

## **ACTINIDE(III)/LANTHANIDE(III) PARTITIONING USING n-Pr-BTP AS EXTRACTANT: EXTRACTION KINETICS AND EXTRACTION TEST IN A HOLLOW FIBER MODULE**

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### **Abstract**

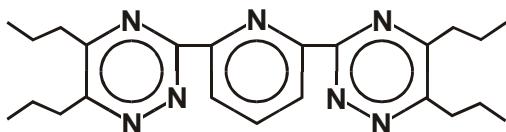
2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP), first developed in our laboratory, is a very promising extractant for the effective separation of actinides(III) from lanthanides(III). It is able to extract actinides(III) with usable distribution coefficient from 1-2 molar nitric acid selectively over lanthanides(III). The Am(III)/Eu(III) separation factor is approx. 135. The performance of this extractant is further elucidated by kinetic investigations and a counter-current extraction experiment in a hollow fiber module (HFM). The kinetic investigations were performed in a stirred cell. The fact that extraction rate is independent of stirring speed reveals a slow chemical complexation reaction. The HFM extraction test on americium(III)/fission lanthanides(III) separation showed good hydrodynamic behavior. Depending on aqueous flow rate, which was varied, up to 94% americium could be removed from the feed phase. Lanthanide co-extraction was in the range of 1%.

## 1. Introduction

Over the recent years, efforts have been made finding extractants capable of separating trivalent actinides from fission lanthanides. This separation task is a key step in the separation of minor actinides from high-level Purex effluents within the P&T strategy [1]. Ideally, such an extractant would selectively extract trivalent actinides over lanthanides from moderately acidic media without the need for pH adjustment or the use of salting-out agents. Furthermore, it would consist only of C, H, O, and N atoms (“CHON principle”), making it fully combustible to gaseous products.

2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP), which was developed in our laboratory [2,3], is an extractant capable of fulfilling this task. It is able to selectively extract actinides(III) over lanthanides(III) from 1-2 molar nitric acid with usable distribution coefficient. Am(III)/Eu(III) separation factor is approx. 135. The extractant complies to the CHON principle.

Figure 1. **2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP)**



In shaking tubes, equilibrium is not attained very rapidly. We feel that this indicates a slow chemical complexation reaction. To further elucidate the kinetics of extraction, we performed experiments on Am(III) extraction in a stirred cell built specifically for our purposes [4].

A constant-interface, Lewis-type stirred cell is the best tool for extraction kinetics studies, if it is calibrated [5,6]. It allows the discrimination of flow-dependent transport processes (diffusional regime) from flow-independent interfacial reactions (chemical regime) as rate determining alternatives by measuring extraction rates at varied stirring speeds. The cell we used in this work is tested on a physical mass transfer system (toluene transfer into water), showing a linear dependency of mass transfer rate on stirring speed over a wide range [4]. Therefore we can be sure that fluxes independent of stirring speed indicate that an interfacial process (i.e. the chemical reaction) is rate determining.

With n-Pr-BTP, a hot mixer-settler test using a synthetic feed solution and a hot test in a 16-stage centrifugal extractor using genuine DIAMEX raffinate for feed solution were performed in other laboratories [7]. These tests were very successful. Americium(III) and curium(III) could quantitatively be extracted (<99.85%) and almost completely be recovered.

Instead of using the above extraction equipment, we performed an extraction test in a hollow fiber module (HFM). Basically, in a HFM, aqueous and organic phases are macroscopically separated by a micro-porous membrane (usually consisting of hydrophobic membrane material). Phase contact is maintained within the pores by the application of a proper pressure difference (with hydrophobic membrane material, pressure in the aqueous phase is kept slightly higher than in the solvent phase). This yields a wide flexibility towards hydrodynamic conditions, overcoming restrictions often encountered with conventional extractors, e.g. entrainment.

The first application of non-dispersive chemical extraction in a HFM was described some 15 years ago [8]. In the meantime, many publications have followed, however, mainly using well-known extractants. To our knowledge, this is the first HFM extraction test on actinide(III)/lanthanide(III) separation using an “exotic” extractant. Tests like this one should eventually allow one to evaluate the capability of non-dispersive extraction in the field of partitioning.

## 2. Experimental

### 2.1 Synthesis and characterisation of n-Pr-BTP

We prepared two batches of 40-50 g n-Pr-BTP each as described in [3]. Melting points were in the range of 105-107°C. NMR data confirmed the products' identities. To further characterise the products, we performed distribution measurements: Contacting a solution of 0.04 M n-Pr-BTP in TPH (a kerosene-type diluent) modified with 1-octanol (70:30 vol.) and 1 M nitric acid labelled with  $^{241}\text{Am}$  or  $^{152}\text{Eu}$ , we found an americium distribution coefficient of approx. 14 and a separation factor,  $SF_{\text{Am(III)}/\text{Eu(III)}}$  of 135. This is in good agreement with results published elsewhere [7].

### 2.2 Extraction kinetics

Kinetic measurements were performed in our special small stirred cell. Its half cell volume is only 60 mL [4]. The aqueous phase was a solution of americium(III) (2 500 Bq/mL) in 1 M nitric acid. Organic phase was a solution of 0.04 M n-Pr-BTP in TPH/1-octanol (70:30 vol.).

The stirred cell was filled with both aqueous and organic phases, and stirrers were started with appropriate stirring speeds (aqueous = organic). The activity in the aqueous phase was continuously detected in a by-pass with a well-type NaI-detector. Measured activity was plotted vs. time and initial metal fluxes were calculated.

### 2.3 HFM extraction test

#### 2.3.1 Feed solutions

Aqueous feed contained  $^{241}\text{Am(III)}$ , fission lanthanides(III) and yttrium(III). Its composition corresponds to a DIAMEX raffinate as used in other n-Pr-BTP tests [7], except that  $^{241}\text{Am}$  was used in trace amount, and Cm, Ru, Pd, Fe were not present. The composition is given in Table 1. The organic phase was a solution of n-Pr-BTP (0.04 kmol/m<sup>3</sup>, 16.2 g/L) in TPH/1-octanol (70:30 vol.).

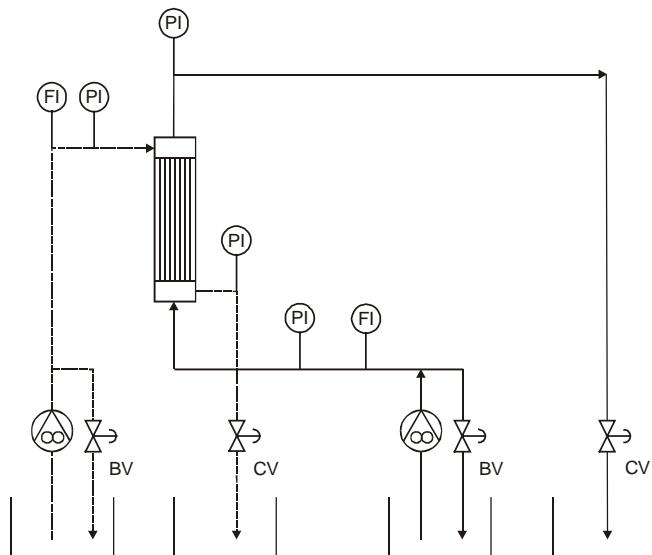
Table 1. Composition of aqueous feed solution

HNO <sub>3</sub>	1.0 kmol/m <sup>3</sup>
Y	89.0 mg/L
La	294 mg/L
Ce	566 mg/L
Pr	264 mg/L
Nd	998 mg/L
Sm	199 mg/L
Eu	35.7 mg/L
Gd	28.2 mg/L
$^{241}\text{Am}$	0.49 MBq/L

### 2.3.2 Set-up

We set up a single HFM extractor inside a glove box. This corresponds to the extraction stages in commonly used extractor batteries, without scrubbing or stripping stages. The HFM set-up is shown schematically in Figure 2. Both phases were passed through the module in counter-current, single-pass mode, i.e. phases were not recycled. The organic phase flowed in the lumen of the hollow fibers (HF). The module used was a Celgard LiquiCel Extra-Flow type module (10 000 HF, membrane material polypropylene, average pore size 0.02 µm, porosity  $\epsilon = 40\%$ , tortuosity  $\tau = 2.6$  [9], HF inner diameter = 0.24 mm, HF outer diameter = 0.30 mm, active length = 0.15 m). Static pressure in the aqueous phase was kept approx. 0.5 bar higher than in the organic phase to maintain proper phase separation. Aqueous flow rate was varied, 0.44 L/h  $Q_{aq} \cdot 1.75$  L/h, organic flow rate was kept constant at  $Q_{org} = 0.50$  L/h. Further details can be found in [10].

Figure 2. Single-pass, counter-current HFM set-up (schematic). — aqueous phase, - - - organic phase, PI = pressure gauge, FI = flow meter (rotameter), CV = control valve, BV = bypass valve



### 2.3.3 Analytic

Samples of aqueous and organic effluents were drawn discontinuously.  $^{241}\text{Am}$   $\gamma$  activity was determined on a  $\gamma$  counter (*Packard Cobra Auto-Gamma*). Lanthanide concentrations were measured with ICP-AES after proper dilution with nitric acid (aqueous samples) or stripping into 0.01 nitric acid (organic samples).

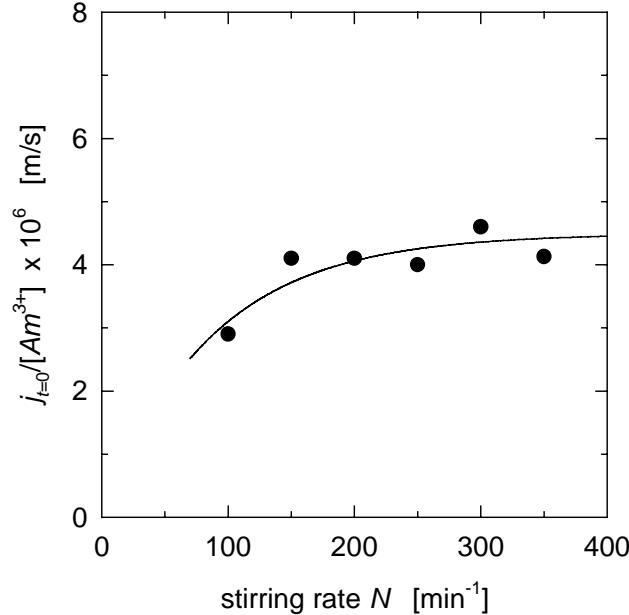
## 3. Results

### 3.2. Extraction kinetics

The plot of normalised initial americium fluxes,  $j_{t=0} / [\text{Am}^{3+}]_{t=0}$ , (Figure 3) characterises the kinetic behaviour of americium extraction with n-Pr-BTP. The flow-independent fluxes (plateau rates) indicate that the interfacial reaction is rate determining (i.e. non-equilibrium at the interface).

Figure 3. Americium(III) extraction into n-Pr-BTP. Stirring rate dependency of normalised initial americium fluxes.

$[Am^{3+}] = 2500 \text{ Bq/mL}$ ,  $[HNO_3] = 1.0 \text{ kmol/m}^3$ ,  $[n\text{-Pr-BTP}] = 0.04 \text{ kmol/m}^3$ .



This means that mass transfer is chemically controlled. This case is very interesting as it allows studying the mechanism of the interfacial reaction. Therefore the dependency of the plateau rate from the concentrations of all participating species ( $Am^{3+}$ ,  $H^+$ ,  $NO_3^-$ , n-Pr-BTP) must be studied. This leads to the reaction orders of the interfacial reaction for each species. If the reaction orders are known a rate equation can be expressed.

Some preliminary measurements indicate a first order dependency on the concentration of n-Pr-BTP. The measurements for the other species are still in progress, therefore a mechanism for the americium extraction with n-Pr-BTP cannot be postulated yet.

### 3.2. HFM extraction test

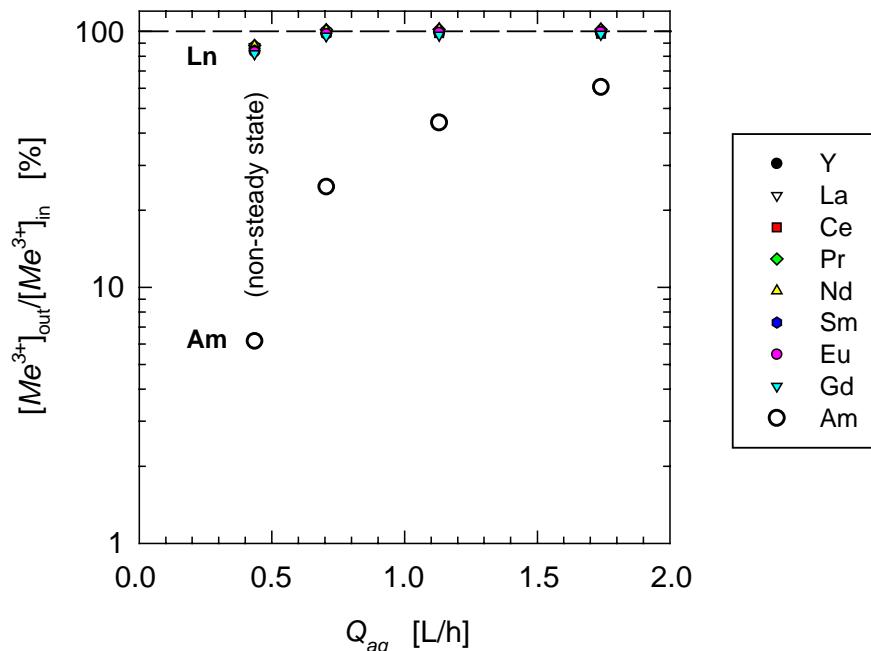
Throughout the experiment, which ran four hours, the hydraulic behaviour was highly satisfactory, i.e. both aqueous and organic effluents were clear without any entrainment. This is a benefit of the macroscopic phase separation by the membrane material.

Except with an aqueous flow rate of  $Q_{aq} = 0.44 \text{ L/h}$ , mass balances were  $(100 \pm 2.5)\%$  for lanthanides, and 90-98% for Am(III). With an aqueous flow rate of  $0.44 \text{ L/h}$ , Am(III) mass balance was 66%, lanthanides mass balances were approx. 88%. This is a sign that, at this flow rate, the experiment was not run sufficiently long to reach steady state.

Aqueous effluent concentrations normalised to feed concentrations,  $[Me^{3+}]_{out}/[Me^{3+}]_{in}$ , over aqueous flow rate,  $Q_{aq}$ , are shown in Figure 4. With an aqueous flow rate of  $0.44 \text{ L/h}$ , 94% of Am(III) could be removed from the aqueous phase. There is a strong dependency of Am(III) extraction efficiency on aqueous flow rate, and hence residence time: With an aqueous flow rate of  $1.75 \text{ L/h}$ , only 40% of Am(III) could be extracted. The steep flow rate dependency indicates that, at significantly

lower flow rates, Am(III) would be extracted almost quantitatively. However, the experimental set-up, regarding the pumps, control valves and flow indicators installed, was not layed out for such low flow rates.

**Figure 4. Am(III)/Ln(III) separation in a HFM using n-Pr-BTP as extractant. Relative aqueous effluent concentrations as a function of aqueous flow rate. Aqueous phase, shell-side: Am(III) + Ln(III) in  $\text{HNO}_3$  1.0 kmol/m<sup>3</sup>. Organic phase, in HF: [n-Pr-BTP] = 0.04 kmol/m<sup>3</sup> in TPH/1-octanol (70:30 vol.).  $Q_{\text{org}} = 0.50 \text{ L/h}$ .**



Except for the non-steady state result with an aqueous flow rate of 0.44 L/h, no lanthanide co-extraction was detectable in the aqueous phase. Lanthanide co-extraction as determined from organic effluent samples was in the range of 1-2% for Sm, Eu, Gd, and well below 0.5% for other lanthanides. We point out these good results concerning lanthanide co-extraction were realised without lanthanide scrubbing, due to the high separation factor of n-Pr-BTP.

#### 4. Conclusion

n-Pr-BTP is a very capable extractant for An(III)/Ln(III) separation from acidic media. Although Am(III) extraction rate is not very fast, results from a HFM extraction experiment are promising. Operation is stable, lanthanide co-extraction is small. Still better results can be expected from a modified experimental set-up which can handle lower flow rates. Tests on lanthanide scrubbing and back extraction will be performed to further evaluate the behaviour of the n-Pr-BTP extraction system in a hollow fiber module.

#### Acknowledgements

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