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Partitioning and Transmutation

Annual Report 2003

S Andersson, C Ekberg, J-O Liljenzin, M Nilsson and
G Skarnemark
Nuclear Chemistry, Department of Materials and
Surface Chemistry, Chalmers University of Technology

February 2004

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Abstract

The long-lived elements in the spent nuclear fuels are mostly actinides, some fission products (^{129}I, ^{99}Tc, ^{135}Cs, ^{93}Zr and ^{126}Sn) and activation products (^{14}C and ^{36}Cl) [1]. To be able to destroy the long-lived elements in a transmutation process they must be separated from the rest of the spent nuclear fuel. The most difficult separations to obtain are the one between trivalent actinides and lanthanides, due to their relatively similar chemical properties, and the one between different actinides themselves. Solvent extraction is an efficient and well-known method that makes it possible to obtain separation factors that fulfil the highly set demands on purity of the separated phases and on small losses.

Chalmers University of Technology is involved in research regarding the separation of actinides and lanthanides and between the actinides themselves as a partner in the European Union project PARTNEW. This project was a part of the fifth framework programme and was concluded in September 2003, but the work is continued in the sixth framework programme under the acronym EUROPART (start January 2004). We mainly cooperate with the University of Reading, which send us new nitrogen containing ligands for evaluation of their extraction properties. The main focus is to understand the basic chemistry of these systems but also to study some process behaviour for future full-scale plants.

Sammanfattning

De långlivade ämnena i det använda kärnbränslet består till största delen av aktinider, en del fissionsprodukter (^{129}I, ^{99}Tc, ^{135}Cs, ^{93}Zr and ^{126}Sn) och aktiveringsprodukter (^{14}C and ^{36}Cl) [1]. För att kunna förstöra de långlivade ämnena i en transmutationsprocess måste de separeras från resten av det använda kärnbränslet. De svåraste separationerna att göra är dem mellan trevärda aktinider och lantanider, på grund av deras relativt liknande kemi, samt dem mellan aktiniderna själva. Extraktionskemi är en effektiv och välkänd metod som gör det möjligt att uppnå separationsfaktorer som uppfyller de högt ställda kraven på renhet i de separerade faserna och små förluster.

Chalmers tekniska högskola deltar i forskningen rörande separationen av aktinider och lantanider och mellan aktiniderna själva, genom att vara en partner i EU-projektet PARTNEW. Detta projekt var en del i EU:s femte ramprogram och avslutades i september 2003, men arbete fortsätter i det sjätte ramprogrammet under akronymen EUROPART (start januari 2004). Vi samarbetar huvudsakligen med universitetet i Reading som skickar nya kväveinnehållande ligander till oss för utvärdering av deras extraktionsegenskaper. Det huvudsakliga målet är att förstå den grundläggande kemin i dessa system men också att studera processtillämpningar för en framtida fullskaleanläggning.

Contents

1 Introduction

The Partitioning and Transmutation (P&T) project at the Department of Materials and Surface Chemistry, Chalmers University of Technology, investigates the separation of different chemical elements in the spent nuclear fuel for purification and/or recovery to a future transmutation process.

Solvent extraction is used already today in *e.g.* France and Japan in the reprocessing of spent nuclear fuel, *i.e.* the recirculation of uranium and plutonium back into the fuel cycle. This means that a lot of expertise on how to deal with highly active aqueous and organic solutions already exists. It is also a good technique to use considering its high efficiency of separation.

Internationally other processes, such as molten salt electrolysis and chromatographic methods, are also investigated.

The PARTNEW project was an international project funded by the European commission of EU. One goal is to design a solvent extraction process for the treatment of spent nuclear fuel with a future transmutation process taken into consideration. The research can be divided into three different areas:

- Co-extraction of actinides and lanthanides from acidic high active raffinate – DIAMEX process.
- Separation of actinides and lanthanides – SANEX process.
- Separation of Am and Cm.

The PARTNEW project was concluded in September 2003, but has continued in 2004 as EUROPART. The new project also involves the former European projects named PYROREP and CALIXPART.

The main laboratory work at Chalmers concerns the extractive properties and other basic chemical properties of the ligands synthesised in Reading, UK. The influence of pH, ionic strength and media, absorbed dose and concentration of the involved species are studied in combination with modelling of the systems using solubility parameters.

2 Research

During 2003 Sofie Andersson and Mikael Nilsson continued their work as PhD students. Mikael also presented his licentiate thesis in April, with the title *Studies of a Synergistic Extraction System for Minor Actinides and the Chemical Properties of 2-bromodecanoic Acid*, see Appendix I. The meetings within PARTNEW were located in Gothenburg (March 17–20) and Keswick (July 29 to August 1), England. Much effort has also been put into writing of the final report (which has not yet been published) for PARTNEW. Two French diploma workers, Hélène Sezgin and Sébastien Goeury, worked partly in the P&T group studying the temperature and relative concentration dependences on the extraction of Eu in a system with 2,2':6',2"-terpyridine and 2-bromodecanoic acid in *tert*-butyl benzene.

2.1 Chemical properties of semi-BTP

The chemical structure of semi (s-) BTP1 and s-BTP2 are shown in Figure 1. (BTP: 2,6-bis(1,2,4-triazin-3-yl) pyridine)

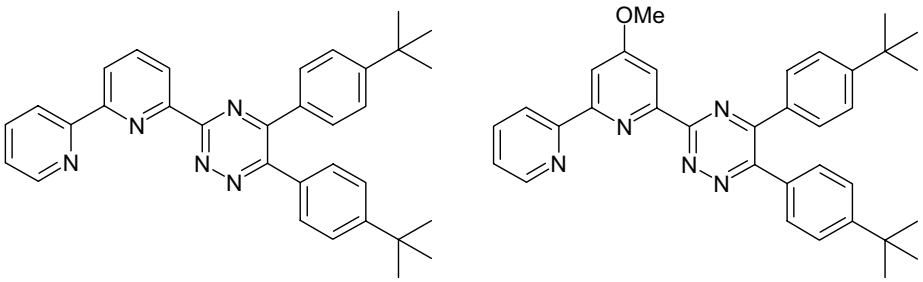

Figure 1. *sBTP1 (left) and sBTP2 (right).*

The extraction system studied has also included the two extracting agents, 2-bromodecanoic acid (HA) and the malondiamide DMDOHEMA (MA), see Figure 2. They have increased the distribution ratio of the metal ions and when using HA also acted as charge neutralizer. In the case of MA another anion from the aqueous phase (nitrate or perchlorate) has to neutralise the charge. These anions can also possibly affect the separation factor of the system.

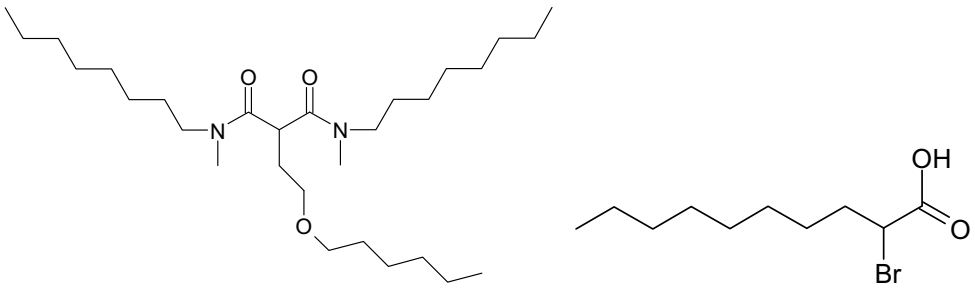

Figure 2. *MA (left) and HA (right).*

The different properties that have been studied are:

- UV-VIS spectra, see Section 2.1.1
- Protonation behaviour, see Section 2.1.2
- Kinetics, see Section 2.1.3
- Extraction behaviour (sBTP, HA, MA), see Section 2.1.4
- Resistance towards radiolysis, see Section 2.1.5
- Varying sBTP-concentration, see Section 2.1.6

2.1.1 UV-VIS spectra

The shape of the UV-VIS spectra of sBTP1, sBTP2 and *tert*-butyl benzene (TBB) can be found in Figure 3.

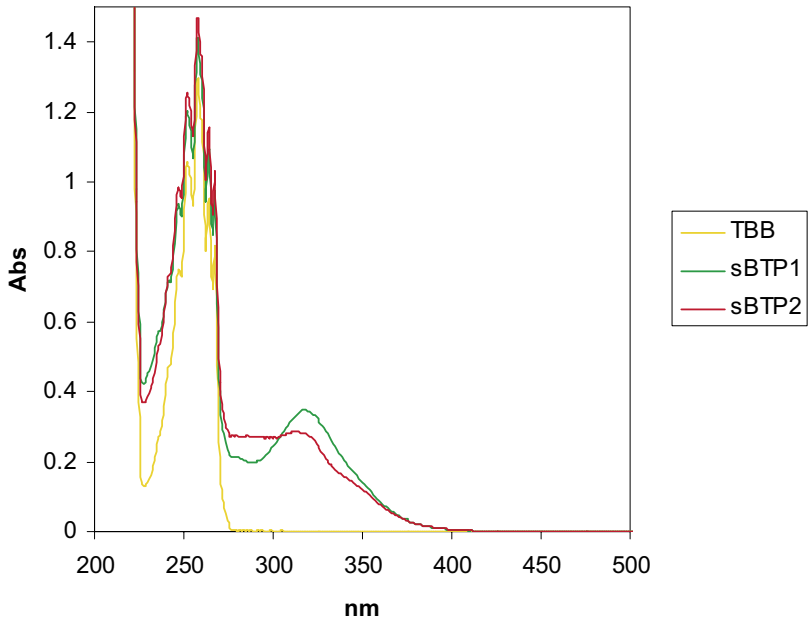

Figure 3. *UV-VIS spectra of sBTP1, sBTP2 in TBB and pure TBB.*

It is clear that the peaks >300 nm are free of influence from the *tert*-butyl benzene peak at 230–260 nm. Using this it is theoretically possible to determine the concentration of sBTP in aqueous and organic phases. The spectrophotometer used was a Perkin Elmer Lambda 19 UV/VIS/NIR. The sample was prepared by taking 10 µl of the organic phase (0.01 M sBPT dissolved in TBB) and then add 1 ml 1 M $HClO_4$ and 95% ethanol to a total volume of 10 ml.

2.1.2 Protonation behaviour

The protonation behaviour of the ligands was tested. The protonated species were assumed to be soluble in the aqueous phase and based on that assumption the distribution of the ligands as a function of the hydrogen ion concentration in the aqueous phase could be used to determine the protonation constants, as has been done previously with 2,2':6',2"-terpyridine [2].

0.5 ml organic phase (0.01 M sBTP dissolved in *tert*-butyl benzene) was contacted with 0.5 ml aqueous phase (1 M ionic strength, various hydrogen ion concentration, $(H,Na)NO_3$) in a 3.5 ml shaking vial. The contact time was 5 minutes and after that the phases were allowed to settle.

The samples prepared for the spectrophotometer were all made up similarly, regardless of whether they originated from the organic or aqueous phases. To a 10 ml volumetric flask 1 ml $HClO_4$ was added together with some 95% ethanol and then 10 µl of the sample from the shaking vial. The flasks were then filled up with ethanol to 10 ml. The reference in the spectrophotometric measurements was 1 ml $HClO_4$ and 9 ml 95% ethanol. Only single samples were made at this stage.

The hydrogen ion concentrations in the aqueous phases were determined by titrations, see Table 1. Also here single samples were made since the results from the spectrophotometric tests were known (see below) and the actual concentrations were not that important. The following hydrogen ion concentrations were used:

Table 1. Hydrogen ion concentrations.

Sample	$-\log[H^+]$	Comments
1	0.33	*1
2	0.81	*2
3	1.24	
4	1.81	
5	3.02	
6	3.51	

*1 Third phase formation, samples NOT evaluated spectrophotometrically, both ligands.

*2 some “unclearness” in the organic phase but the samples were measured on the spectrophotometer, both ligands.

The yellow colour of the organic phases was not changed by contact with the acidic aqueous phases (this indicates that no immediate transport of ligand between the phases took place, as far as one can detect with the naked eye). Both ligands had the same behaviour with third phase formation at the highest hydrogen ion concentration in the aqueous phase. The precipitation made the distinction between the organic and aqueous phases impossible and in the case of sBTP2 the shaking vial could be held up side down without the precipitate falling out from the vial.

Samples two to six were tested spectrophotometrically, but it was not possible to detect any sBTP in the aqueous phases in any of the samples. This indicates that less than detectable amounts of the ligands are transported into the aqueous phase at those hydrogen ion concentrations due to protonation, which is positive. At the highest hydrogen ion concentration the protonation occurs and the ligands are transported from the organic phase, but since their solubility in the aqueous phase is very low third phases are formed. The third phase for sBTP2 is more white and dense than the one formed with sBTP1.

In close relation with these experiments a two-phase titration with sBTP1 was done. 15 ml of 0.01 M sBTP1 in TBB was added to a titration cup together with 20 ml of 0.1 M nitric acid. The phases were contacted by magnetic stirring. pH was measured while sodium hydroxide (1 M + 0.1 M $NaNO_3$) was added. The results can be found in Figure 4.

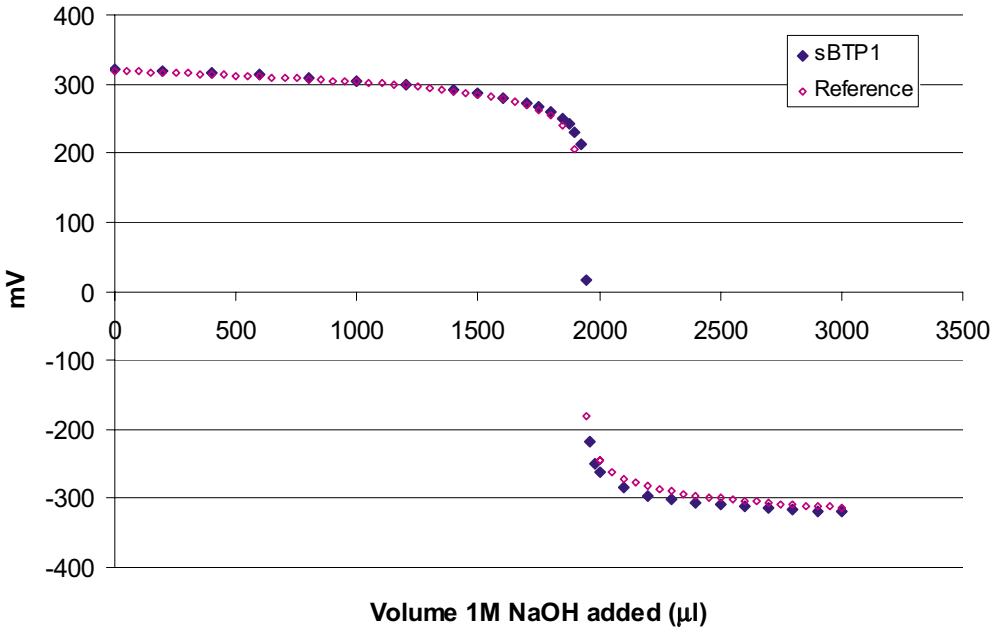

Figure 4. *Two phase titration with sBTP1 and a reference two phase titration with pure TBB.*

This graph shows that the presence of sBTP1 in the system does not affect the outcome of the titration in the used pH range, approximately above pH 1. This pH was chosen from the earlier tests showing that a precipitation forms at lower pH. The same curve is obtained doing a two-phase titration with 0.1 M nitric acid and pure TBB in the organic phase.

2.1.3 Kinetics

Tests investigating the kinetics of the extraction were done with sBTP2 and 2-bromodecanoic acid.

0.5 ml of 0.01 M sBTP2 with 0.5 M 2-bromodecanoic acid in TBB was contacted with 0.5 ml of an aqueous phase containing 1 M $NaNO_3$, 0.01 M H^+ and trace amounts of Am or Eu. The contact times were varied between 3 s and 24 h. For shaking times above 10 minutes a shaking device was used.

When using Eu all samples were centrifuged for 15 minutes after contact. When using Am only one of the samples was centrifuged for investigating the difference between samples centrifuged and samples allowed to settle with only the help of gravity.

A contact time longer than 5 minutes does not seem to be required to reach equilibrium for neither Am or Eu, see Figure 5. Further investigations are needed to give conclusive evidence for the extraction kinetics.

The goal of this investigation was to know what the minimum contact time could be and thereby reduce the time of the experiments to come.

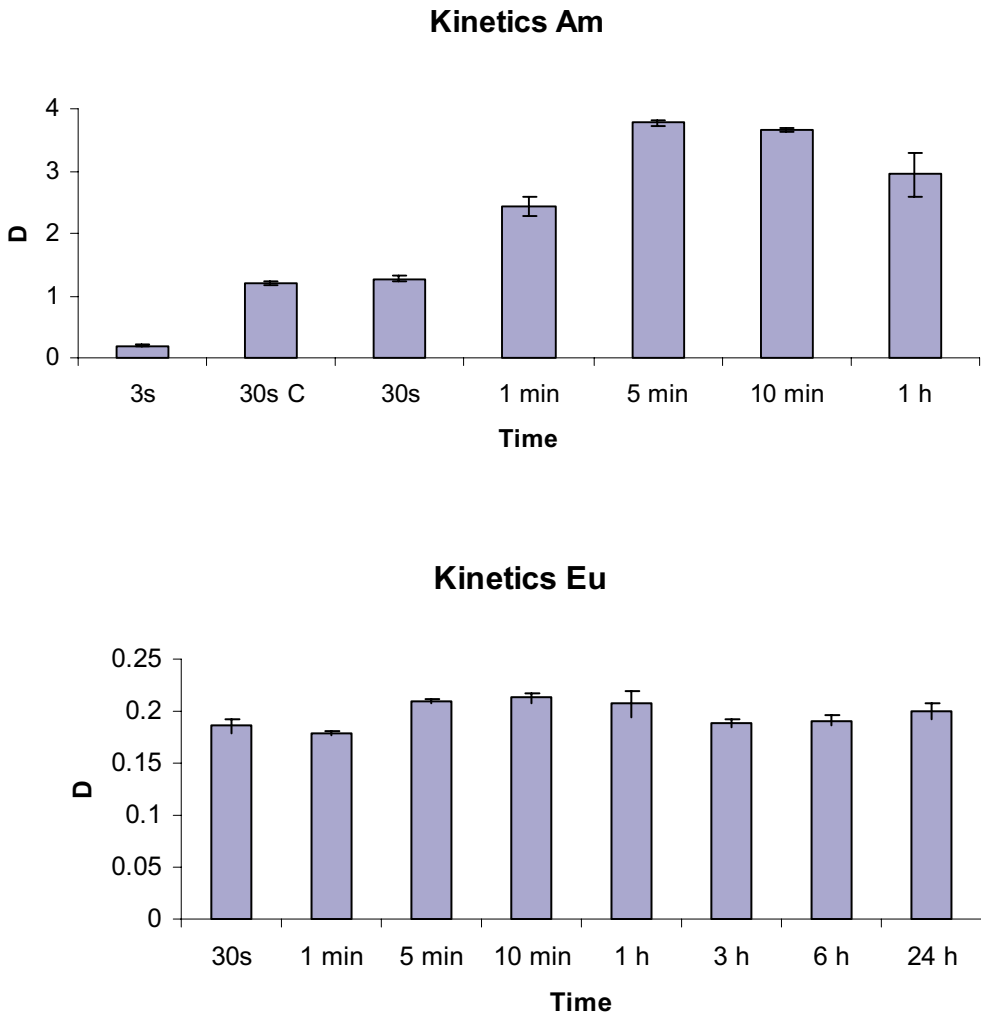

Figure 5. *Results from the kinetic tests. C in the top figure means that the sample has been centrifuged. This is the case for all samples in the lower figure.*

2.1.4 Extraction behaviour

Extraction experiments have been made. The aqueous phases have, if not stated otherwise, consisted of 0.01 M H^+ and a total ionic strength of 1 M (nitrate or perchlorate) and tracer amounts of Am(III), Cm(III) and Eu(III) in separate aqueous solutions. Triple test were standard procedure during these experiments. Only the mean value of these triple samples will be presented if not stated otherwise. There were some problems with precipitation, indicated in the results.

The distribution ratios from the extraction experiments with nitrate containing aqueous phase can be found in Table 2. The corresponding separation factors are shown in Table 3. The organic phase always consisted of 0.01 M s-BTP1 or s-BTP2 and 0.5 M extracting agent (MA or HA) in TBB. Experiments were also done with s-BTP1 and s-BTP2 alone (without any extracting agent) but the results were very low distribution ratios (not included in the tables below). The corresponding tests with perchlorate were only made with s-BTP1 and the results are given in Table 4 and Table 5.

Table 2. Distributions ratios from extraction experiments with nitrate.

Organic phase	D (Am)	D (Eu)	D (Cm)
s-BTP1 + HA	1.61±0.098	0.15±0.002	1.06±0.061
s-BTP1 + MA	0.0069±0.0001	0.0033±0.00005	0.0038±0.0001
s-BTP2 + HA	2.94±0.36	0.21±0.01	2.00±0.37
s-BTP2 + MA	0.0072±0.0001	0.0030±0.00002	0.0041±0.0001

Table 3. Separation factors from extraction experiments with nitrate.

Organic phase	SF (Am/Eu)	SF (Am/Cm)	SF (Cm/Eu)
s-BTP1 + HA	10.5±0.64	1.53±0.13	6.84±0.40
s-BTP1 + MA	2.12±0.04	1.83±0.07	1.16±0.04
s-BTP2 + HA	14.2±1.93	1.47±0.34	9.64±1.99
s-BTP2 + MA	2.35±0.03	1.76±0.02	1.33±0.02

Table 4. Distributions ratios from extraction experiments with perchlorate.

Organic phase	D (Am)	D (Eu)	D (Cm)
s-BTP1 + HA	5.07±0.25	0.49±0.006	4.55±0.29
s-BTP1 + MA	692±62	270±17	202±6.2
s-BTP1 + HA + MA	60.9±1.2	13.9±0.31	33.3±2.2
MA	188±15	178±4.4	77±1.5

Table 5. Separation factors from extraction experiments with perchlorate.

Organic phase	SF (Am/Eu)	SF (Am/Cm)	SF (Cm/Eu)
s-BTP1 + HA	10.4±0.53	1.12±0.09	9.35±0.60
s-BTP1 + MA	2.56±0.28	3.41±0.32	0.75±0.05
s-BTP1 + HA + MA	4.37±0.13	1.84±0.13	2.39±0.17
MA	1.05±0.09	2.45±0.20	0.43±0.01

The uncertainties in the distribution ratios are the standard deviations of the triple samples. The uncertainties in the separation factors have been calculated using (1).

$$\sigma_{SF(A/B)} = SF\sqrt{\left(\frac{\sigma_{DA}}{D_A}\right)^2 + \left(\frac{\sigma_{DB}}{D_B}\right)^2} \qquad (1)$$

There is a big difference in distribution ratios between the perchlorate and nitrate systems when MA is used as extracting agent, indicating that the anion (used to neutralize the charge of the metal ions) is important. The separation factor between actinides and lanthanides is higher when using HA than MA, which is opposite the behaviour of separation factors between the actinides themselves. When using 0.01 M s-BTP1 in combination with 0.5 M MA, the separation factor between Am and Cm is 3.41±0.32.

Finally a set of extraction experiments investigating the influence of the molar ratio of the s-BTP1 and MA on the extraction was done. The results from these experiments are shown in Figure 6. There were some problems with precipitation, especially at the lower molar ratios of MA to s-BTP1.

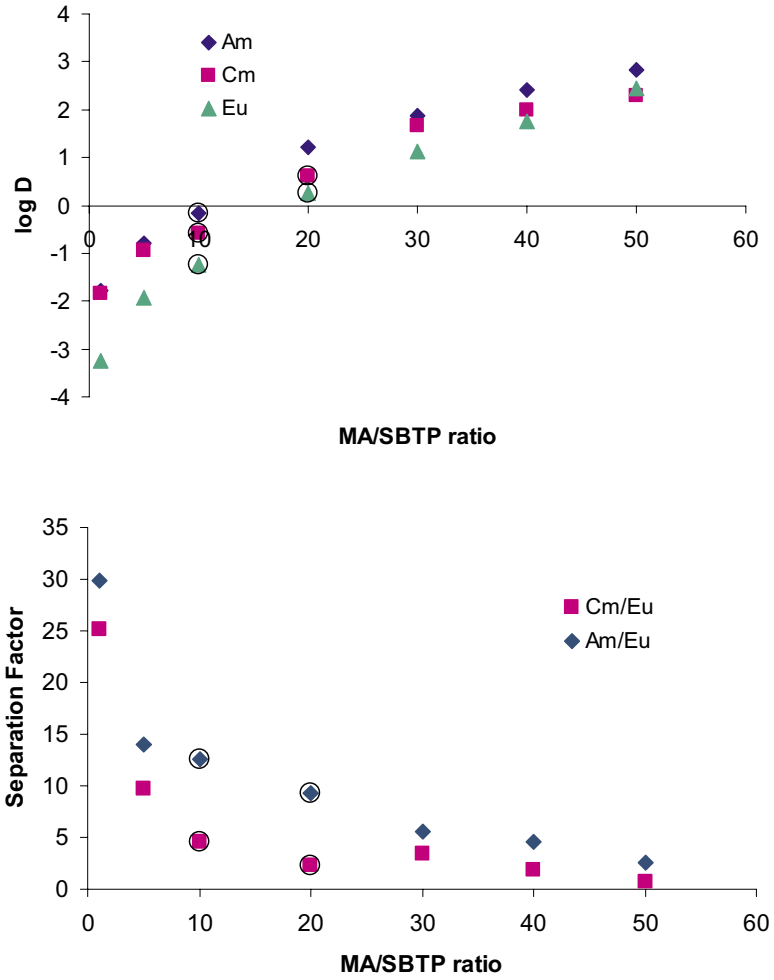

Figure 6. *Distribution ratios of Am, Cm and Eu (to the left) and separation factors of Am/Eu and Cm/Eu (to the right) at different molar ratios of MA and s-BTP1. The points with circles around are when precipitation occurred.*

The results show an increase in extraction for all tested elements when the molar ratio between MA and s-BTP1 increased. The results also clearly indicate a decrease in the separation of actinides and lanthanides when increasing the concentration of MA. The separation between Am and Cm on the other hand is increased when the concentration of MA is high.

2.1.5 Resistance towards radiolysis

Organic phases with 0.01 M sBTP in TBB were prepared. Half of them were taken away to be used as references and the rest was irradiated in a Co-60 gamma source. The approximate exposition rate to air was 70.4 R/min and the total irradiation time was 262 h for sBTP1 and 256 h for sBTP2. This corresponds to an absorbed dose of ~9.7 kGy for sBTP1 and 9.5 kGy for sBTP2.

After radiation 2-bromodecanoic acid was added to a total concentration of 0.5 M. Extraction experiments were performed to see if there was any change in distribution ratio due to the irradiation. As aqueous phase 1 M $NaClO_4$, 0.01M H^+ and trace amount of Am was used. No significant change in distribution ratios was found.

Pure TBB was also irradiated, but no indication of any degradation was found. Spectrophotometric measurements were also performed before and after irradiation with the same results. The sBTP:s seem to be resistant towards irradiation up to at least ~10 kGy.

2.1.6 Varying s-BTP concentration

Extraction experiments were done with varying concentration of sBTP in the organic phase. The concentrations tested were 0.005 M, 0.025 M, 0.050 M, 0.075 M and 0.1 M. The concentration of HA was kept constant at 0.5 M and the diluent was TBB. The aqueous phase consisted of 1 M $NaNO_3$, 0.01 M H^+. The results are shown in Figure 7, Figure 8 and Figure 9

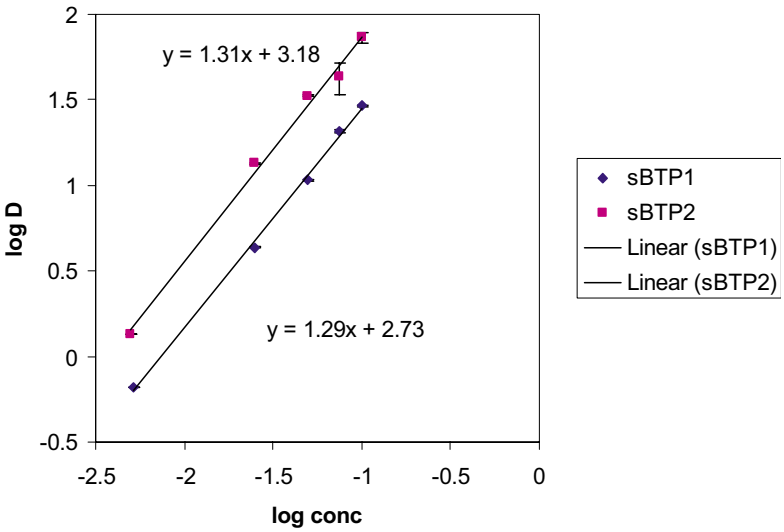

Figure 7. *Concentration dependence for Am.*

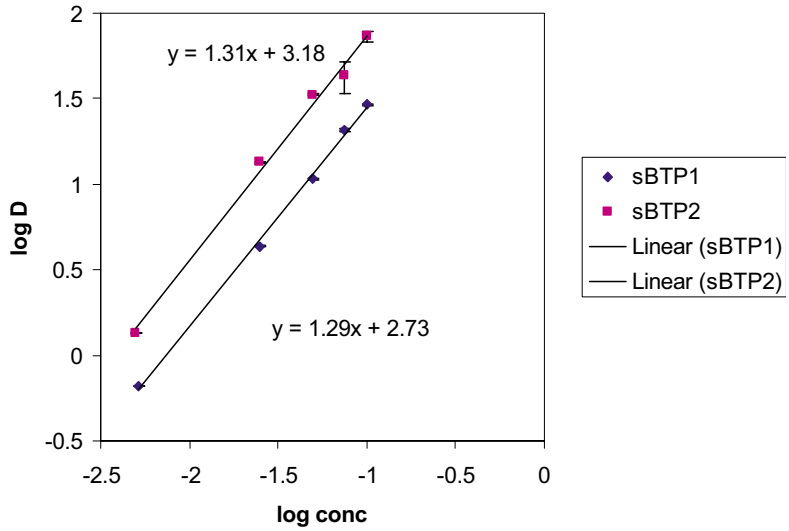

Figure 8. *Concentration dependence for Eu.*

The regression lines for Am and Cm seem to have the same slope (same concentration dependence). The corresponding line for Eu has a slightly lower slope. This could indicate that the complex with the lanthanide involves one sBTP per extracted complex. In the case of Am and Cm there is more than one sBTP molecule involved, but it is impossible to say what the complex looks like from this investigation.

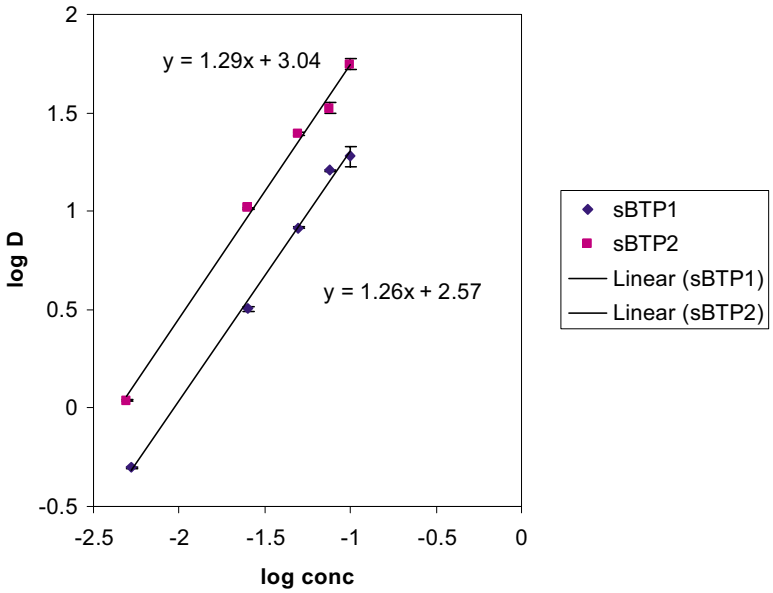

Figure 9. *Concentration dependence for Cm.*

2.2 Nitrate complex formation with various actinides and lanthanides

The nitrate complex formation with La, Pr, Nd, Pm, Sm, Eu, Gd, Dy, Ho, Er, Lu, Am and Cm has been studied using a solvent extraction system consisting of 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine (BODO), see Figure 10, in TBB and an aqueous phase of varying composition (0.01 M hydrogen ions, 5 M constant ionic strength of sodium nitrate and sodium perchlorate).

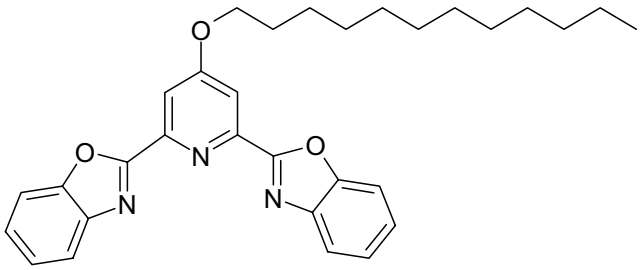

Figure 10. *2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine (BODO).*

The distribution ratio of the metal ion can be described using (2). Here it is assumed that the distribution ratio of the metal-nitrate complex is very low.

$$D_M = \frac{D_0}{1 + \sum_i \beta_i^* [NO_3^-]^i} \qquad (2)$$

where D_0 is the metal distribution in the absence of nitrate ions and is assumed to be constant in the system studied and the modified stability constants equal (3):

$$\beta_i^* = \frac{\left[M(NO_3)_i^{3-i}\right]}{\left[M^{3+}\right]\left[NO_3^-\right]^i} \qquad (3)$$

These equations give a means to relate the theoretical and experimental data and to calculate the stability constants of the nitrate complex formation.

2.2.1 Experimental

The organic phase consisted of 0.01 M BODO, 1 M HA in TBB. BODO was synthesized in Reading, England, and its purity (>99%) was tested with H-NMR. The ionic strength of the aqueous phase was kept constant at 5 M using nitrate and perchlorate ions. The hydrogen ion concentration, which affects the extraction properties of the system significantly, was 0.01 M throughout all experiments. Trace amounts of the metals ions, Pm^{3+}, Eu^{3+}, Am^{3+} and Cm^{3+} were used ensuring negligible effect on the composition of the organic phase.

0.5 ml of each phase was contacted through vigorous shaking in a 3.5 ml glass vial for 5 minutes. The phase separation was facilitated using a centrifugation at $2x10^4$ m/s^2 (which is ~2000 g) for 15 minutes. 100 µl of each phase was taken out and measured with an Intertechnique model CG-4000 NaI(Tl)-scintillation well detector with automatic sample changing.

After the first four elements had been analysed another nine lanthanides were investigated (La, Pr, Nd, Sm, Gd, Dy, Ho, Er and Lu). The same experimental procedure (described below) was used. The radioactive isotopes were produces in the TRIGA Mainz research reactor.

2.2.2 Results and discussion

The logarithms of the experimental distribution ratios for some of the studied elements are shown in Figure 11.

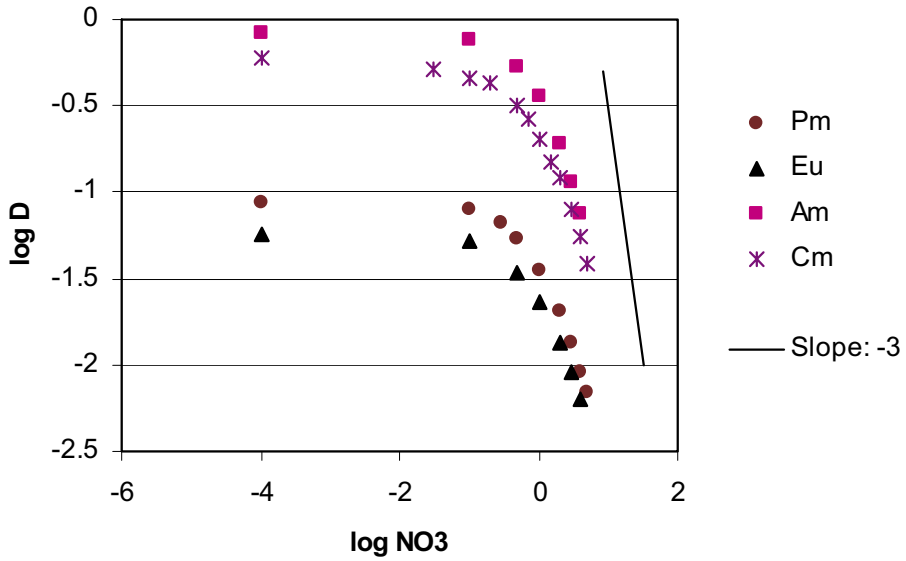

Figure 11. *Experimental distribution ratios for Pm3+, Eu3+, Am3+ and Cm3+ as a function of nitrate ion concentration (298K, 5M constant ionic strength (nitrate and perchlorate ions)).*

In Table 6 the determined stability constants are given. In the case of Am and Eu they are in good agreement with earlier published results. It was more problematic to find reliable data for Pm and Cm.

Table 6. Stability constants found in this work.

	D_0	β_1	β_2	β_3	Ionic radius (Å)
Pm	0.09±0.001	1.20±0.05	0.24±0.01	-	0.979
Eu	0.06±0.0004	1.33±0.05	0.13±0.04	-	0.950
Am	0.84±0.004	1.02±0.03	0.29±0.03	0.02±0.006	0.982
Cm	0.56±0.008	1.42±0.06	0.22±0.02	-	0.970

The higher D_0 for the actinides can be explained by the system conditions themselves. Nitrogen coordinating ligands form stronger complexes with actinides than lanthanides due to the 4f and 5f electron interactions. The nature of the complex between metal and the oxygens in the nitrate ions will although be mainly electrostatic. This can be explained by the fact that both the oxygens and the metal ions can be considered to be hard acids.

The comparison between the stability constants must be made within the two groups. The stability constants for the first complex formed is increased with decreasing ionic radius. A metal ion with higher surface charge (smaller ionic radius) will form a stronger complex with the nitrate ion. When it comes to the second stability constant the order is reversed, something that possibly can be explained by the smaller size of Cm and Eu, thereby increasing the influence of steric hindrance. This is a possible explanation since the differences in sizes are fairly small. The differences in stability constants are significant, even considering the uncertainties, see Table 6.

In Figure 12 the experimental and calculated separation factors between Am and Eu, Pm and Cm are shown as a function of nitrate ion concentration. In the case of Am/Eu, the separation factor first increases when the nitrate ion concentrations is increased. At higher nitrate ion concentrations the separation factor decreases due to the different strength of the complexes between the metal and the nitrate ions. The second nitrate complex with Am is stronger than corresponding one with Eu. At higher nitrate ion concentration the influence of these complexes is significant and thus gives a decrease in separation factor as Am is hold stronger in the aqueous phase. The same explanation can describe the increase in separation factor at lower nitrate ion concentration, where the first Eu complex with nitrate is stronger than corresponding one with Am. The same results are found for Pm, although the effect is not as pronounced as in the case with Eu.

At higher ionic strength the influence of the polynitrate metal complexes on the extraction is increased and the higher uncertainties in the stability constants give large uncertainties in the calculated distribution ratios and thereby also separation factors. Here the third stability constant for Am has been included.

Once the stability constants of the nitrate complexes are known, it is possible to calculate the concentration of the different species formed. In Figure 13 the speciation of nitrate complexes with Am are shown, assuming no correlation between the calculated stability constants. This assumption is a simplification

The results for the rest of the lanthanides are not yet finished but will be presented in the next annual report.

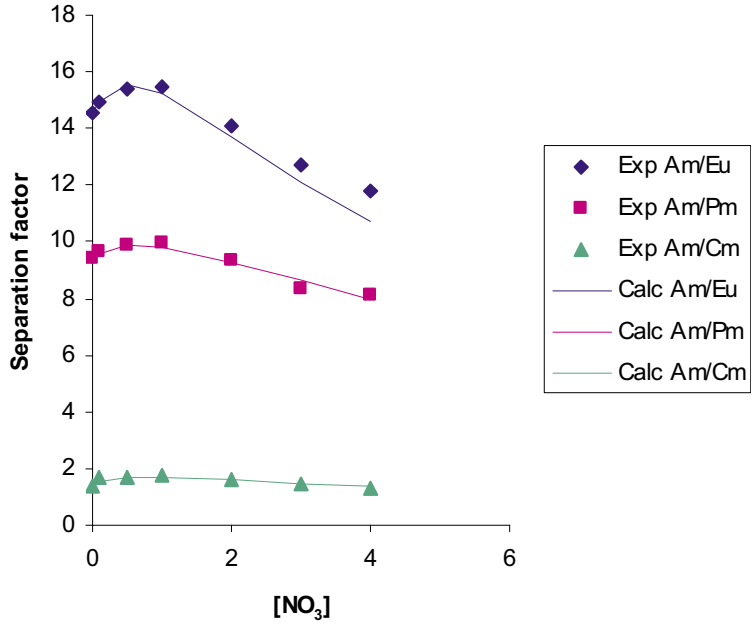

Figure 12. *Experimental and calculated separation factors as a function of nitrate ion concentration.*

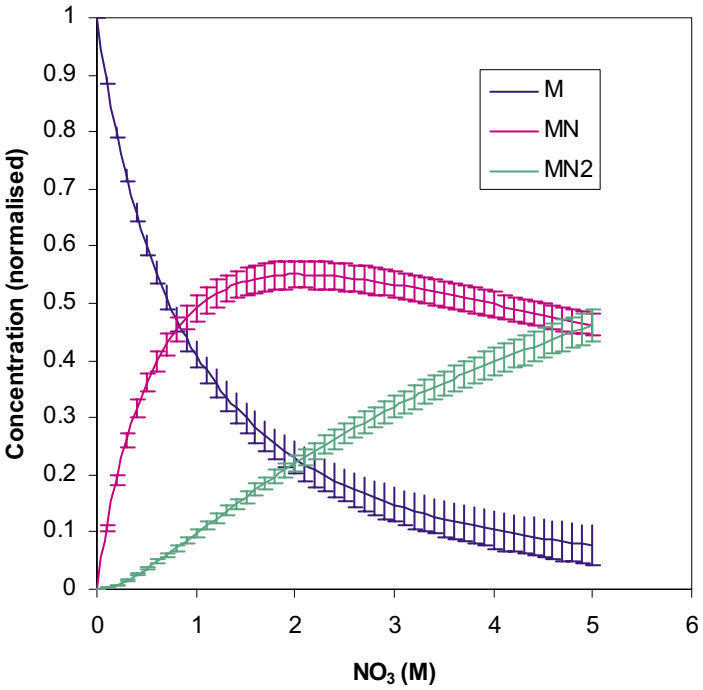

Figure 13. *Different relative concentrations of Pm/nitrate species.*

2.3 Chemical behaviour of 2-bromodecanoic acid (HA)

In order to understand and model a liquid-liquid extraction system several input data are needed. Among these are the chemical properties of the extracting agent. If an acidic extraction agent with lipophilic character is used the acid formation constant, k_a, and the distribution constant between the two phases, k_d, are particularly important. For this reason the equilibrium constants for 2-bromodecanoic acid were investigated using a combination of several different analysis methods described below.

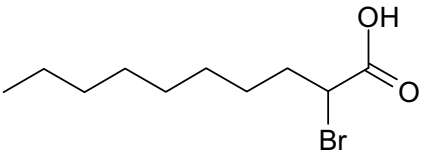

Figure 14. *2-bromodecanoic acid (HA).*

2.3.1 IR measurements

HA, see Figure 14, was dissolved in *tert*-butyl benzene (TBB), to a number of different concentrations. A sample from each solution was taken for measurements on an IR-spectrometer, Bruker 66v/S connected to a computer. Pure TBB was used as reference for these measurements. All experiments were performed at ambient temperature.

2.3.2 Activation analysis

120 ml of organic solution consisting of 0.1 M HA in TBB was contacted with 120 ml aqueous solution consisting of 0.1 M HNO_3 in an AKUFVE. pH was measured continuously. 1 M LiOH with 0.1 M $LiNO_3$ was added to the system in small controlled amounts. When the pH electrode was stable, samples of 2 ml were taken from both phases for activation analysis. 150 µl of organic phase and 1 ml of aqueous phase were introduced into Mainz TRIGA reactor. The biggest amount of HA was suspected to be in the organic phase. Therefore the organic phase was irradiated for 10 minutes and the aqueous phase for 60 minutes. After the samples were taken out they were left to cool for around 20 h, so that any short lived nuclides would have decayed, and then the amount of Br in the samples was measured using a HPGe-detector for 30 minutes.

2.3.3 Potentiometric two-phase titrations

A number of potentiometric two-phase titration was carried out with 3 different volume ratios, Θ, for the initial aqueous and organic phases. The different initial volume ratios used were 0.75, 1 and 1.5.

20 ml of aqueous phase consisting of 0.1 M HNO_3 was added to a titration vessel. After that the organic phase, consisting of 0.002 mol of HA dissolved in TBB to a volume corresponding to the desired initial volume ratio, was added.

1 M NaOH with 0.1 M $NaNO_3$ was added in controlled amounts. After every addition the pH was given time to stabilise before a new addition was made. A two-phase titration using a similar aqueous phases but an organic phase of pure TBB was performed to get a reference.

2.3.4 Results from the HA studies

Spectra were obtained from the IR-measurements on 2-bromodecanoic acid dissolved in TBB. A part of one of the IR-spectra is showed in Figure 15.

The carbonyl peak is very distinct for a carboxylic acid. A closer look of this peak indicated a second broader peak at higher wave number, close to the dominating peak, see Figure 16.

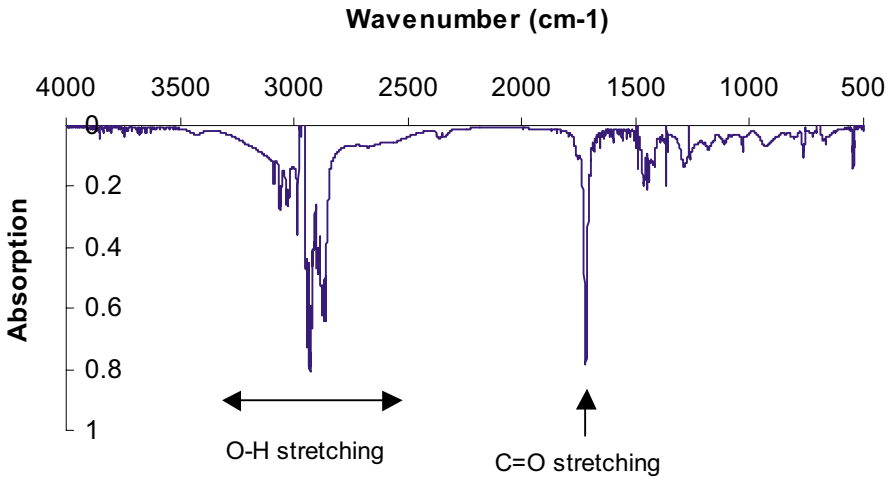

Figure 15. *A sample of an IR-spectrum from a measurement using 0.1M 2-bromodecanoic acid in TBB. Some interesting peaks for carboxylic acids are indicated.*

The smaller peak at higher wave number was assigned to C=O stretching of the monomeric form of 2-bromodecanoic acid and the large peak at lower wave number was assigned to the dimeric form of the same stretching.

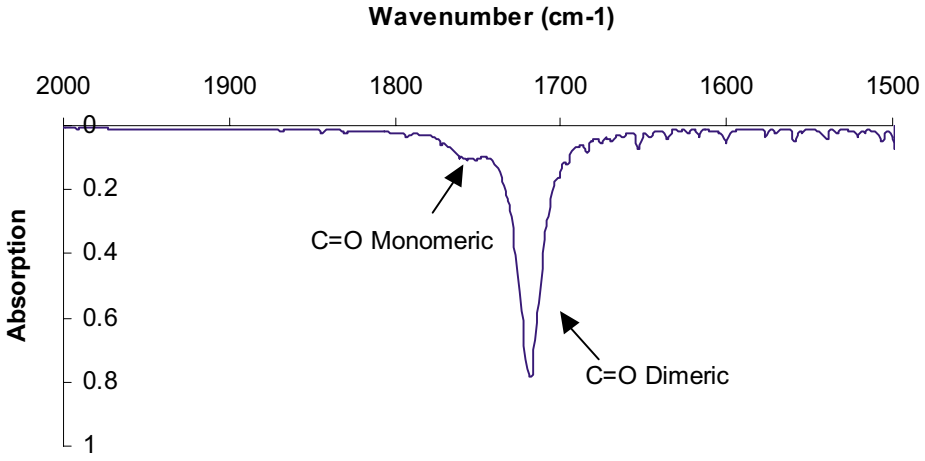

Figure 16. *A closer look of the 0.1 M spectrum displaying two separate carbonyl stretchings, indicated in the graph.*

To find the absorption of the individual peaks, two Lorenzian distributed peaks, one for the dimer and the other for the monomer, were fitted to the spectrum for each total concentration of acid. The respective absorbances, A, calculated from the Lorenzian function, for each peak along with the corresponding total concentrations are displayed in Table 7.

Table 7. Absorption at different acid concentrations.

Total concentration of HA in the organic phase, C^0 (M)	Absorption of the monomer peak, A_M	Absorption of the dimer peak, A_D
0.025	0.0287	0.1635
0.05	0.0419	0.3561
0.1	0.0771	0.7877
0.5	0.1550	4.096
1.0	0.2578	8.3724

By using Beer-Lamberts law the resulting molar absorptivity coefficients, ε, were found to be: ε_M = 434 (+21.8, –12.2) ($M^{-1}cm^{-1}$) and ε_D = 1405 (+6.3, –6.2) ($M^{-1}cm^{-1}$).

The individual concentrations and the dimerisation constant for the molar scale k_2 were calculated according to:

$$k_2 = \frac{\left[\overline{(HA)_2}\right]}{\left[\overline{HA}\right]^2} \qquad (4)$$

From the activation analysis, the bromine concentration and hence the HA concentration in each sample was determined. From this, distribution ratios of HA were calculated.

When pH is low, all HA present in the aqueous phase is assumed to be in the undissociated form. From the distribution ratios at the lowest pH and the dimerisation constant, it is therefore possible to calculate the distribution constant expressed in concentrations, k_D, see Table 8.

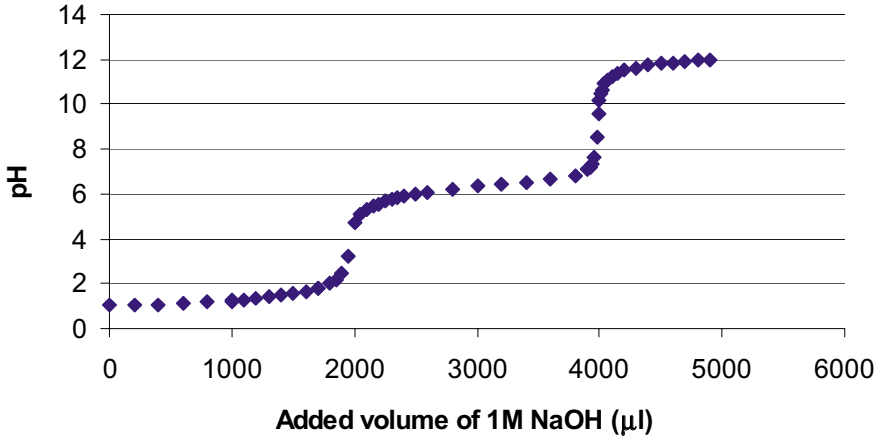

Figure 17. *The titration curve from a potentiometric two phase titration using an initial volume ratio of 1. This figure gives an example of when the stripping of HA takes place.*

Figure 17 shows that the amount of NaOH added during the central near-horizontal portion of the titration curve is the same molar amount as the total HA in the system. This means that during this part of the two-phase titration the HA is dissociated.

At the centre of the horizontal part of the curve in Figure 17, the mass balance can be expressed as:

$$\frac{n_{HA,0}}{2} = n_{A^-} = 2 \cdot n_{\overline{(HA)_2}} + n_{\overline{HA}} + n_{HA} \qquad (5)$$

Since half of the total amount of HA will be deprotonated and the other half will consist of a mix of the three other possible species. Expressing this in concentrations will result in:

$$\frac{n_{HA,0}}{2 \cdot V_{aq}} = \left[A^-\right] = 2 \cdot \left[\overline{(HA)_2}\right] \cdot \Theta^{-1} + \left[\overline{HA}\right] \cdot \Theta^{-1} + [HA] \qquad (6)$$

By expressing the concentrations of the three undissociated species in (6) in molar equilibrium constants and $[H^+]$ the last unknown equilibrium constant, k_a, can be calculated if $[H^+]$ is calculated from (7), [3].

$$-\log\left[H^+\right] = pH - 0.09 \qquad (7)$$

(7) holds for 0.1 M perchlorate media at 25ºC, in this work it is assumed that (7) also holds for 0.1 M nitrate media at 25ºC. The value of pk_a is found in Table 8.

Table 8. Molar equilibrium constants for HA.

Dimerisation constant, k_2	278 ± 60
Distribution constant, k_d	799 ± 105
Acid dissociation constant, pk_a	2.68 ± 0.09, –0.07

2.4 Improved apparatus for automated vapour pressure measurements

The apparatus developed earlier [4], [5] is being fitted with additional instruments for easier handling and evaluation. This involves a valve for quick and easy switching of samples and two HPLC pumps for transporting liquids into the systems.

2.5 Experiments with a synthetic waste solution

A synthetic high level waste (HLW) solution was prepared according to [6], see Table 9. This 6 M HNO_3 solution was used to prepare solutions with 1, 2, 3, 4 and 5 M HNO_3 concentration by addition of Milli-Q water. Thus, in the diluted solution the metal ion concentrations were lower than in the original one, but the ratios between the metals were the same. The dilution should not affect the distribution ratios, since the organic phase was far from being significantly loaded. Even if all metals were quantitatively extracted from the most concentrated solution, the 1 M DMDOHEMA would only be loaded to about 9%. In reality the maximum loading was approximately 5%.

Fe, Cr and Ni are difficult to determine by ICP-MS. Therefore ^{59}Fe, ^{51}Cr and ^{63}Ni tracers were added in the same chemical form as the macro amounts of these elements. In addition, trace amounts of ^{239}Np, ^{238}Pu or ^{241}Am were added to some samples to gain additional information about actinide extraction. These elements were added as Np(V), Pu(IV) and Am(III).

The concentrated HLW solution is stable for a few days. Then a small amount of black precipitation is formed. Most of this precipitation can be redissolved by heating. The diluted solutions are stable for at least 4 months.

The organic phase was prepared by dissolution of DMDOHEMA in TPH.

Four series of extraction experiments were performed:

M1. HLW solutions (1,2,3,4,5,6 M HNO3)
M2. HLW solutions (1,2,3,4,5,6 M HNO3) + 59Fe, 51Cr, 241Am
M3. HLW solutions (1,2,3,4,5,6 M HNO3) + 63Ni, 239Np
M4. HLW solutions (1,2,3,4,5,6 M HNO3) + 238Pu

In series M1 1.0 ml of the aqueous phases were shaken with 1.0 ml of the organic phases in 3.5 ml glass test tubes. In series M2–M4 these volumes were reduced to 0.4 ml not to waste the limited amount of extractant. The contact time was 1 h in all experiments. All extractions were performed in triplicate. After extraction, the phases were separated by centrifugation for 15 min at 2000 g. No precipitations or third phase formations were observed for 1–5 M HNO_3, while for 6 M HNO_3 there was a weak indication of haze at the liquid-liquid interface.

Table 9. Composition of the HLW solution.

Element	Conc. (mM)	Added chemical	Dissolved in
Se	0.086	SeO_2	6 M HNO_3
Rb	1.46	$RbNO_3$	6 M HNO_3
Sr	2.98	$Sr(NO_3)_2$	6 M HNO_3
Y	1.86	$Y(NO_3)_3 \cdot 2H_2O$	6 M HNO_3
Zr	14.1	$ZrO(NO_3)_2 \cdot 2H_2O$	6 M HNO_3
Mo	12.3	$(NH4)_6Mo_7O_{11} \cdot 4H_2O$	Milli-Q water
Ru	7.16	$RuCl_3$*	6 M HNO_3
Rh	1.41	$RhCl_3$*	6 M HNO_3
Pd	4.15	$Pd(NO_3)_2 \cdot 2H_2O$	6 M HNO_3
Ag	0.20	$AgNO_3$	6 M HNO_3
Cd	0.21	$Cd(NO_3)_2 \cdot 4H_2O$	6 M HNO_3
In	0.005	In_2O_3	conc. HNO3
Sn	0.066	Sn	conc. HNO3
Sb	0.026	Sb_2O_3	6 M HNO_3
Te	0.31	Te	8 M HNO_3
Cs	6.07	$CsNO_3$	6 M HNO_3 (hot)
Ba	4.43	$Ba(NO_3)_2$	Milli-Q water
La	3.10	$La(NO_3)_3 \cdot 6H_2O$	6 M HNO_3
Ce	5.94	$Ce(NO_3)3 \cdot 6H_2O$	conc. HNO_3
Pr	2.94	Pr_6O_{11}	conc. HNO_3
Nd	9.74	$Nd(NO_3)_3 \cdot 6H_2O$	6 M HNO_3
Sm	1.79	Sm_2O_3	conc. HNO_3
Eu	0.28	Eu_2O_3	6 M HNO_3
Gd	0.25	Gd_2O_3	conc. HNO_3
Tb	0.005	Tb_2O_3	6 M HNO_3
U	1.01	$UO_2(NO_3)_2 \cdot 6H_2O$	6 M HNO_3
Fe	3.07	$Fe(NO_3)_3 \cdot 6H_2O$	6 M HNO_3
Cr	0.66	$Cr(NO_3)_3 \cdot 9H_2O$	6 M HNO_3
Ni	0.58	$Ni(NO_3)_2 \cdot 6H_2O$	6 M HNO_3
PO_4	0.21	H_3PO_4	Milli-Q water
H	$6 \cdot 10^3$	HNO_3	

After phase separation 100 µl aliquots were taken and analyzed in the following way:

M1: Since the ICP-MS instrument (a Perkin-Elmer Elan 6000) is less suited for measurements of organic phases, the distribution ratios were determined by comparison of the metal concentrations in the aqueous phases before and after extraction. A prerequisite for this method is the assumption that no sorption occurs on the walls of the test tubes and also that no significant amounts of material stay at the liquid-liquid interface. There are strong reasons to believe that these assumptions are realistic in this case, *i.e.* strong acid solutions containing macro amounts of the metals. These assumptions are valid also for the series M2–M4.

The 31 solutes present in the samples make them a very complicated matrix. In order to study possible interferences between mass numbers another 31 samples were prepared. These samples contain either 6 M or 1 M HNO_3 and each sample lacks one solute. In this way it is possible to see interferences at the mass of the missing solute.

The results show that Zr, Mo, U and the lanthanide elements can be extracted with high separation factors. The extraction from 1 M HNO_3 is rather low while the distribution ratios are in the range 10–100 when using 6 M HNO_3 as the aqueous phase. The other elements in the HLW solution are not extracted to any significant amount (distribution ratios < 0.01).

M2: ^{59}Fe, ^{51}Cr and ^{241}Am were all determined by γ-spectrometry using HPGe detectors. Both the aqueous and the organic phases were measured.

M3: ^{239}Np was measured by γ-spectrometry using a NaI(Tl) detector. Both phases were measured. Thereafter ^{239}Np ($t_{½}$ = 2.355 d) was allowed to decay, and the pure β-emitter ^{63}Ni was determined by liquid scintillation counting.

M4: ^{238}Pu was determined by liquid scintillation counting. No severe quenching was observed in these measurements.

The results are shown in Figure 18.

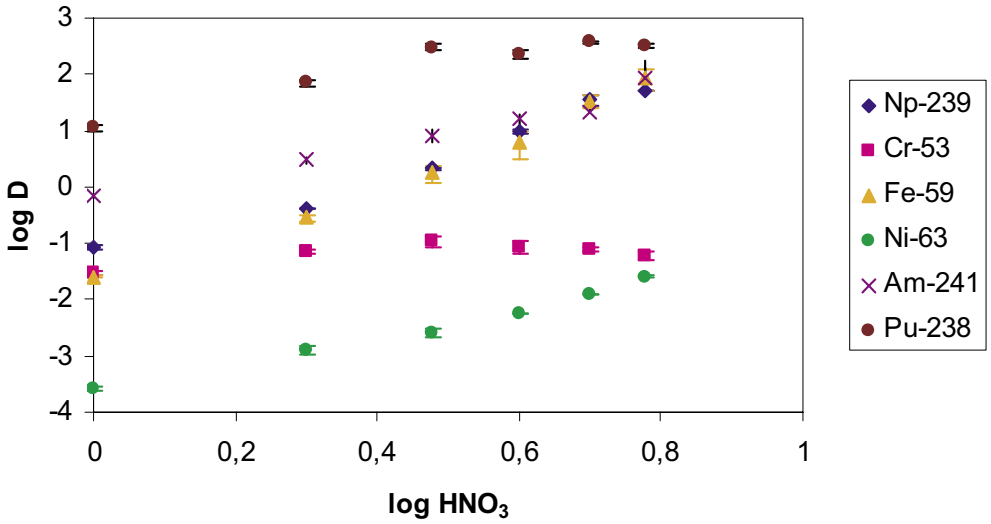

Figure 18. *Distribution ratios of some of the investigated elements as a function of acidity.*

2.6 Influence of temperature on the extraction

Studies of the temperature dependence on the extractive properties of DMDOHEMA have been reported earlier, *e.g.* M.-C. Charbonnel, M.-T-Presson [7]. There, the extraction of Nd(III) into dodecane was studied.

The temperature dependence of DMDOHEMA together with sBTP1 and sBTP2 was investigated. Three different organic solutions were prepared for this investigation:

I: 0.5 M DMDOHEMA in TB
II: 0.01 M sBTP1 + 0.5 M DMDOHEMA in TBB
III: 0.01 M sBTP2 + 0.5 M DMDOHEMA in TBB

Three aqueous solutions were prepared containing, 0.01 M H^+ and 3 M (H, Na)NO_3 and tracer amounts of ^{241}Am, ^{152}Eu and ^{244}Cm respectively. The reason for choosing a high nitrate concentration was that the extraction of actinides and lanthanides with the use of malondiamides gives distribution ratios close to the detection limit in a 1 M nitrate solution. The nitrate ions act as neutralizers in the extracted species.

0.5 ml of each phase was introduced into a 3.5 ml shaking vial. The vial was sealed and strapped onto a plastic plate. The plastic plate was inserted and fastened to a shaking device connected to a temperature bath. The temperature was regulated with an uncertainty of approximately 1°C. All nine combinations of aqueous and organic phases were tested at three different temperatures, 10° C, 25°C and 40° C. Double samples were made in all cases.

The samples were shaken for 1 h and after that time one vial at a time was taken out from the bath and aliquots of 100 µl of each phase were taken. The shaking vials were not centrifuged before sampling since there was no possibility to centrifuge at the same temperature as the vials had been shaken at. There were little or no problems with phase separation except in one case, the samples containing sBTP2 shaken at 10° C. Here the phases would not separate until after some time at a somewhat higher temperature. It was assumed that this would not influence the equilibrium to any great extent.

The americium and europium samples were measured on a NaI(Tl) scintillation detector. The curium samples were mixed with 10 ml of Hionic-Fluor™ scintillation cocktail and measured in a liquid scintillation detector. The results from these experiments are displayed in Figure 19, Figure 20 and Figure 21.

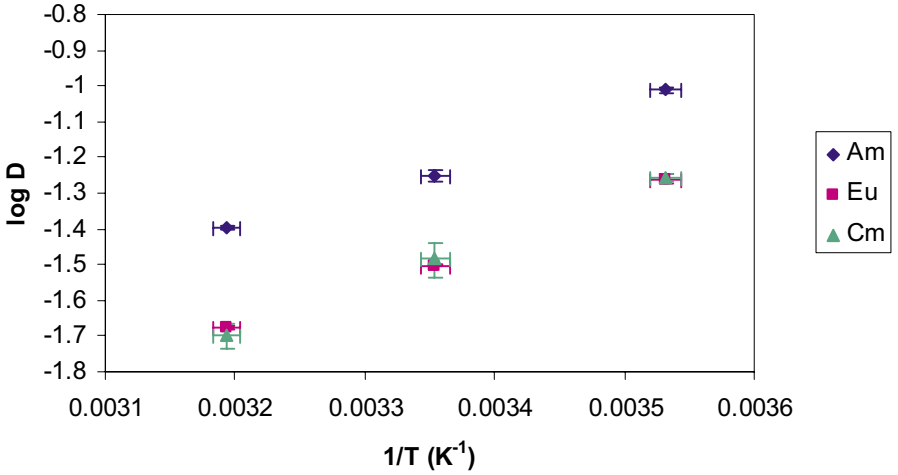

Figure 19. *Temperature dependence on the extraction, 0.5 M DMDOHEMA in TBB.*

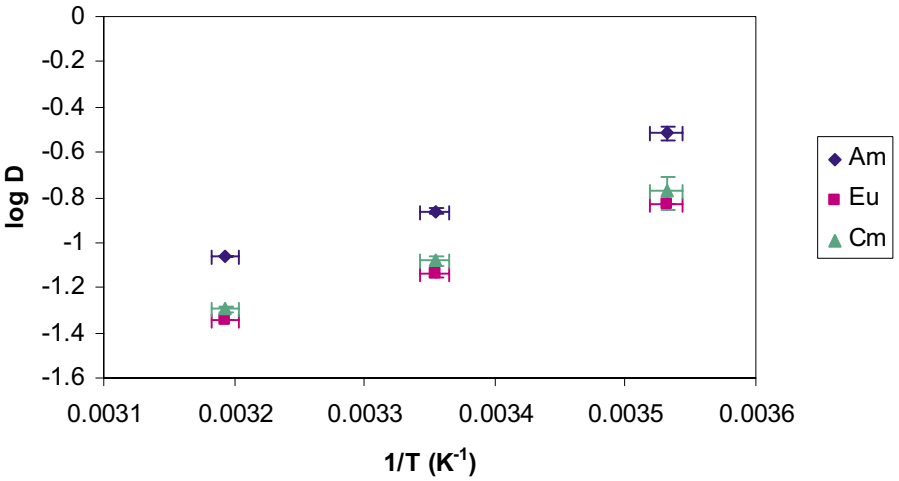

Figure 20. *Temperature dependence on the extraction, 0.01 M sBTP1 and 0.5 M DMDOHEMA in TBB.*

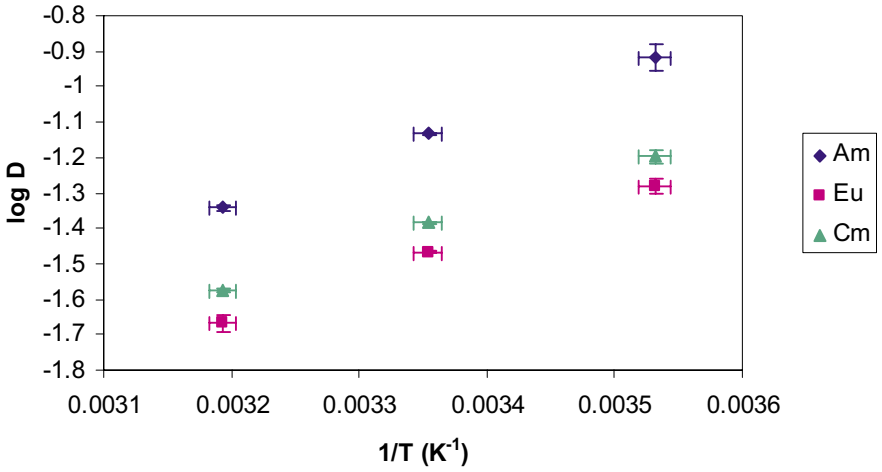

Figure 21. *Temperature dependence on the extraction, 0.01 M sBTP2 and 0.5 M DMDOHEMA in TBB.*

The results indicate that the extraction is increased as the temperature is decreased. The separation factors between the three elements seem to be constant as the temperature changes, but more experiments must be made in order to make any substantial conclusions. There seems to be no or very low separation between Cm and Eu except for the experiments when sBTP2 was used. The highest distribution ratios are obtained with sBTP1. Comparing these results with extraction results using 1 M NO_3^- in the aqueous phase the distribution ratios are approximately a factor 10 higher with 3 M NO_3^-.

2.7 Radiolysis nitrobenzene

The radiolysis of a BTP molecule was studied and at the same time the effect of changing the organic diluent on the radiolysis was also studied. The work was divided into two parts.

2.7.1 Part 1

Three organic solutions comprising 0.0018 M tetraethyl-BTP, see Figure 22, were prepared.

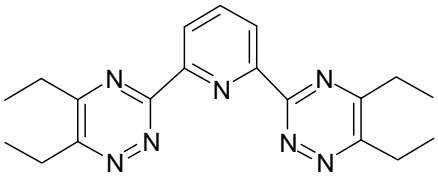

Figure 22. *Schematic picture of tetraethyl-BTP.*

The organic diluent was 1-hexanol in all three samples but in two of the samples 10% per volume of *tert*-butyl benzene and nitrobenzene were added, respectively. The solutions were transferred to glass flasks, which were sealed by a lid. These flasks were placed in a gamma-irradiating cobalt source (Gamma cell 220 from Atomic Energy of Canada ltd) with an activity of 0.99 TBq ^{60}Co and an estimated dose rate to water of ~40 Gy/h at the time of the irradiation. The flasks were connected via tubes to a bubble flask to avoid any pressure build up. As a reference, three vials containing solutions of the same composition were placed outside the gamma source during the irradiation time. Samples were taken during a time period of ~500 h. At each sampling two samples of 0.5 ml were taken from each of the three flasks containing BTP and only one sample of 0.5 ml from each of the three reference vials.

The samples were contacted with 0.5 ml of an aqueous phase containing trace amounts of ^{241}Am, 0.99 M $NaClO_4$ and 0.01 M $HClO_4$. The contact time was 5 min, shaking vigorously by hand. After contact the phases were separated by centrifugation for 15 min at 2000 g and aliquots of 100 µl were taken from each phase for gamma measurements in a NaI(Tl) detector (Intertechnique Gamma Counter 4000).

The distribution ratios (D) observed show that the extraction decreases with increasing dose to the solutions. There is also a big difference between the solution containing 10% nitrobenzene and the two other solutions, see Figure 23. The solution containing nitrobenzene does not show the same rapid decrease in americium extraction, indicating that nitrobenzene somehow inhibits the degradation of BTP. None of the reference solutions shows any significant reduction in americium extraction.

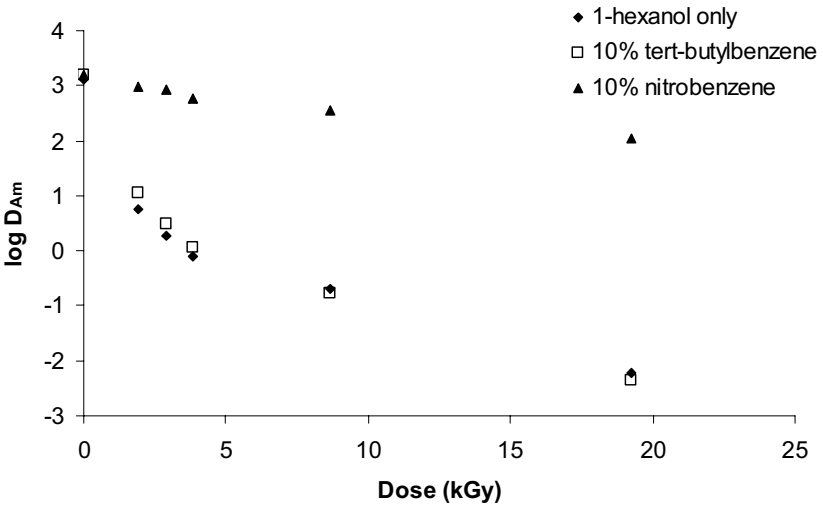

Figure 23. *Distribution ratios of americium as a function of dose to irradiated samples.*

2.7.2 Part 2

Noting that nitrobenzene somehow inhibited the radiolysis a new experiment was conducted. New organic solutions were prepared, similar to those used in part 1, containing BTP dissolved in 1-hexanol with different amounts of nitrobenzene, ranging from 0 to 10% per volume, see Figure 24. The organic solutions were transferred to glass vials, which were sealed with a lid and parafilm. These vials were placed in the same Co-source as was used before. Along with the vials with BTP were two vials without BTP, containing samples of pure nitrobenzene and a mixture of 10% per volume of nitrobenzene in 1-hexanol, respectively. Samples were taken during a time period of ~500 h. At each sampling two samples of 0.5 ml were taken from each of the eight vials containing BTP and one sample of 0.5 ml from each of the other two vials.

The samples containing BTP were contacted with an aqueous phase containing americium, according to the method described in part 1, and distribution ratios were measured. These measurements show that there is an impact on the BTP degradation depending on the amount of nitrobenzene added to the system, see Figure 24. It is, however, unclear if there is a saturation level where any extra nitrobenzene will make no difference to the degradation.

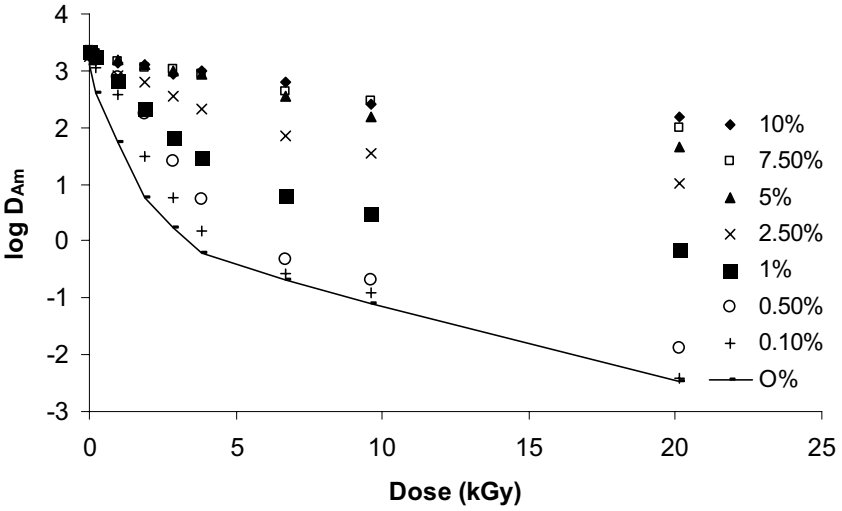

Figure 24. *Distribution ratios of americium as a function of dose to irradiated solutions. The different concentrations of nitrobenzene in the solutions are displayed in the picture.*

The samples without BTP were used for spectrophotometric studies. 10 µl of each sample was taken and diluted a factor 100 000 and 10 000, for the samples containing pure nitrobenzene and 10% nitrobenzene in 1-hexanol respectively, with 10 ml with 95% EtOH. From this solution ~1 ml was withdrawn for measurements on a spectrophotometer (Perkin Elmer Lambda 19 UV/VIS/NIR using a 1 cm quartz cells).

The results from the spectrophotometer studies showed no differences in the spectra of nitrobenzene between different doses. This may indicate that the nitrobenzene is not destroyed during irradiation of the solution containing nitrobenzene and 1-hexanol.

The full mechanism behind the radiolysis of BTP and stabilisation effect of nitrobenzene is not yet fully understood but may include complexation between the •OH-radical and nitrobenzene [8]. Nitrobenzene may also act as a scavenger of the solvated electrons [8]. The influence of the aromatic ring alone seems to have little impact on the stabilisation effect since *tert*-butyl benzene was unable to stabilise the BTP-molecule.

3 Collaborations

The following laboratories are involved in PARTNEW. More information can also be found as http://www.nc.chalmers.se/PARTNEW.HTM.

- Commissariat á l'Énergie Atomique (France).
- The University of Reading (United Kingdom).
- Chalmers University of Technology (Sweden).
- European Commission, DG-JRC, Institute for Transuranium Elements (Germany).
- Ente per le Nuove Technologie, l'Energia e l'Ambiente (Italy).
- Politecnico di Milano (Italy).
- Forschungszentrum Karlsruhe, GmbH (Germany).
- Forchungszentrum Jülich, GmbH (Germany).
- Centro de Investigaciones Energeticas, Medioambientales y Technologicas (Spain).
- Universidad Autonoma de Madrid (Spain).

In EUROPART 24 different partner laboratories will participate. They are:

- Commissariat à l'énergie atomique (France).
- British Nuclear Fuels (United Kingdom).
- Chalmers University of Technology (Sweden).
- Centro de investigaciones energeticas medioambientales y tecnologicas (Spain).
- Czech Technical University in Prague (Czech Republic).
- Centre National de la Recherche Scientifique (France).
- Electricité de France (France).
- Ente per le Nuove Tecnologie, l'Energia, l'Ambiente (Italy).
- Forschungszentrum Jülich (Germany).
- Consejo Superior de Investigaciones Cientificas (Spain).
- Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic (Czech Republic).
- Forschungszentrum Karlsruhe (Germany).
- European Commission, Joint Research Centre, Institute of Transuranium Elements (Germany).
- Johannes Gutenberg-Universität (Germany).
- Katchem spol. S.r.o. (Czech Republic).
- Nuclear Research Insitute Rez plc (Czech Republic).
- Politecnico di Milano (Italy).
- Universidad Autonoma de Madrid (Spain).
- Université de Liège (Belgium).
- Université Louis Pasteur I (France).
- Università degli studi de Parma (Italy).
- University of Reading (United Kingdom).
- University of Twente (The Netherlands).
- Instytut Chemii I Techniki Jadrowej (Poland).

4 Meetings and lectures

EC cluster meeting on Partitioning and Transmutation, Göteborg, March 17–20.
S. Andersson, C. Ekberg, J-O. Liljenzin, M. Nilsson and G. Skarnemark attended.

Every year a study tour for the students taking our basic nuclear chemistry course is arranged. This year they visited e.g. CEA Marcoule and their facilities dealing with the separation of the elements in the spent nuclear fuel.
S. Andersson and G. Skarnemark attended the study tour.

Scientific visit to Institut für Kernchemie, Johannes Gutenberg-Universität Mainz.
Activation analysis of bromine as a part of the study of bromodecanoic acid, May 12–14.
Mikael Nilsson

EC cluster meeting on Partitioning and Transmutation, Keswick, July 29–August 1.
S. Andersson, C. Ekberg, J-O. Liljenzin and M. Nilsson participated.

International Workshop on P&T and ADS development 2003, Mol Oct 6–8.
S. Andersson, C. Ekberg, M. Nilsson and G. Skarnemark attended and presented a poster.

Christian Ekberg was invited speaker at the Fourth International Conference on Cryogenics, Sep 16–19 2003, Valcea, Rumania

Scientific visit to Institut für Kernchemie, Johannes Gutenberg-Universität Mainz to activate lanthanides and make nitrate complex formation studies, November 24–28.
S. Andersson, C. Ekberg and G. Skarnemark participated.

5 Articles and publications

During the past year several reports and articles have been published or submitted for publication.

The abstract of M. Nilsson licentiate thesis can be found in Appendix 1.

The abstract of the article *Extraction Behaviour of the Synergistic System 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine and 2-bromodecanoic Acid Using Am and Eu as Radioactive Tracers* is given in Appendix II. The authors are S. Andersson, C. Ekberg, M.R.S. Foreman, M.J. Hudson, J-O. Liljenzin, M. Nilsson, G. Skarnemark and K. Spahiu and it was published in Solvent Extraction and Ion Exchange, **21**(5), pp. 621–636, 2003.

The abstract of the article *Determination of $H_2TPTZ_2^{2+}$ Stability Constant by TPTZ Solubility in Nitric Acid* is given in Appendix III. The authors are C. Mesmin and J-O. Liljenzin and it was published in Solvent Extraction and Ion Exchange, **21**(6), pp. 783–795, 2003.

The article *Study of Nitrate Complex Formation with Pm, Eu, Am and Cm Using a Solvent Extraction Technique* by S. Andersson, C. Ekberg, J.-O. Liljenzin, M. Nilsson and G. Skarnemark. Submitted to Radiochimica Acta.

We have also written half-yearly reports to the PARTNEW project and participated in the preparation of the final report. This has not yet been published.

The abstracts of the diploma works by H. Sezgin and S. Goeury are available at Chalmers University of Technology.

We have also submitted abstracts to NRC6. Five different papers (in preparation) in which we are involved will be presented there.

6 Future work

The EUROPART project has started (1 Jan 2004) and we will participate in the work concerning:

- Partitioning of actinides (Am to Cf) from High Active Raffinates and High Active Concentrates issued from the reprocessing of UOX and MOX spent fuels using extracting agents belonging to the families of polyamides and polydendate N or S-bearing molecules and cosan
- Partitioning of actinides for advanced dedicated future fuel cycles, like for example ADS nuclear systems. The co-extraction of actinides of different oxidation states will be studied. Mixtures of ligands, bitopic extractants and chromatographic techniques will be used.

Mikael Nilsson will go to Forschungszentrum Jülich to work with process development of some promising ligands.

Sofie Andersson will go to Lawrence Berkeley National Laboratory to study extraction chemistry with californium and berkelium.

A new PhD student, Daniel Magnusson started his work in the group on January 1. He will go to Germany and ITU after one year, stay there for three years and then come back to Göteborg again to make his final year here.

We will also have a new French diploma worker in our group, Francois Drouet, who will probably continue the work of the two former diploma workers from France.

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Appendix I

Studies of a synergistic extraction system for minor actinides and the chemical properties of 2-bromodecanoic acid

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Abstract

Spent fuel from nuclear power plants contains long-lived radionuclides, which are the main reason for its long storage time. These long-lived elements can be converted into short-lived or stable nuclides by neutron irradiation. For this transmutation process to be successful, a good separation of the long-lived elements, the actinides, from the rest of the waste must be ensured. Special consideration must be given to the difficult task of separating the trivalent actinides from the chemically similar lanthanides.

In this work a model for describing the influence of the organic diluent on the extraction of Am(III), Cm(III) and Pm(III) is presented. One of the reagents used in this extraction system, 2-bromodecanoic acid, was further investigated in order to find some important chemical properties describing the extraction mechanism.

The model is based on Charles Hansen's extension of the Schatchard-Hildebrands regular solution theory and was tested by performing a number of extraction experiments using reagents 2,2':6',2"-terpyridine and 2-bromodecanoic acid in synergy. The model proved to be in good agreement between experimental and theoretical results in most of the tested extraction cases.

In order to better understand this metal extraction system the chemical properties of 2-bromodecanoic acid were thoroughly investigated. In particular the equilibrium constants for the acid were studied using a number of different analytical methods.

The extent of the dimerisation of the acid in the organic phase was investigated using IR-spectroscopy. The distribution of the acid between organic and aqueous phase was found using ordinary solvent extraction experiments. Finally the acid dissociation constant in the aqueous phase was found by performing two-phase titrations.

To further investigate the system, solvent extraction of Eu(III) was carried out in order to find the stability constants for the Eu(III)-2-bromodecanoic acid complexes.

Keywords: Solvent extraction, Partitioning, Transmutation, Synergistic extraction, Solubility parameters, 2-bromodecanoic acid, 2,2':6',2"-terpyridine, Actinides, Lanthanides

Appendix II

Extraction behaviour of the synergistic System 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine and 2-bromodecanoic acid using Am and Eu as radioactive tracers

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[3] Svensk Kärnbränslehantering AB, SE-102 40 Stockholm, Sweden

Abstract

In this study, the extraction properties of a synergistic system consisting of 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine (BODO) and 2-bromodecanoic acid (HA) in *tert*-butyl benzene have been investigated as a function of ionic strength by varying the nitrate ion and perchlorate ion concentrations. The influence of the hydrogen ion concentration has also been investigated. Distribution ratios between 0.03–12 and 0.003–0.8 have been found for Am(III) and Eu(III) respectively, but there were no attempts to maximise these values. It has been shown that the distribution ratios decrease with increasing amounts of $ClO4^-$, $NO3^-$ and H^+. The mechanisms, however, by which the decrease occurs, are different. In the case of increasing perchlorate ion concentration, the decrease in extraction is linear in a log-log plot of the distribution ratio versus the ionic strength, while in the nitrate case the complex formation between nitrate and Am or Eu increases at high nitrate ion concentrations and thereby decreases the distribution ratio in a non-linear way. The decrease in extraction could be caused by changes in activity coefficients that can be explained with specific ion interaction theory (SIT); shielding of the metal ions, and by nitrate complex formation with Am and Eu as competing mechanism at high ionic strengths.

The separation factor between Am and Eu reaches a maximum at ~1 M nitrate ion concentration. Thereafter the values decrease with increasing nitrate ion concentrations.

Appendix III

Determination of $H_2TPTZ_2^{2+}$ stability constant by TPTZ solubility in nitric acid

Mesmin C and Liljenzin J-O, Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg, Sweden

Abstract

The protonation constants for 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ), a well known extractant in partitioning of An(III)/Ln(III), were calculated from the solubility of TPTZ in aqueous solutions of varying acidity in equilibrium with either solid TPTZ or a nitrobenzene phase containing TPTZ. The values obtained are log K_1 = 3.55 ± 0.07, log K_2 = 2.72 ± 0.06. For the first time the existence of the dimmer form, $H_2TPTZ_2^{2+}$, has been proven and its stability constant, $K_{2,2}$, was found to be (1.79 ± 0.21) x 10^4 in the acidity range $2 < -\log[H^+] < 5$.

Keywords: TPTZ, Solubility, Stability constant, $H_2TPTZ_2^{2+}$, Protonation constant, Polymer form.