentally friendly and efficient methods for extraction REE from secondary sources) [3].

6.1 Complexation of Cm(III) and Eu(III) with PTD

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Over the years, we have developed and studied solvent extraction systems capable of separating trivalent actinides, An(III), from chemically similar lanthanides, Ln(III). The chemistry applied is based on the use of polydentate nitrogen donor heterocycles such as 2,6-(bis-1,2,4-triazin-3-yl)pyridines (BTP) and 6,6'-(bis-1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBP) [4]. Initially such compounds were used as lipophilic extracting agents, selectively extracting An(III) from aqueous solutions containing HNO₃.

More recently, water soluble derivatives were developed and tested. For example, SO₃-Ph-BTP (Fig. 1 top) selectively back-extracts An(III) from an organic phase loaded with An(III) and Ln(III) while Ln(III) remain in the organic phase [5,6]. Successful lab-scale process tests have been performed using this compound [7, 8].

Unfortunately, the presence of Sulphur poses issues with the management of secondary waste. Preferably,

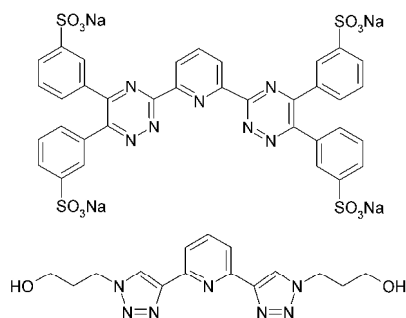


Fig. 1: Top, SO₃-Ph-BTP; bottom, PTD.

all chemicals used should be composed of only C, H, O and N atoms, making them combustible to gaseous products.

Addressing this issue, PTD (Fig. 1 bottom) has recently been synthesized and evaluated by our colleagues from Università di Parma and Politecnico di Milano. This compound is a CHON alternative to SO₃-Ph-BTP. It appeared that a solvent extraction system using PTD to strip An(III) from a TODGA organic phase loaded with An(III) and Ln(III) [9] is slightly less selective than the SO₃-Ph-BTP/TODGA system [5].

To understand this difference and explore possible ways of improvement, the complexation of Cm(III) and Eu(III) with PTD was studied by TRLFS [10].

This study concluded that PTD is not intrinsically less selective than SO₃-Ph-BTP; the stability constants of the 1:3 Cm(III) complexes are approximately two orders of magnitude higher than those of the Eu(III) complexes, for both ligands. However, PTD is a weaker and more easily protonated ligand, as inferred from the Cm(III) 1:3 complex stability constants (corrected for ligand protonation) and pK_a values (see Table 1).

Tab. 1: Cm(III) 1:3 complex stability constants (corrected for ligand protonation) and pK_a values for PTD and SO₃-Ph-BTP.

Ligand	lg β ₃ (Cm)	pK _a
PTD	9.9 ± 0.3	2.1 [9]
SO ₃ -Ph-BTP	12.2 ± 0.3 [6]	0.5 [11]

As a consequence, PTD does not exclusively form the 1:3 complexes under conditions applicable to the PTD/TODGA solvent extraction system, i.e. at a PTD concentration of 80 mmol/L in approx. 0.5 mol/L HNO₃. Indeed, a mixture of Cm(III) 1:2 and 1:3 complexes in a concentration ratio of approx. 1:4 is present, as probed by TRLFS. This significant fraction of

the Cm(III) 1:2 complex is responsible for the system's lower selectivity.

Building on the otherwise excellent properties of PTD [9], future work aims at finding PTD derivatives which form more stable metal ion complexes and/or are less prone to protonation.