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SANEX-BTP PROCESS DEVELOPMENT STUDIES

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ABSTRACT

Among the different *bis*-triazinyl-pyridine molecules studied at CEA-Marcoule, the 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine (*n*Pr-BTP) was chosen to carry out a counter-current SANEX[a] test, the feed solution of which was a genuine back-extraction solution issued from a DIAMEX process. Although the observed performances were very satisfactory for the separation of actinides(III) from lanthanides(III), the extraction and back-extraction yields of americium and curium were lower than expected from calculation. The hot test actually pointed out the strong sensitivity of *n*Pr-BTP towards air oxidation and acidic hydrolysis. Further investigations will thus be devoted to the strengthening of the molecule towards hydrolysis and hopefully lead to the formulation of a new solvent, which would be tested during year 2001 in the Atalante facility.

INTRODUCTION

The separation of minor actinides (*i.e.*: neptunium (Np), americium (Am) and curium (Cm)) from the wastes issuing the reprocessing of nuclear spent fuels should allow the long-term radiotoxic inventories of the waste packages to be substantially reduced, if these nuclides are removed from the waste before conditioning and subsequently transmuted into short-lived fission products by nuclear reactions (1). However, this separation is very difficult, particularly for the trivalent actinides (An(III) = Am(III) and Cm(III)), which exhibit very similar chemical properties to the trivalent lanthanides (Ln(III)), accounting for about one third of the total amount of fission products. The separation of An(III) from Ln(III) by liquid-liquid extraction using specific extractants (*e.g.*: synergistic mixtures based on nitrogen containing ligands and carboxylic acids, dithiophosphinic acids) has been studied for the last two decades in France. Recently, a new family of extractants, the *bis*-triazinyl-pyridines (BTP, Fig. 1), was developed by Dr. Z. Kolarik (2) in the framework of a European collaboration led by CEA-Marcoule. These BTP molecules are very efficient extracting agents and remain selective towards An(III) in highly acidic conditions ([HNO$_3$] $\geq$ 2 mol/L).
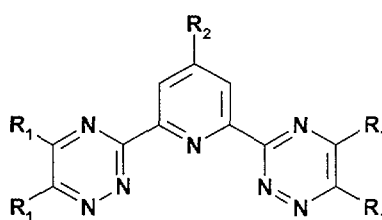
with R$_1$ = H, Methyl, *n*-Propyl, *i*-Propyl, *n*-Butyl, *i*-Butyl
and R$_2$ = H, *i*-Nonyl

Fig. 1: General formula of BTP*s*

Various BTP*s* have been studied at CEA-Marcoule. Among them, the 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine (Fig. 1: R$_1$ = *n*-Propyl and R$_2$ = H, hereafter named *n*Pr-BTP) was chosen to perform a counter-current test in 1999 on a genuine highly active effluent issued from the DIAMEX process. Preliminary to the hot test, numerous series of experiments were carried out in micro-tubes on synthetic aqueous solutions simulating DIAMEX back-extraction solutions. The influence of the

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[a] SANEX : Separation of ActiNides(III) from lanthanides(III) by EXtraction

composition of the organic solvent (concentration of nPr-BTP, TPH[b] or n-octanol volume ratios) on the extraction yields and extraction kinetics of An(III) was assessed.

RESULTS AND DISCUSSION

Preparation of the hot test: formulation of the solvent

The reasons why nPr-BTP was chosen to perform the hot test were the following:
- The kinetics of extraction of Am(III) and Eu(III) (used to simulate An(III)/Ln(III) separation), was faster than with any other BTP,
- nPr-BTP was fairly soluble (up to 0.05 mol/L) in mixtures of TPH and n-octanol, the organic diluents used to prevent precipitate formation,
- nPr-BTP could be easily synthesized on large scales (the implementation of the hot test required approximately 50 g).

In order to investigate the extraction properties of nPr-BTP towards nitric acid and other metallic cations such as lanthanides(III) or palladium(II), also present in the feed, the following series of synthetic solutions were used as aqueous phases in batch experiments:
- Nitric acid solutions ($0.01 \leq$ [HNO$_3$]$_{initial} \leq 1$ mol/L), without or with palladium(II) at a concentration of 400 mg/L,
- Molar nitric acid solutions containing seven lanthanides (i.e.: La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III)), and some transition metals such as yttrium, palladium, iron and molybdenum, spiked with alpha and gamma emitters (i.e.: ^{59}Fe, ^{103}Ru, ^{152}Eu, ^{241}Am and ^{244}Cm at about 10 MBq/L each) to simulate DIAMEX stripping solutions,
- Molar nitric acid solutions containing americium(III) in nominal amounts ([^{241}Am] = 120 mg/L).

It appeared that 30%$_{vol}$ of n-octanol were at least necessary to prevent palladium complexes from precipitating at the liquid interface, but an increase of n-octanol content in TPH lowered the extraction performances of nPr-BTP. The mixture "TPH (70%$_{vol}$)/n-octanol (30%$_{vol}$)" was thus chosen for the hot test. In these conditions, the log-log variation of the distribution ratios (D$_{M(III)}$) of both ^{152}Eu(III) and ^{241}Am(III) with the initial concentration of nPr-BTP in the organic phase (ranging from 0.01 to 0.05 mol/L) followed a linear relationship with a slope value close to 3, in good agreement with the expected stoichiometry of the extracted complexes (2).The separation factor remained fairly constant (SF$_{Am/Eu}$ = D$_{Am}$/D$_{Eu}$ ~ 120) whatever the initial concentration of nPr-BTP in the organic phase. However, the concentration of nPr-BTP was set at 0.04 mol/L for the hot test, because:
- the solvent precipitated after several weeks when the initial concentration of nPr-BTP exceeded 0.05 mol/L,
- the distribution ratio of Am(III) was respectively high enough (D$_{Am}$ ~ 10, Fig. 2) in concentrated nitric acid solutions ([HNO$_3$] = 1 mol/L) and small enough (D$_{Am}$ < 0.5, Fig. 2) in diluted nitric acidic solutions ([HNO$_3$] < 0.06 mol/L) to allow a suitable process flowsheet to be elaborated. Higher D$_{Am}$ would indeed disfavour its stripping.

The study of the extraction of nitric acid and palladium(II) revealed that:
- a 1:1 complex was formed in the case of nitric acid,
- a 1:2 complex (i.e.: Pd(NO$_3$)$_2$L$_2$ with L = nPr-BTP) was formed when saturating the organic solution with palladium(II). Considered as a "soft" acid, palladium(II) was undoubtedly well extracted by nPr-BTP.

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[b] TPH : Hydrogenated Tetra Propylene, the industrial organic diluent used in the PUREX and DIAMEX processes
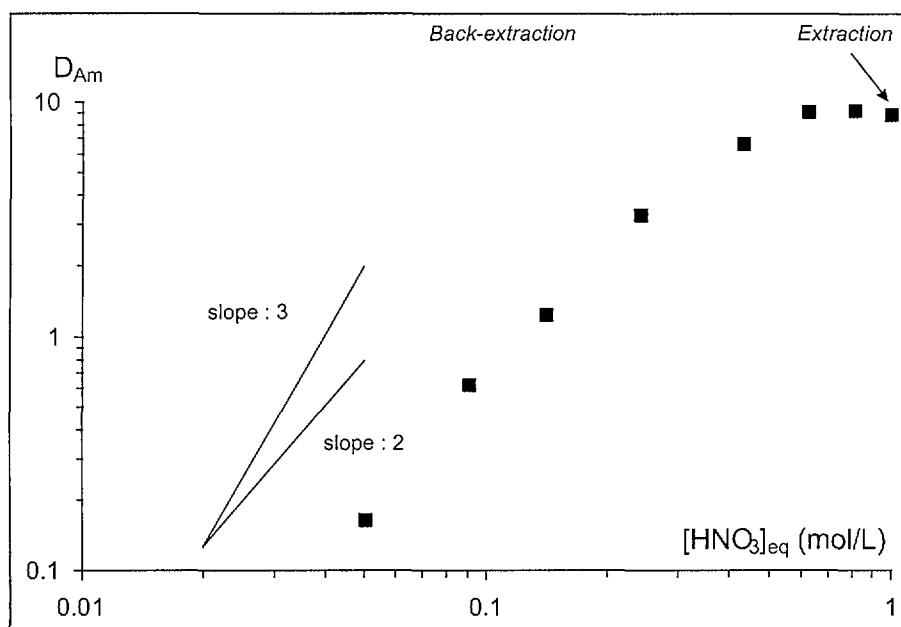
Aqueous extraction solution: synthetic solution simulating a DIAMEX stripping solution , $[Am^{241}]_{initial}$ = 120 mg/L
Organic extracting solution: $[nPr\text{-}BTP]_{initial}$ = 0.04 mol/L in TPH/ n-octanol ($70/30\%_{vol}$)
Aqueous back-extraction solution: diluted nitric acid - Temperature = (22 ± 0.5) °C

Fig. 2: Extraction and back-extraction of macro amounts of americium(III) by nPr-BTP

The extraction of ^{59}Fe(III), ^{103}Ru(III), ^{152}Eu(III), ^{241}Am(III) and ^{244}Cm(III) was determined by alpha and gamma spectrometric analyses, both in the presence and absence of palladium(II). As expected, macro amounts of Pd(II) in the aqueous feed solution ($[Pd]_{initial}$ = 400 mg/L) induced a decrease of the distribution ratios of all other elements.

Although iron(III) and ruthenium (RuNO(III)) seemed to be slowly extracted as compared to europium(III), americium(III) and curium(III), the affinity of nPr-BTP towards iron(III) was fairly high at equilibrium (which required more than one hour to be reached). Besides, curium(III) was always better extracted than americium(III).

All these acquired thermodynamic data were computed in order to elaborate and design the proper flowsheet to be applied during the hot test.

Feed-back of the hot test and future research program

Concerning the separation of An(III) from Ln(III), the performances of the hot test carried out in the Atalante facility in 1999 were very satisfactory ($1,400 < DF_{Ln(III)} < 450,000$), but the extraction and back-extraction yields of Am(III) and Cm(III) were lower than expected by calculation. This hot test actually pointed out that the SANEX-BTP solvent was sensitive to air oxidation and to a larger extend to acidic hydrolysis.

Under normal conditions (capped bottle, room temperature, absence of contacting aqueous phase), the extraction performances of the SANEX-BTP solvent (nPr-BTP in a mixture of TPH and n-octanol ($70/30\%_{vol}$)) steadily decrease over time. Indeed, the distribution ratio of Am(III) is divided by 6 after two months and by 13 after four months.

The degradation of the nPr-BTP is worse under acidic hydrolysis. The more acidic the aqueous solution, the faster the degradation of the molecule : the solvent degrades after a few days of contact with a molar nitric acid solution. However, its hydrolysis strongly depends on the nature of the organic diluent (Fig. 3). Thus, chlorinated and aromatic diluents limit the degradation of the nPr-BTP up to 30 days of contact with molar nitric acid solutions, although they do not completely prevent the molecule from degrading upon ageing.

Fig. 3: Influence of the nature of the organic diluent on the acidic hydrolysis of nPr-BTP
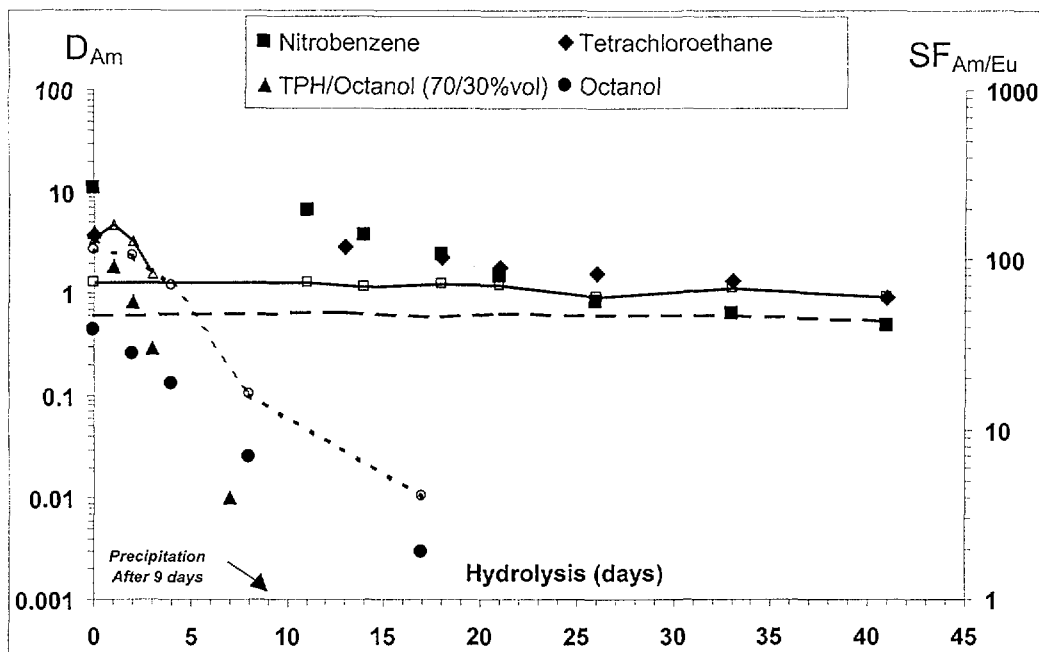
Hydrolysis conditions: $[nPr\text{-}BTP]_{initial} = 0.02$ mol/L vs $[HNO_3]_{initial} = 1$ mol/L - Temperature = (25 ± 0.5) °C
Extraction tests conditions (Temperature = (25 ± 0.5) °C):
Organic solution: Hydrolysed solutions of nPr-BTP in different organic diluents
Aqueous solution: $[HNO_3]_{initial} = 1$ mol/L, spiked with ^{152}Eu and ^{241}Am

Qualitative determination of the degradation compounds of nPr-BTP by means of Gas Phase Chromatography and/or Electro-spray Ionisation Mass Spectrometry allowed a better understanding of its degradation mechanism. Apparently, the nPr-BTP molecule mainly degrades into alcoholic derivatives through the oxidation of its propyle substituents (probably through radical reactions). Besides, the triazinyl rings may also break and open.

Thus, attempts should be made to strengthen the skeleton of the nPr-BTP molecule towards hydrolysis, by changing the nature of the alkyl groups substituting the triazinyl rings. However, our experience in the field of extraction behaviour of BTP molecules has shown that the more lipophilic the groups attached to the triazinyl rings of the BTP molecules (e.g.: groups with more than 3 carbon atoms), the slower their kinetics of extraction. Thus, a compromise will have to be found between the stability of the BTP molecule towards nitric acid hydrolysis and its kinetics of extraction, may be by optimising the mixture of organic diluents used to dissolve it: simultaneous use of radical scavengers and phase transfer catalysts.

CONCLUSION

The SANEX hot test carried out at CEA-Marcoule in 1999 with the 2,6-bis(5,6-n-propyl-1,2,4-triazin-3-yl)-pyridine pointed out the strong sensitivity of this extractant towards air oxidation and acidic hydrolysis. Further investigations will be devoted to the strengthening of the extractant towards hydrolysis and to a new formulation of SANEX-BTP solvent, which should be tested during year 2001 in the Atalante facility.

REFERENCES
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