

KINETICS OF NOVEL EXTRACTION SYSTEMS USED IN THE PARTITIONING OF NUCLEAR WASTE

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Abstract

Both 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP), and a synergistic mixture of di(chlorophenyl)dithiophosphinic acid and tri-n-octyl phosphine oxide, are able to selectively extract trivalent actinides over lanthanides from 0.5-1 M nitric acid. We focused on clearly identifying the extraction regime (chemical or diffusional) of these extraction systems. The dependency of extraction rates from stirring speed was measured in our special stirred cell. The n-Pr-BTP system showed extraction rates independent from stirring speed. This reveals that the mass transfer is controlled by a slow chemical complexing reaction. On the other hand the synergistic mixture showed a linear relationship between fluxes and stirring rate indicating that mass transfer is controlled by diffusion. Furthermore extraction rates are about ten times higher than for the n-Pr-BTP system.

Introduction

The Partitioning & Transmutation (P&T) strategy is to separate long-lived radioisotopes from spent nuclear fuel arising from electric power production (Partitioning) and then to transmute them into short-lived radionuclides and eventually stable nuclides. Thus, the long-term impact from the final disposal of spent nuclear fuel could be alleviated. [1]

In the European research on minor actinide partitioning a two step liquid/liquid extraction process is an option to achieve this goal. The first step is the DIAMEX (DIAMide EXtraction) process, designed for the selective co-extraction of trivalent minor actinides and trivalent fission lanthanides from HLLW. [2] In the second step, actinides(III) must be selectively recovered from the DIAMEX product containing both trivalent actinides (americium, curium) and fission lanthanides. This separation task is a difficult challenge due to the chemical similarity of the two groups and is the key step in partitioning. To make this step process compatible, a feed acidity in the range of 0.1 to 1 kmol/m³ HNO₃ must be processed. Furthermore very high extraction efficiency over the whole separation process (extraction, scrubbing, stripping) is required to produce a product containing at least 99.9% of the minor actinides and less than 5% of lanthanides. This effort is necessary since some of the fission lanthanides are strong neutron absorbers, and due to their relative abundance compared to the trivalent actinides. Effective transmutation requires a good decontamination regarding the fission lanthanides. [3]

Two novel extractants for this task were developed in German laboratories:

- a) 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP) (see Figure 1), a solvating extractant which was developed in our laboratory. [4] It is able to extract trivalent actinides from 1-2 kmol/m³ HNO₃ with usable distribution coefficient and an Am(III)/Eu(III) separation factor of approx. 130. The so-called *SANEX-III* process (selective actinide extraction) [2] is based on this extractant.
- b) A synergistic mixture of di(chlorophenyl)dithiophosphinic acid (see Figure 2) and tri-n-octyl phosphine oxide (TOPO). [5] Depending on the diluent used, this mixture extracts actinides from 0.5 kmol/m³ with an Am(III)/Eu(III) separation factor of approx. 30. This mixture is used as extractant in the *SANEX IV* process. [2]

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

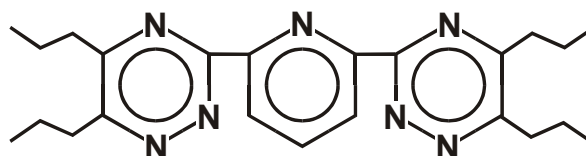
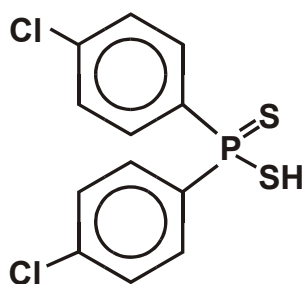


Figure 2. **di(chlorophenyl)dithiophosphinic acid**



These extractants have already proven their potential in mixer-settler and centrifugal extractor battery tests performed in other laboratories. [2] Instead of using multistage contactors, we perform tests on americium(III)-lanthanide(III) separation in hollow fiber modules (HFM). [6] The design of the hollow fiber extraction experiments is based on mass transfer calculations. Therefore an evaluation of mass transfer kinetics is necessary.

This contribution concerns the evaluation of the kinetic regime (chemical or diffusional) of these two extraction systems introduced above. A kinetic study can conveniently be performed with mass transfer experiments in a constant-interface stirred cell of appropriate design. [7, 8] The stirred cell we used was calibrated on a physical mass transfer system (toluene-water), showing a linear increase of mass transfer with stirring speed. [7] Therefore we can be sure that, in a chemical mass transfer system, a linear increase of mass transfer with stirring speed indicates diffusional regime. Mass transfer rate independent of stirring speed indicates other processes than transport (e.g. the chemical reaction) control the mass transfer rate. [8]

Knowledge of the mass transfer controlling step (chemical reaction or diffusion) is essential for calculating extraction rates (especially in the HFM). Furthermore knowledge of the extraction regime leads to a better understanding of the physical and chemical fundamentals of an extraction system.

Experimental

Reagents and solutions

2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP) was synthesised according to [4]. A solution of n-Pr-BTP (0.01 to 0.04 kmol/m³) in TPH/1-octanol (70:30 vol.) was used for the first set of kinetic experiments (TPH is a French highly-branched kerosene-type diluent). A solution of 0.5 kmol/m³ di(chlorophenyl)dithiophosphinic acid (synthesised by an external laboratory according to [5])+0.25 kmol/m³ TOPO in tert.-butylbenzene was used for the second set of experiments.

Aqueous phase was a solution of tracer amounts of ²⁴¹Am(III) or ¹⁵²Eu(III) in either 1.0 kmol/m³ HNO₃+2.0 kmol/m³ NH₄NO₃ (BTP system) or 0.1 kmol/m³ HNO₃ (synergistic mixture). The radiotracers were received from *Blaseg Isotopendienst*, Germany (radionuclide purity > 99%). For one set of experiments a solution of inactive fission lanthanides traced with ²⁴¹Am(III) (see Table 1) was used. Lanthanide(III) nitrates were reagent grade with better than 99% purity.

Table 1. **Composition of inactive fission lanthanide solution**

HNO ₃	0.1 kmol/m ³
Y	89 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

Kinetic experiments

Kinetic measurements were performed at 293 K in a constant interface stirred cell. The cell's half volume is 60 cm³. In general the used stirred cell is a scaled-down version of the Nitsch-type stirred cell. It is described in detail in [7]. The stirred cell was filled with both aqueous and organic phases, and stirrers were started with the same stirring speed in both phases ($n_{\text{aq}} = n_{\text{org}}$). Experiments were carried out at varied stirring speed. The change in the activities of the radiotracers in the aqueous phase was detected continuously in a by-pass with a well-type NaI-detector. Measured concentration change was plotted vs. time and initial extraction rates were calculated. Details about this calculation are reported in [9].

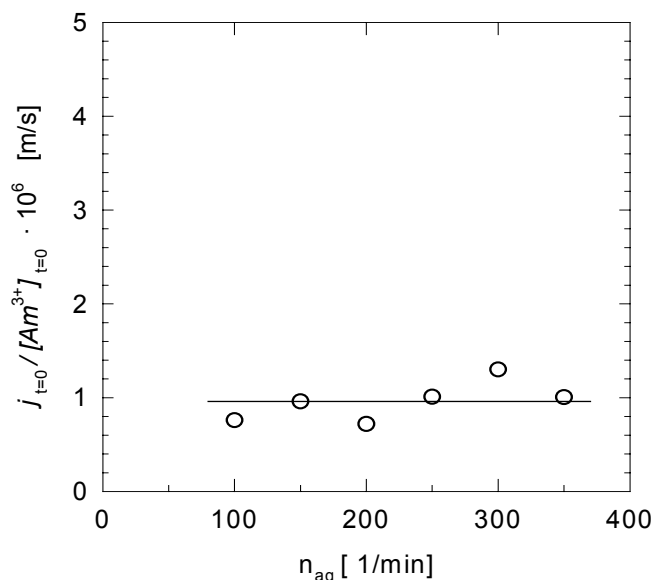
Results and discussion

Kinetics of the 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP) system (SANEX III)

The plot of normalised initial americium fluxes, $j_{t=0}/[Am^{3+}]_{t=0}$, (Figure 3) characterises the kinetic behaviour of Am(III) extraction with n-Pr-BTP. The flow independence of the initial fluxes indicates that the interfacial reaction is rate determining. This means that mass transfer is chemically controlled.

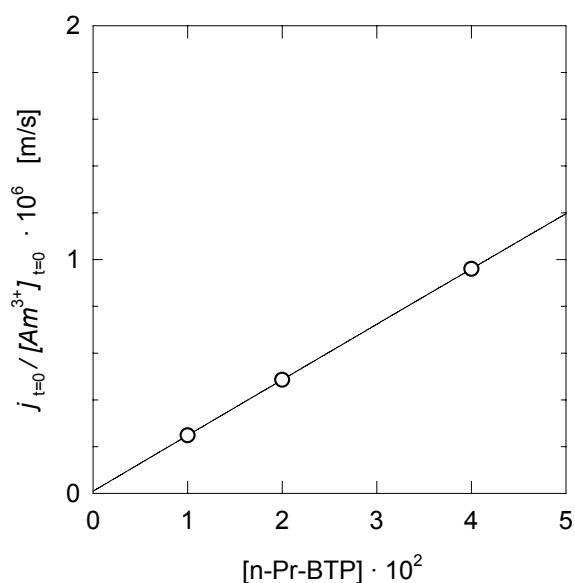
In the case of an extraction system controlled by the chemical reaction a study of the chemical extraction mechanism is possible. Therefore, analogously to a former reported successful procedure, the dependency of initial fluxes at a given stirring speed (in the plateau region) from the concentrations of all participating species (Am^{3+} , H^+ , NO_3^- , n-Pr-BTP) must be studied [9]. The influence of the complexing agent concentration on the extraction rate is shown in Figure 4. The linear dependency of initial fluxes on n-Pr-BTP concentration indicates that the interfacial reaction is of first order for the complexing agent (n-Pr-BTP). The measurements for the other species are still in progress. Some preliminary measurements concerning the influence of nitrate concentration on the extraction rate indicate that extraction rate is independent of the nitrate anion concentration. This means that the nitrate anion is not involved in the rate determining step.

Figure 3. **Stirring rate dependency of normalised initial americium (III) flux.**
Aqueous phase: 1 MBq/L Am(III) in 1 kmol/m³ HNO₃+2.0 kmol/m³ NH₄NO₃;
Organic phase: 0.04 kmol/m³ n-Pr-BTP in kerosene/1-octanol (70:30 vol.)



With the above result and the assumption of a bimolecular reaction between the metal ion and the complexing agent as rate determining step we can calculate an overall rate constant $k = 3 \cdot 10^{-5}$ [-]. Calculations of a HFM experiment taking in to account the limitation by the chemical reaction and using this rate constant were successful. [6] The investigation of the influence of the proton concentration will lead to a complete understanding of this extraction system.

Figure 4. **Dependency of normalised initial americium(III) flux on n-Pr-BTP concentration.**
Aqueous phase: 1 MBq/L Am(III) in 1 kmol/m³ [HNO₃]+2 kmol/m³ [NH₄NO₃];
Organic phase: n-Pr-BTP (varied concentration) in kerosene/1-octanol (70:30 vol.)

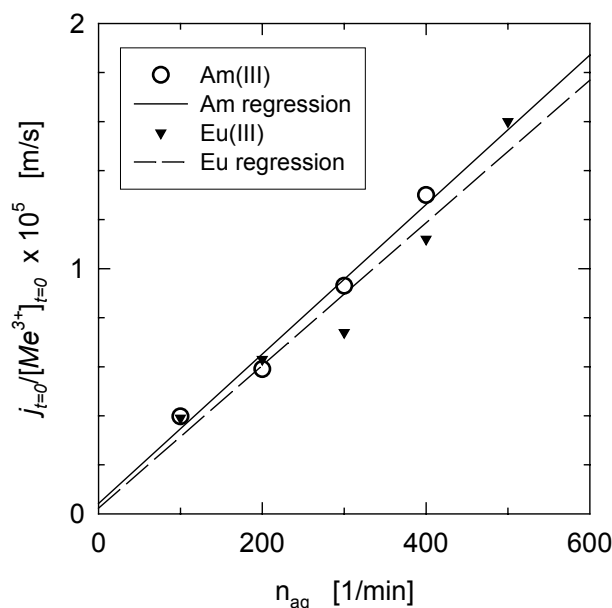


Kinetics of the synergistic mixture of di(chlorophenyl)dithiophosphinic acid and tri-n-octyl phosphine oxide (TOPO) (SANEX IV)

Figure 5 shows the stirring rate dependencies of initial americium and europium fluxes. In either case, extraction rate is found to linearly increase with stirring speed. Hence, the rate of extraction is controlled by diffusion in the range of hydrodynamic conditions investigated. The rate of the chemical complexation reaction is fast compared to diffusion in this system. Experimental conditions were chosen in a way to maintain mass transfer resistance in the aqueous phase. Hence, individual Am (III) and Eu(III) mass transfer coefficients for a given stirring rate are accessible. [10] Their values can directly be taken from the y-axis values in Figure 5.

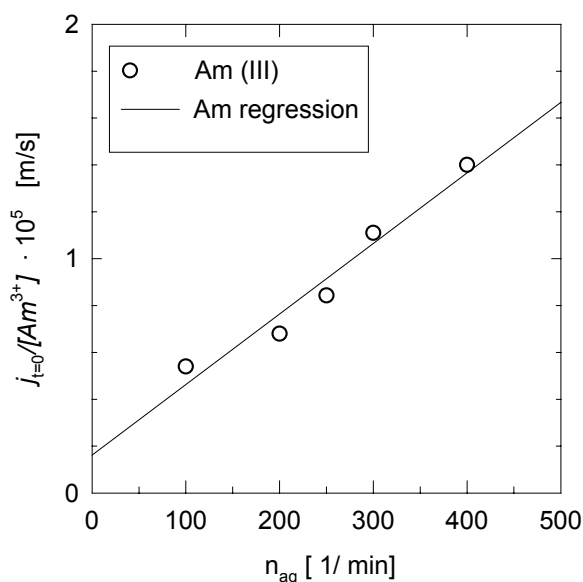
This is important as it allows to verify that the stirred cell experiments cover the hydrodynamic conditions in the HFM extraction experiments: Individual mass transfer coefficients in the HFM are well below those from the stirred cell experiments. As mass transfer is limited by diffusion an additional mass transfer resistance from the chemical reaction does not need to be implemented in the HFM calculations for extraction with the synergistic system. [6]

Figure 5. **Stirring rate dependency of normalised initial americium(III) and europium(III) fluxes.**
Aqueous phase: 0.5 MBq/L Am(III) or 80 kBq/L Eu(III) in 0.1 kmol/m³ [HNO₃];
Organic phase: 0.5 kmol/m³ di(chlorophenyl)dithiophosphinic acid+0.25 kmol/m³ TOPO in tert.-butyl benzene



From a study by Giuseppe Modolo [11] we know that there is an influence of the lanthanide concentrations on Americium distribution ratio. Therefore we wanted to identify a possible effect of macro amounts of lanthanides on extraction rate (see Figure 6). These experiments were performed with an aqueous solution of inactive lanthanides (see Table 1) traced with ²⁴¹Am(III).

Figure 6. **Influence of inactive lanthanides.**
Aqueous phase according to Table 1+0.5 MBq/L Am(III);
Organic phase: 0.5 kmol/m³ di(chlorophenyl)dithiophosphinic acid+0.25 kmol/m³ TOPO in tert.-butyl benzene



The linear increase of initial flux with stirring speed shows that americium extraction is not influenced by the presence of macro amounts of lanthanides. The observed extraction rates are almost identical, cf. Figure 5. This means that the concentration of lanthanides has no influence on the driving force. Therefore a correction in the calculation of mass transfer in the HFM regarding kinetics is not necessary if we want to extract actinides from real HLLW.

Conclusion

We investigated mass transfer kinetics of two novel extraction systems used in the minor actinide partitioning. The tool used for these investigations was a calibrated stirred cell. The important feature of this study is that the kinetic regime of the 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP) extraction system and the synergistic mixture of di(chlorophenyl)dithiophosphinic acid and tri-n-octyl phosphine oxide (TOPO) are different. The extraction rates of the former system are independent from stirring speed and this means that it is controlled by a slow chemical reaction. On the other hand the extraction rates of the latter system depend on stirring speed, the chemical reaction is fast, and the extraction rate is controlled by diffusion. Nevertheless both extraction systems are well suited for americium(III)/lanthanide(III) separation in a HFM. This was shown by HFM extraction experiments [6, 12, 13] designed with the use of mass transfer calculations which are based on these studies.

Acknowledgements

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REFERENCES

- [1] OECD Nuclear Energy Agency (1999), *Status and Assessment Report on Actinide and Fission Product Partitioning and Transmutation*, (www.nea.fr/html/pt/pubdocs.htm).
- [2] C. Madic, M.J. Hudson, J.O. Liljezin, J-P. Glatz, R. Nannicini, A. Facchini, Z. Kolarik, R. Odoj (2000), *New Partitioning Techniques for Minor Actinides*, EUR 19149, European Commission, Luxembourg, ISBN 92-828-9696-X.
- [3] OECD Nuclear Energy Agency (2002), *Accelerator-driven System (ADS) and Fast Reactors (FR) in Advanced Nuclear Fuel Cycles*, OECD-NEA, Paris, France, ISBN 92-64-18482-1 (www.nea.fr).
- [4] Z. Kolarik, U. Müllich and F. Gassner (1999), *Extraction of Am (III) and Eu (III) Nitrates by 2,6-Di (5,6-dipropyl-1,2,4-triazin-3-yl)pyridine*, Solvent Extr. Ion Exch. 17 (5), 1155-1170.
- [5] G. Modolo, R. Odoj (1999), *Synergistic Selective Extraction of Actinides over Lanthanides from Nitric Acid Using New Aromatic Diorganylthiophosphinic Acids and Neutral Organophosphorus Compounds*, Solvent Extr. Ion Exch. 17 (1), 33-53.
- [6] A. Geist, M. Weigl, U. Müllich, K. Gompper (2002), *Application of Novel Extractants for Actinide(III)/Lanthanide(III) Separation in Hollow Fiber Modules*, Proceedings of the International Solvent Extraction : ISEC 2002, Cape Town, ZA, March 18-21, 2002. Ed.: Sole, K. C., South African Inst. of Mining and Metallurgy, Johannesburg, S.693-98.
- [7] M. Weigl, A. Geist, K. Gompper, J.I. Kim (2001), *Kinetics of Lanthanides/Actinides Co-Extraction with N,N'-dimethyl-N,N'-dibutyl-tetradecylmalonic Diamide (DMDBTDMA)*, Solvent Extr. Ion Exch. 19 (2), (2001) 215-229.
- [8] P.R. Danesi (1992), in *Principles and Practices of Solvent Extraction*. Eds: J. Rydberg, C. Musikas, G.R. Choppin, Marcel Dekker: New York, Basel, Hongkong.
- [9] W. Nitsch and M. Weigl (1999), *Action of Amphiphilic Layers on the Kinetics of Interfacial Reactions at Liquid/Liquid Interfaces*, Langmuir, 14 (23), 6709-6715.
- [10] A. Geist, P. Plucinski, W. Nitsch (2000), *Mass Transfer Kinetics of Reactive Multi-cation Co-extraction into Bis(2-ethylhexyl)phosphoric Acid*, Solvent Extr. Ion Exch. 1 (3), (2000) 493-515.
- [11] Table 94 and Table 98 in Ref. 2.
- [12] A. Geist, M. Weigl, K. Gompper (2002), *Actinide (III)/Lanthanide (III) Separation by Non-dispersive Extraction with a Synergistic Mixture of bis(Chlorophenyl)dithiophosphinic Acid and TOPO*. Sep. Sci. Technol. 37 (15) 3369-3390 (in press).
- [13] A. Geist, M. Weigl, U. Müllich, K. Gompper (2002), *Separation of Actinides from Fission Lanthanides by Non-dispersive Liquid-liquid Extraction*. Lecture at the Actinide 2001, International Conference, 4-9 November 2001, Hayama, Japan (to be published in a special issue of the Journal of Nuclear Science and Technology).