THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

On the Diluent and Solvent Effects in Liquid-Liquid Extraction Systems based on Bis-triazine-bipyridine (BTBP) ligands

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Cover: Nicely separated phases in a liquid-liquid extraction system (left). That picture can be compared to phases that do not separate due to similar densities (right).

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LIST OF PUBLICATIONS

This thesis is based on the work in the following papers, referred to in the text by their Roman numbers

I. Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg and Gunnar Skarnemark: A reinterpretation of C5-BTBP extraction data, performed in various alcohols, *Journal of Radioanalytical and Nuclear Chemistry*, 296: 733–737 (2013)

II. Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg, Mark Foreman and Gunnar Skarnemark: A comparison of americium extractions as a function of time using two bis-triazine-bipyridine ligands in long chained alcohol diluents, *Separation Science and Technology,* 49: 2060-2065 (2014)

III. Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg, Mark Foreman and Gunnar Skarnemark: Comparison of the Extraction as a Function of Time in Two GANEX Solvents: Influence of Metal Loading, Interfacial Tension and Density, *Solvent Extraction and Ion Exchange*, 31: 604-616 (2013)

IV. Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg, Nathalie Mabile and Gunnar Skarnemark: Solvent effects on the extraction rate in proposed GANEX processes, Proceedings of the 19th international solvent extraction conference, ISEC, Santiago de Chile (2011)

V. Elin Löfström-Engdahl, Christian Ekberg, Mark Foreman, Jenny Halleröd, Gunnar Skarnemark and Emma Aneheim: The influence of acidity, TBP addition and $CyMe_4$-BTBP concentration on the rate of extraction in a GANEX solvent based on hexanol, *Manuscript*

VI. Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg, Hanna Elfverson, Mark Foreman and Gunnar Skarnemark: Hexanoic acid as an alternative diluent in a GANEX process: feasibility study, *Journal of Radioanalytical and Nuclear Chemistry*, 299: 1261-1266 (2014)

VII. Elin Löfström-Engdahl, Emma Aneheim, Christian Ekberg, Mark Foreman, Jenny Halleröd and Gunnar Skarnemark: Extraction thermodynamics of Am(III) and Eu(III) using $CyMe_4$-BTBP in various organic diluents, *Journal of Chemical Thermodynamics*, 76:64-69 (2014)

Contribution report

I, II, III, IV, V, VII	All experimental work, author of the paper
VI	Part of the experimental work, author of the paper

On the Diluent and Solvent Effects in Liquid-Liquid Extraction Systems based on Bis-triazine-bipyridine (BTBP) ligands

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ABSTRACT

Used nuclear fuel is dangerous for mankind and her environment for a long time. If however, the minor actinides together with uranium and plutonium could be transmuted, i.e. transformed, into more shortlived or stable isotopes, the volume of the waste could be significantly reduced together with a reduction in the long term radiotoxicity. In order to be able to transmute the actinides they need to be separated from fission and corrosion/activation products. One way of achieveing such a separation is through liquid-liquid extraction. One group of specially designed ligands that can achieve a separation of the trivalent actinides from the chemically similar lanthanides is the so called BTBPs (biz-triazine-bi-pyridine). By combining a BTBP type of ligand with tributyl phosphate, TBP, an extraction of all the actinides as one group, (Grouped ActiNide EXtraction) GANEX, can be achieved. As of today, cyclohexanone has been the diluent of choice in this solvent. The solvent has shown very promising extraction and separation results, however, both cyclohexanone and TBP have some drawbacks as parts in a process solvent why alternative diluents to cyclohexanone (hexanol and hexanoic acid) and an alternative ligand to TBP, di(2-ethylhexyl) butyramide (DEHBA), have been investigated in this work. Thermodynamic extraction data for a BTBP ligand in three diluents (cyclohexanone, hexanol and nitrobenzene) have been presented and the influence of the interfacial tension between the aqueous and organic phase on the rate of mass transfer of americium in the extraction systems have also been investigated.

Hexanoic acid did not work as a process diluent, since the extraction of americium and curium was much lower compared to that of plutonium. Hexanol would probably be a better choice, however, not as good as the cyclohexanone based solvent, due to mainly solubility issues of the ligand. For process development, the thermodynamic data shows that the extraction of americium and europium as well as their separation decreases as the temperature increases in several diluents. During the work it was also shown that a short phase contact time favors the separation of americium from europium.

Keywords: GANEX, Solvent effects, Diluent effects, Interfacial tension, Density

1 INTRODUCTION

“Nothing is to be feared, only to be understood, so that we may fear less” Marie Curie

1.1 Nuclear power in a sustainable world

Industrialisation and a globally increasing population are generating increasing energy demands (Brundtland, 1987). In order to fulfill the need for energy and electricity, society currently utilises several energy sources. One of these sources is nuclear power. Several analyses of nuclear energy indicate that it can hopefully be an option to fossil fuels as part of the development of a more sustainable energy route for society (e.g. Sailor, 2000; Bruggink, 2002), particularly if the technology can be modernised (Zwaan, 2013). During normal operation, its employment is consistent with one of the central aim of sustainable development, to avoid major environmental impacts through carbon dioxide emissions (Sailor, 2000; Bruggink, 2002; Zwaan, 2013). However, even a properly working and safe nuclear power plant produces radioactive waste in the form of used nuclear fuel, which is considered to be one of the major issues associated with nuclear power. The used fuel is radiotoxic to mankind and its environment for a long time. At present, the fuel is stored in water pools, using the water to shield the radiation and for cooling, while awaiting final storage deep down in the bedrock (IAEA, 2011). It will take more than 100,000 years before the radiotoxicity (described as Sv/TWhe in figure 1) from the used nuclear fuel reaches the same level as the uranium used to fabricate it. The data in the figure is calculated by RADtox, (Holm, 2012).

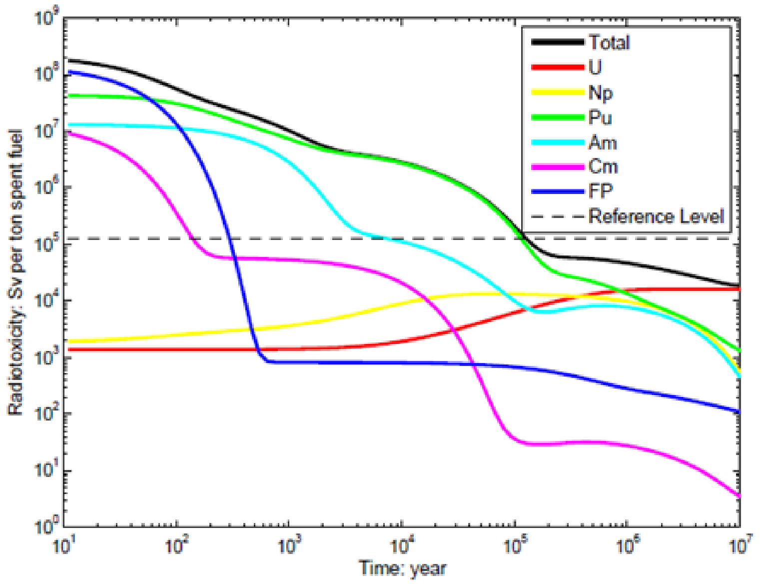


Figure 1. The radiotoxicity (Sv/tonne) of used nuclear fuel (“once through” fuel cycle, 4% enrichment, burnup 45GWd/tHM of initial uranium) as a function of time. Cooling time is 10 years. The dose is calculated from the International Commission on Radiological Protection (ICRP) dose coefficients (ingestion), and integrated for all prodigies from the parent nuclide; reference is the amount of natural uranium needed to produce 1 tonne of enriched fuel. Calculated using RADtox (Holm, 2012).

1.2 Nuclear energy today

The Organisation for Economic Co-operation and Development (OECD) countries currently use nuclear energy to meet approximately 20 % of their electricity requirements. Some countries, Sweden (around 40 %), Belgium (around 50 %) and France (nearly 80 %) use even more (OECD, 2012). Table 1 lists some important figures concerning the status of nuclear reactors and their electricity generation.

Table 1. Some important figures concerning nuclear energy production in OECD countries as per 2012 (OECD, 2012).

	Reactors connected to grid	**Nuclear electricity generation 2012 (Twh)**	**Percentage nuclear**
Sweden	10	58.0	37.9
OECD America	125	869.3	18.0
OECD Europe	133	849.0	24.0
OECD Pacific	73	165.7	10.3

1.3 Current status of the nuclear fuel

At the end of 2012, 360,500 tonnes of used fuel from the world's nuclear facilities had been discharged (IAEA, 2013), which can be compared to 320,000 tonnes at the end of 2010 (IAEA, 2011). As of today, this fuel is only in temporary storage. Final storage is under consideration for example in Sweden and Finland. The Swedish method is based on three protective barriers. Initially, the used fuel is encapsulated in copper. The copper canisters are placed deep down in the bedrock at a depth of about 500 meters and finally the canisters are embedded in bentonite clay (SKB, 2014A). The application of this design is currently under review by the Swedish Radiation Safety Authority (with respect to nuclear safety and radiation protection) and the Land and Environmental Court (with respect to the environmental code) in Stockholm (SKB, 2014B). A complement to direct final storage of the used fuel is to reuse the actinides that are still present within the fuel. The plutonium and uranium can today be used for the production of so-called Mixed Oxide Fuel (commonly known as MOX fuel) (Choppin, 2013A). Using MOX fuel increases the utilisation of the energy in the uranium from 1 to around 1.2 %, however the need for uranium mining and enrichment services is reduced by around 30 % (Choppin, 2013A). MOX fuel is today used in for example United Kingdom and France. In addition to the uranium and plutonium, the used nuclear fuel contains minor actinides (americium, curium and neptunium), as well as fission and corrosion/activation products. The minor actinides contribute to the long term radiotoxicity of the used fuel and are therefore a subject for research concerning a so-called transmutation, which has the potential to transform them into more short-lived or stable isotopes.

1.4 Transmutation

“Don´t call it transmutation, they´ll have our heads of as alchemists!” Ernest Rutherford

Transmutation is a nuclear process that transforms one element into another. The transmutation attempts were initially conducted by alchemists, with the aim of producing gold. Rutherford and Soddy concluded in 1895 that transmutation occurs naturally (Royal society, 2009). Transmutation also occurs continuously in nuclear reactors when the uranium nuclei are being transformed into fission and transuranium elements by the neutron irradiation. Transmutation can be useful when handling the radiotoxic elements in the used nuclear fuel. Transmutation of used nuclear fuel in a fast (neutron spectrum) reactor actually has the potential to reduce the radiotoxicity of the used fuel by e.g. fission of the minor actinides. The energy utilization of the initial uranium is simultaneously increased. By separating and transmuting the minor actinides, the strain on the final repositories could be significantly reduced, both in storage time and capacity (Aoki, 2002; Bond, 1975; Choppin, 2013A; Madic, 2000). Another possible way of transmuting the minor actinides is by using accelerator driven systems (ADS). A similar fast neutron spectrum is used in order to transmute the actinides, however, such a system is subcritical, and instead of producing energy, energy has to be inserted to the system. In order to be able to transmute the minor actinides they need to be separated from the fission and corrosion/activation products, since these consume neutrons. One way of achieving such a separation is through liquid-liquid extraction.

One concept for a complete reactor park is double strata (described by Salvatores (1998) for example). The first layer then deals with reactors, fuel cycles and fuel production of standard design as well as fast reactors and recirculate uranium, plutonium and in some cases also neptunium. The second layer is dedicated to the transmutation of americium and curium. A schematic figure of a possible nuclear power cycle, with a separate transmutation part can be seen in figure 2.

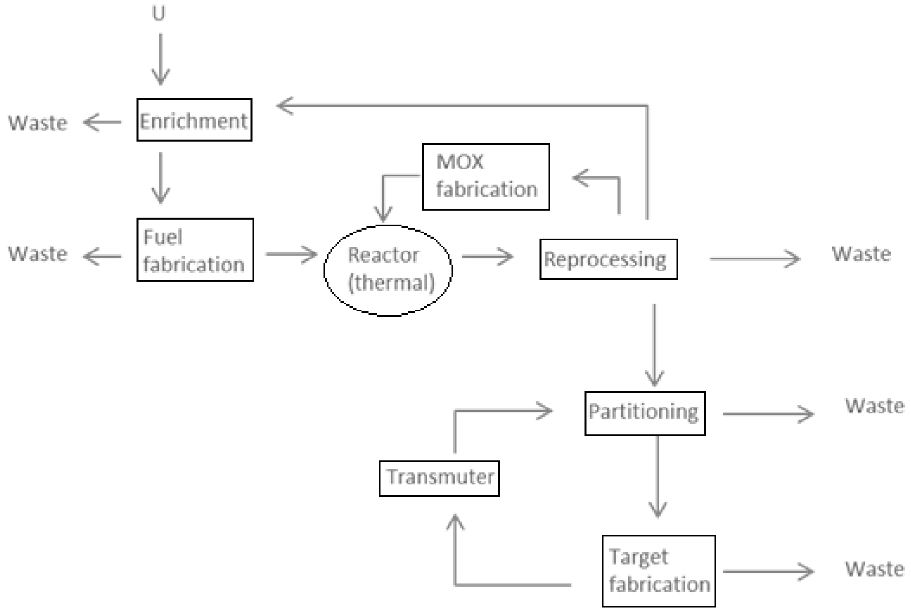


Figure 2. Schematics of a proposed nuclear fuel cycle.

1.5 Objectives

The objective of this work is the separation of actinides from the rest of the used nuclear fuel using solvent extraction. The main focus is the effect of the diluent and solvent on the extraction of (mostly) trivalent actinides, lanthanides and other fission, corrosion and activation products when using the so-called BTBP class of ligands. The importance of the interfacial tension of these extraction systems is systematically investigated and discussed in paper I and II with a focus on its influence on the rate of mass transfer of americium. More focus was put on the rate of mass transfer in paper III and IV, with a discussion of the effects of solvent composition as well as metal loading in Chalmers GANEX solvents. Papers V and IV focus on alternative and for the system novel diluents for process application in such a GANEX solvent, and place a specific focus on the density of the solvents. Paper VII presents the thermodynamic parameters of the extraction of americium into three diluents (cyclohexanone, hexanol and nitrobenzene).

2 BACKGROUND

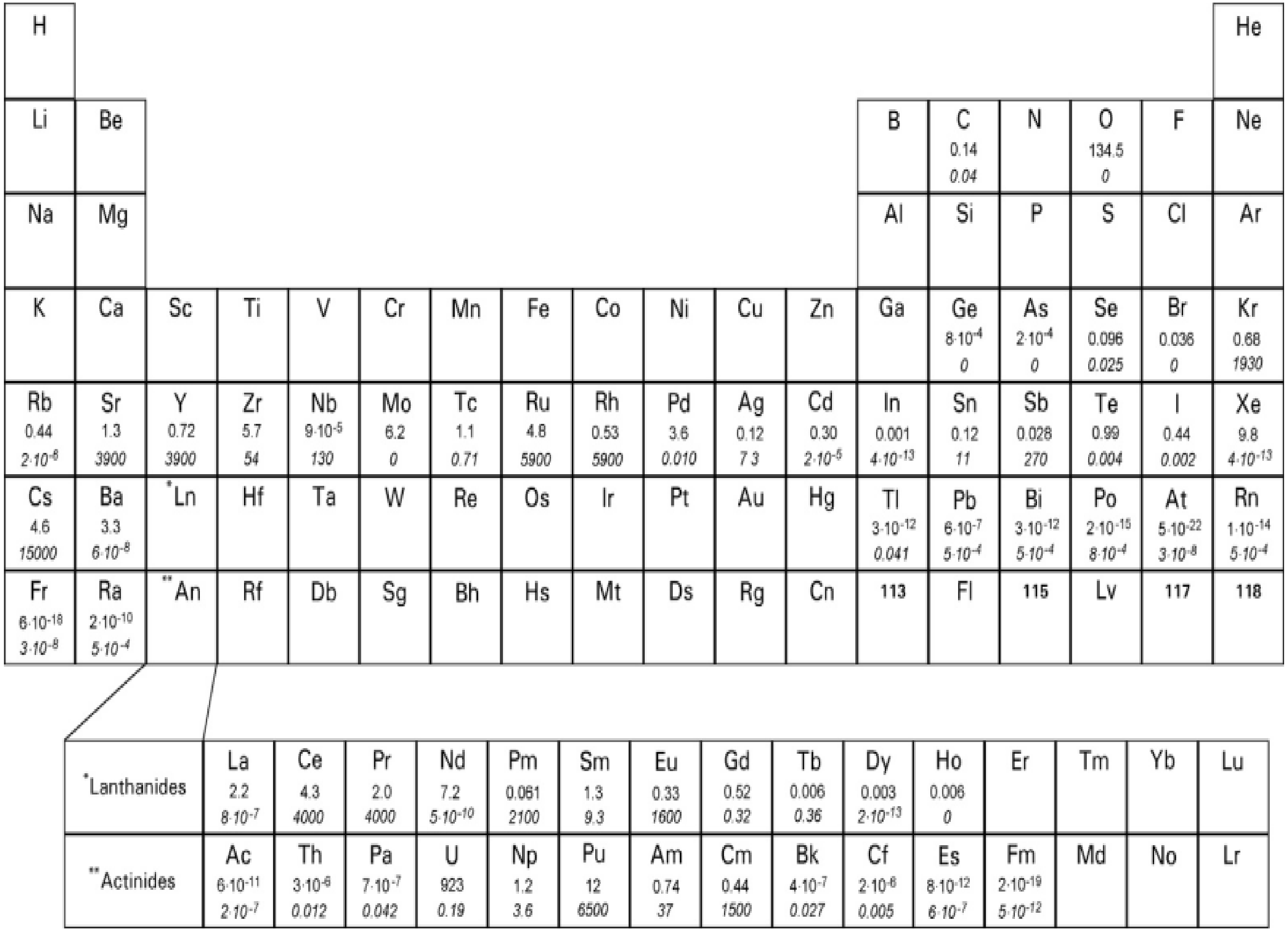
2.1 The nuclear fuel cycle

The nuclear fuel mostly used in commercial reactors today is ^{238}U enriched with respect to ^{235}U (up to a few percent). During the operation of the reactor, thermal neutrons induce fission in the fissile material

$$^{235}\text{U} + \text{n} \rightarrow \text{FP} + \text{vn}$$

where n denotes the neutron and v the number of neutrons released per fission and FP is the fission products produced. An average of 2.5 neutrons are released for each neutron consumed (Choppin, 2013B). This chain reaction is controlled in a reactor so that each fission only generates one new fission, not more. The energy released per fission is around $3.2 \cdot 10^{-11}$ J (200 MeV). However, not all the uranium isotopes are fissile. Neutron capture and β decay build up heavier actinides. Some of the higher actinides do fission and contribute to the overall energy production (^{239}Pu and ^{241}Pu (Choppin, 2013A)), but unfortunately not all, leaving a used fuel containing fission products as well as the minor actinides that have built up.

The composition of used nuclear fuel varies according to factors such as input composition, neutron spectrum, flux, burn up, design of fuel elements and position in the reactor. However, some approximate numbers can be given. Every tonne of irradiated (33 MWd/kg) uranium generates about 34 kg of fission products (included gaseous) (Choppin, 2013A). A schematics of the elements present in the fuel from a pressurised water reactor after 1 year of cooling (3.6 % enrichment, 60 MWd/kg U burn up, where the n-flux changes yearly after fuel rearrangement), is seen in figure 3. The picture is from borrowed Choppin et al (2013A).



H																	He
Li	Be											B	C 0.14 *0.04*	N	O 134.5 *0*	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge $8\cdot10^{-4}$ *0*	As $2\cdot10^{-4}$ *0*	Se 0.096 *0.025*	Br 0.036 *0*	Kr 0.68 *1930*
Rb 0.44 *$2\cdot10^{-8}$*	Sr 1.3 *3900*	Y 0.72 *3900*	Zr 5.7 *54*	Nb $9\cdot10^{-5}$ *130*	Mo 6.2 *0*	Tc 1.1 *0.71*	Ru 4.8 *5900*	Rh 0.53 *5900*	Pd 3.6 *0.010*	Ag 0.12 *7.3*	Cd 0.30 *$2\cdot10^{-5}$*	In 0.001 *$4\cdot10^{-13}$*	Sn 0.12 *11*	Sb 0.028 *270*	Te 0.99 *0.004*	I 0.44 *0.002*	Xe 9.8 *$4\cdot10^{-13}$*
Cs 4.6 *15000*	Ba 3.3 *$6\cdot10^{-8}$*	*Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl $3\cdot10^{-12}$ *0.041*	Pb $6\cdot10^{-7}$ *$5\cdot10^{-4}$*	Bi $3\cdot10^{-12}$ *$5\cdot10^{-4}$*	Po $2\cdot10^{-15}$ *$8\cdot10^{-4}$*	At $5\cdot10^{-22}$ *$3\cdot10^{-8}$*	Rn $1\cdot10^{-14}$ *$5\cdot10^{-4}$*
Fr $6\cdot10^{-18}$ *$3\cdot10^{-8}$*	Ra $2\cdot10^{-10}$ *$5\cdot10^{-4}$*	**An	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	113	Fl	115	Lv	117	118

*Lanthanides	La 2.2 *$8\cdot10^{-7}$*	Ce 4.3 *4000*	Pr 2.0 *4000*	Nd 7.2 *$5\cdot10^{-10}$*	Pm 0.061 *2100*	Sm 1.3 *9.3*	Eu 0.33 *1600*	Gd 0.52 *0.32*	Tb 0.006 *0.36*	Dy 0.003 *$2\cdot10^{-13}$*	Ho 0.006 *0*	Er	Tm	Yb	Lu
**Actinides	Ac $6\cdot10^{-11}$ *$2\cdot10^{-7}$*	Th $3\cdot10^{-6}$ *0.012*	Pa $7\cdot10^{-7}$ *0.042*	U 923 *0.19*	Np 1.2 *3.6*	Pu 12 *6500*	Am 0.74 *37*	Cm 0.44 *1500*	Bk $4\cdot10^{-7}$ *0.027*	Cf $2\cdot10^{-6}$ *0.005*	Es $8\cdot10^{-12}$ *$6\cdot10^{-7}$*	Fm $2\cdot10^{-19}$ *$5\cdot10^{-12}$*	Md	No	Lr

Figure 3. Composition (Choppin, 2013A) of used fuel after 1 year of cooling (3.6 % enrichment, 60 MWd/kg U burn up, where the n-flux changes annually after fuel rearrangement). The picture is taken from Choppin et al (2013A). The straight figures are weight in kg/t IHM and italics are radioactivity in TBq/t IHM. The total weight is 63 kg FPs and 14 kg transuranium elements.

2.2 Separation of used nuclear fuel

There are various ways to achieve the separation of used nuclear fuel. The main categories are the “dry” route and the “wet” route. Today, the dry routes are only at the research stage, and include for example *Halide volatility*, where fluorides of uranium (UF_6) are separated from a molten fluoride salt eutectic in presence of HF (Choppin, 2013A). Another “dry” way of separating actinides from the rest of the used fuel is through “*Molten salt extraction*”. Molten salt extraction is also based on an eutectic salt melt in combination with a low volatility heat resistant solvent. The actinides and fission products then distribute themselves between the two phases. Examples of applications of the later technique include continuous reprocessing of molten salt reactor fuel (Choppin, 2013A). Pyro processing technology is under development for example in the US, Russia, France and Japan (Madic, 2001).

On the other hand, the so-called “wet route”, implies the separation of elements through their different capacities to forming organic soluble complexes. This technique is called *liquid-liquid* extraction. Liquid-liquid extraction is based on the principle that organic and aqueous liquids do not mix. By adding specially designed molecules, ligands, to the organic phase, selected elements can be extracted from the aqueous phase, leaving the unwanted metals in the aqueous solution. When comparing the “dry” and “wet” route it can be noted that the *Molten salt extraction* is more radiation resistant as well as safer with respect to criticality compared to aqueous based systems (Choppin, 2013A). However, the “wet” route has, compared to the dry route (IAEA, 2007), been used over a substantial period of time for the separation of uranium and plutonium from used nuclear fuel in the so-called PUREX process, thus demonstrating its functionality in the harsh environment that the used nuclear fuel make up.

2.3 Solvent extraction of used nuclear fuel

The liquid-liquid extraction treatment of used nuclear fuel is complicated. The fission and corrosion/activation products from the equipment together with uranium, plutonium and minor actinides make up a delicate mixture of a number of elements (Choppin, 2013A). Several elements are also chemically similar, for example the trivalent actinides (americium and curium) and the lanthanides, which are a large part of the fission products.

Liquid-liquid extraction for nuclear applications has traditionally been used for the production of plutonium. One process used for the separation of plutonium from the rest of the used nuclear fuel is described and patented by Anderson et al (1960). This procedure was then developed to the so called Plutonium Uranium REdoX process (PUREX). The PUREX process separates uranium and plutonium from a highly acidic dissolution liquor by using the extractant tributylphospate (TBP). The use of TBP developed out of a study presented by Warf (1949) showing that butyl phosphate extracted tetravalent cerium, uranium and thorium as nitrate complexes. After the PUREX extraction the rest of the used fuel, such as fission, corrosion activation products, as well as minor actinides, are still present in the aqueous phase, the raffinate. The plutonium is recovered by reduction. Such a reduction then has the ability to selectively strip the plutonium from the uranium (Thomas, 1949). Research concerning more advanced partitioning and transmutation previously focused on developing processes aimed at following a PUREX separation in order to treat the raffinate, a so called double strata.

Trivalent actinides and fission product lanthanides can be separated from the rest of the fission and corrosion/activating products through for example DIAMEX, TRUEX or TRPO processes (summarized by Nilsson (2007)). After such a separation the Trivalent Actinide – Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes

(TALSPEAK) process (Weaver, 1964) can be applied. A co-stripping is then followed by a selective extraction of the lanthanides (Weaver, 1964). The TALSPEAK process is still today under investigation. The basic science in particular is currently being studied by researchers including Nilsson and Nash (Nilsson, 2009).

Another example of processes with the aim of treating the PUREX raffinate is the DIAMide EXtraction/Selective ActiNide EXtraction (DIAMEX/SANEX) process (Madic, 2000; Madic, 2004). In the DIAMEX process the minor actinides and lanthanides are co-extracted from the PUREX raffinate using diamides. The next step is a co-stripping of the two groups of elements (Baron, 2004). Several variations of heterocyclic nitrogen donor ligands have been developed and tested for the SANEX part of the process. A modification of this concept has also been presented in the so-called CTH process (Liljenzin, 1984), which also included a hot test (Persson, 1984). A schematic figure of the processes is seen in figure 4. The boxes in the top row represents the PUREX part of the separation while the three boxes in the bottom part are the more advanced separation options, which deal with the PUREX raffinate.

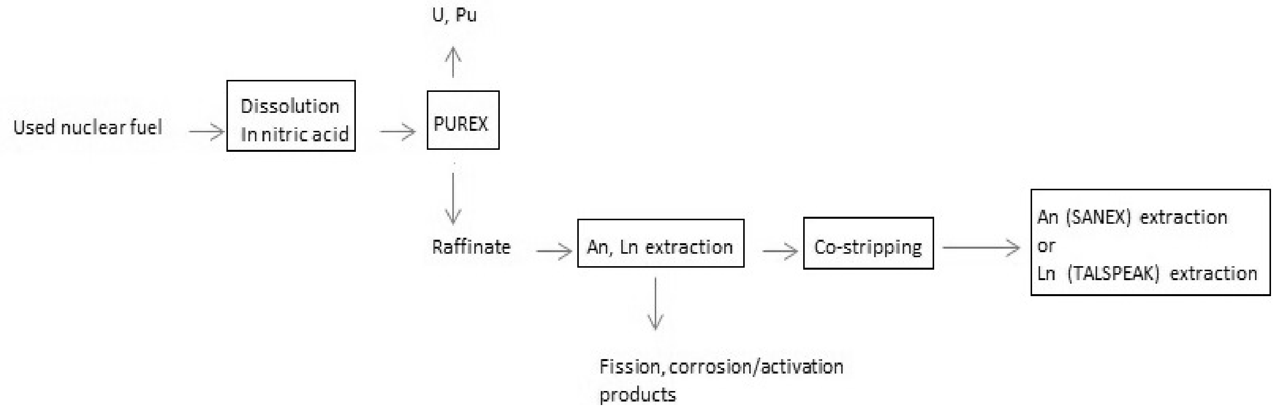


Figure 4. Schematics of a possible way of treating used nuclear fuel. The initial part is the so-called PUREX process, which is followed by more advanced options.

However, current research in Europe is targeting for a more proliferation resistant separation process. One way of increasing the resistance towards proliferation is to avoid a pure plutonium stream. One possibility of doing so is to extract all the actinides as one group, a single stratum. This kind of extraction is a Grouped ActiNide EXtraction (GANEX) (Adnet, 2005; Miguirditchian, 2007), thereby replacing the PUREX process. Another advantage of such a group actinide extraction is that the number of extraction stages is reduced. A reduction in the number of process stages reduces for example the waste streams, the capital investment and the area needed for the plant (Rydberg, 2004A).

3 THEORY

3.1 Definition of distribution ratio and Separation factor

The focus in a liquid-liquid extraction operation is the partition of the solute between the phases and the separation between two, or more, different solutes. Terminology for solvent extraction can be found in IUPAC documents (Rice, 1993). The extraction is given by the distribution ratio, the D. This distribution ratio is the ratio between the total analytical concentration of a species, M, in the organic phase divided by the total analytical concentration of the species in the aqueous phase. For radioactive nuclides, the concentration is proportional to the activity of the nuclide, thus

Equation 1

$$\mathrm{D} = \frac{\text{Total concentration of M in the organic phase}}{\text{Total concentration of M in the aqueous phase}} = \frac{[\mathrm{M}]_{\mathrm{Org}}}{[\mathrm{M}]_{\mathrm{Aq}}}$$

$$\propto$$

Equation 2

$$\frac{\text{Specific activity of M in the organic phase}}{\text{Specific activity of M in the aqueous phase}}$$

Equation 3

$$\mathrm{D} = \frac{\psi_{\mathrm{org}} \mathrm{R}_{\mathrm{org}}/\mathrm{V}_{\mathrm{org}}}{\psi_{\mathrm{aq}} \mathrm{R}_{\mathrm{aq}}/\mathrm{V}_{\mathrm{aq}}}$$

where R is the count rate. The detector efficiency (ψ) in γ-counting is usually similar for the organic and aqueous phases. However, different sample volumes (V) can affect the detector efficiency through different geometries of samples, which is why similar volumes were always measured in this work. In liquid scintillation counting and alpha spectrometry a high nitric acid concentration for example can influence the efficiency of the measurement. The distribution ratio can be measured both at equilibrium as well as after various times of phase contact. However, in order to discuss the thermodynamic behaviour of elements in an extraction system, equilibrium data shall be used. The separation factor (SF) is defined as the ratio of the distribution ratios for different solutes that are to be separated, and is defined to be >1. The denotation SF followed by an index naming the elements is commonly used, for example

Equation 4

$$\mathrm{SF}_{\mathrm{Am/Eu}} = \frac{\mathrm{D}_{\mathrm{Am}}}{\mathrm{D}_{\mathrm{Eu}}}$$

if the distribution ratio is higher for americium than for europium.

3.2 The GANEX concept

The GANEX concept typically consists of two cycles. Initially the bulk uranium is extracted. In the second cycle the rest of the actinides are separated as one group. The schematics of the GANEX process is seen in figure 5. The first stream then consists of pure uranium, which makes it easy to control the uranium content in a potential outgoing solution aimed at the production of new reactor fuel. In addition, uranium loading in the grouped extraction step is avoided by reducing the uranium concentration before the second extraction stage. Different formulations of GANEX solvents have been presented. A solvent that has been suggested and successfully applied for the 1st cycle is N,N-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) dissolved in Hydrogenated TetraPropylen (HTP) (Miguirditchian, 2008), in that study, more than 99.999 % of the uranium was recovered. Different ligand combinations and diluents have been used to achieve a satisfactory solvent for the 2nd GANEX cycle. One example is the one based on *N,N N',N'*-tetraoctyl diglycolamide (TODGA) and N,N'-dimethyl-N,N'-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA), which is a promising solvent composition that has been shown to extract all actinides together with the lanthanides (Bell, 2012). The concept has successfully been tested using genuine used nuclear fuel (Malmbeck, 2014), the recovery was for example 99.99 % for americium and plutonium. Another example is the so-called Chalmers GANEX solvent.

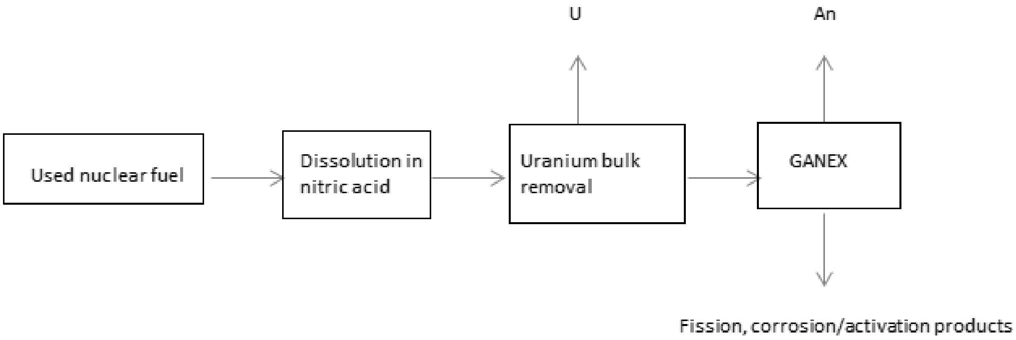


Figure 5. Schematics of a possible GANEX process.

3.3 The Chalmers GANEX process

The GANEX process that has been developed at Chalmers in recent years has proven to be promising, both with respect to extraction and separation (Aneheim, 2010) and hydrolytic and radiolytic stability (Aneheim, 2011). This process utilises a ternary solvent. The well-known PUREX ligand TBP is combined with a heterocyclic nitrogen donor, 6.6’-bis(5.6-dialkyl-[1,2,4-]triazin-3-yl)-2.2’-bipyridine ($CyMe_4$-BTBP), which belongs to the BTBP class of ligands that has been shown to extract tri- (Foreman, 2005; Nilsson, 2006A) and pentavalent actinides (Retegan, 2007A). In the Chalmers GANEX solvent, the ligands are dissolved in ($CyMe_4$-BTBP) and mixed with (TBP) the diluent cyclohexanone. Using this combination of extractants, the tetra- and hexavalent actinides (plutonium and uranium) are extracted by the TBP together with the tri- and pentavalent actinides that are extracted by the $CyMe_4$-BTBP. Also fission product treatment has been successfully handled during the development of the process, for example palladium precipitation can be prevented by the addition of methionine (Aneheim, 2012B) or together with molybdenum and zirconium be kept in the aqueous phase (preventing unwanted extraction) by the additions of 2S,2S)-4,4-(ethane-1,2-diylbis(sulfanediyl)) bis(2-aminobutanoic acid, BIMET, or mannitol (Aneheim, 2013). Also the technetium extraction in the system has been investigated (Aneheim, 2013B).

3.3.1 The BTBP class ligands

BTBP is an abbreviation of bis-triazin-bi-pyridine, which refers to the nature of the central core common to all molecules in the family. This is a group of molecules that act as tetradentate ligands for metal ions and also facilitate high selectivity towards trivalent actinides over trivalent lanthanides (Foreman, 2005; Nilsson, 2006A). This separation is especially hard to achieve, since the trivalent actinides are chemically similar to the lanthanides. $CyMe_4$-BTBP has proven to be quite resistant towards both gamma (low dose rate) (Retegan, 2007C) and alpha-radiolysis (Magnusson, 2009). Also C5-BTBP has been investigated (Fermvik, 2012), for example with focus on degradation products after radiation (Fermvik, 2009).

It is assumed that the difference in the soft-hard acid character of the actinides and lanthanides is the reason for the separation achieved when using nitrogen donor ligands. This theory is called the hard soft acid base (HSAB) theory. The principle indicates that metal ions that are soft Lewis acids form strong complexes with soft Lewis bases and vice versa. Mixed complexes, such as hard metal ions and soft Lewis bases, on the other hand, do not form such strong complexes (Pearson, 1968). Both actinides and lanthanides are assumed to be hard Lewis acids, however, actinides display a more covalent character in their complexation (Miguirditchian 2005; Ionova, 2001; Ionova, 2001B) and are therefore preferred over lanthanides by the N-donors in the BTBP ligands. Depending on the side groups and different attachments to the BTBP core molecule the extraction properties change such as distribution ratio (Retegan, 2007A; Ekberg, 2007). Two BTBP ligands, $CyMe_4$-BTBP and C5-BTBP are seen in figure 6. This work has focused on the differences in rate of mass transfer of americium into long chained alcohol diluents using these two BTBP ligands in order to add new insights to the side group influence on the rate of mass transfer of americium into various diluents.

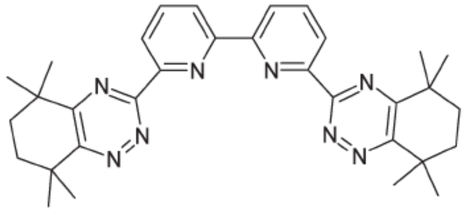
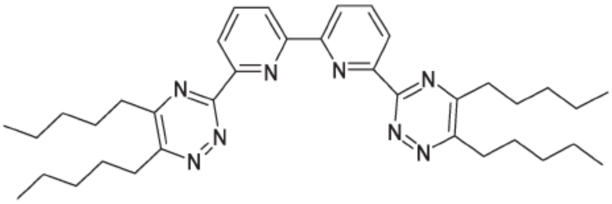



Figure 6. Molecular structures of CyMe$_4$-BTBP (left) and C5-BTBP (right).

3.3.2 TBP

TBP is an O-donor that extracts tetra and hexavalent actinides (Warf, 1949; Anderson, 1960). The ligand is an “oldie but goldie” that has served its purpose in the PUREX process for several years. A thorough review of the technology and applications of TBP has been made by Schulz and Navratil (1989). However, using TBP as a part in a reprocessing solvent has some drawbacks; the molecule contains a phosphorous atom, making it hard to incinerate without producing secondary wastes and it also has a troublesome degradation chain. For example, the TBP molecule decomposes during hydrolysis and radiolysis into, for example dibutyl phosphoric acid, which can interfere with extraction processes (Shevchenko, 1958). A group of ligands that have been pointed out as possible successor for TBP is aliphatic amides (Nair, 1994) and especially the extractant di(2-ethylhexyl) butyramide (DEHBA) (Prabhu, 1997). The DEHBA has also been tested for initial extraction studies in a cyclohexanone based solvent containing CyMe$_4$-BTBP (Aneheim, 2012). Both TBP and DEHBA are shown in figure 7. In order to add important new information concerning the choice of one of the ligands, the focus for this work has been the rate of mass transfer in the two different solvent compositions, as this is important knowledge when designing the process plant. The metal concentration has also been increased in order to investigate how this affects the rate of mass transfer of americium and europium as well as influence their separation.

The water as well as nitric acid solubility in organic phases containing TBP was studied as early as 1956 by Alcock et al (1956) and also later by Davis (1961). Alcock et al showed that the extraction of nitric acid into TBP was through the formation of 1:1 compounds as $TBP \cdot HNO_3$. At low (or zero) concentration of nitric acid a H_2O:TBP complex was suggested to be formed in the organic phase. The nitric acid extraction of n,n-dialkylamides has been investigated by Condamines (1988) and Prabhu (1997). Prabhu did show that DEHBA does extract nitric acid to some extent, however, when cyclohexanone based extraction systems containing TBP and DEHBA were investigated by Aneheim et al (Aneheim, 2012), it was shown that in a cyclohexanone based system the nitric acid extraction from both of the ligands could be neglected, as cyclohexanone itself extracts around 0.65 M nitric acid from a 3 M nitric acid solution.

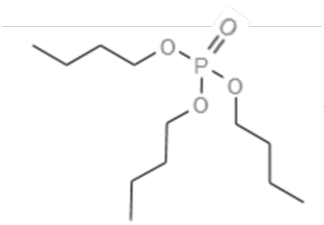
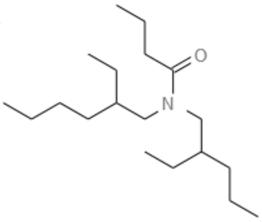



Figure 7. Molecules of TBP (left) and DEHBA (right)

3.4 Diluents in solvent extraction

3.4.1 Diluent classification

One of many useful classification schemes for liquids has been described by Marcus (Rydberg, 2004B). Using the molecules' capability of forming hydrogen bonds Marcus defines five classes of liquids. Class one includes liquids capable of forming three-dimensional networks of strong hydrogen bonds (water, polyamino alcohols, hydroxi acids etc.). Class two includes other liquids that have both active hydrogen atoms and acceptor atoms, however, rather than three dimensional networks they prefer forming chainlike oligomers (primary alcohols, carboxylic acids, primary and secondary amines etc.). Long chained primary alcohols are included in class two. These are denoted "protic" or "protogenic" substances. Class three includes polar aprotic substances. They are solvents containing donor atoms, but no active hydrogen atoms (ethers, ketones, aldehydes etc.). Class four covers liquids composed of molecules containing active hydrogen atoms, but no donor atoms (e.g. chloroform). Finally, class five includes liquids without hydrogen bonding capability and without donor atoms, such as hydrocarbons, carbon disulfide and carbon tetrachloride.

The classification described by Marcus results in different outcomes relevant to solvent extraction. For example; the diluents in class 1 are highly soluble in water and could not be used as organic phases, while diluents from class 3, ketones and aldehydes, sometimes react directly with inorganic compounds, forming extractable organic complexes. In many extraction systems the aqueous phase is aggressive towards the diluent and the extractant. This may affect both the long term behaviour of the extraction system as well as subsequent processes such as scrubbing or stripping. In this work a thermodynamic study has been made using a diluent from class 2 (hexanol) and class 3 (cyclohexanone and nitrobenzene). Nitrobenzene and cyclohexanone was both used as nitrobenzene is aromatic and therefore different compared to cyclohexanone.

3.4.2 Demands on diluents

The following demands on a suitable diluent for partitioning purposes in the present context are summarised by Retegan (Retegan, 2009)

- It should only contain carbon, hydrogen, oxygen and nitrogen (i.e. fulfill the so-called CHON principle) in order to be totally incinerable. This is important for nuclear systems where the secondary waste shall be reduced (Madic, 1998)
- It should have a high flash point and preferably a high boiling point.
- It should have a low freezing point as well as low water solubility and a low chemical transformation rate with water, extractants and solute.
- The formation of a third phase should be avoided, thus diluents should not form third phases during loading conditions.
- A diluent used in a partitioning process should be resistant towards irradiation and, if not, be regenerable.
- The density shall be different compared to that of the aqueous phase. Here it should be added that this shall be the case also during metal loading conditions.

In this work, two diluents have been investigated as alternatives to cyclohexanone as diluent in a GANEX solvent based on TBP and $CyMe_4$-BTBP, as it has a quit low flash point and high water solubility. It also degrades in contact with acid. The alternative diluents used in this work are hexanol and hexanoic acid. Hexanol was used since it is a cheap alternative to cyclohexanone. Hexanol belongs to the group of long chained alcohols from which octanol has been used in similar process development (Modolo, 2013; Wilden, 2013). Hexanol was used instead of octanol as it has been shown that $CyMe_4$-BTBP is more soluble in hexanol compared to octanol (Ekberg, 2010), the data from Ekberg (2010) is shown in table 2. Hexanoic acid was used since it has an easy degradation chain during irradiation and a low solubility in water.

Table 2. Solubilities (mM) of CyMe4-BTBP (and C5-BTBP) in hexanol and octanol at 293 K (data retrieved from Ekberg, 2010).

	Hexanol	±	**Octanol**	±
$CyMe_4$-BTBP	10	2.1	8.2	2.8
C5-BTBP	26.6	2.2	23.9	2.1

3.4.3 Density of Diluents in solvent extraction

The density of the diluent in a solvent extraction system is of major importance when designing a process (Retegan, 2009). The difference in density between the phases is of primary importance for achieving a phase separation when utilising gravity or centrifuging. Instead of separating perfectly (left in figure 8) two phases with similar density will have the phases beside each other (middle figure 8) or sometimes split into three phases (right figure 8). It should also be noted that the density of the phases can be dramatically altered after phase contact due to mutual (partly) solubilities of the two phases. The extraction process can also affect the phase density due to the variations in metal concentration in the two phases. One example is that the aqueous phase contains a high metal concentration before extraction, while during extraction the metals are transferred into the organic phase, thus increasing the density of the organic phase and simultaneously decreasing the density of the aqueous phase. If not treated accordingly, such a scenario can cause a phase inversion or problems in achieving phase separation. A calculation of the influence of the metal extraction on the density in a Chalmers GANEX solvent can be made by summarizing the feed concentrations and the extraction for the various elements. Feed concentrations for a typical PUREX feed can be found in Appendix A. In order to adjust such a calculation to a 2nd cycle GANEX feed it should be noted that only 0.103 mg * L^{-1} of the initial uranium is left after the 1st GANEX cycle (Miguirditchian, 2008).

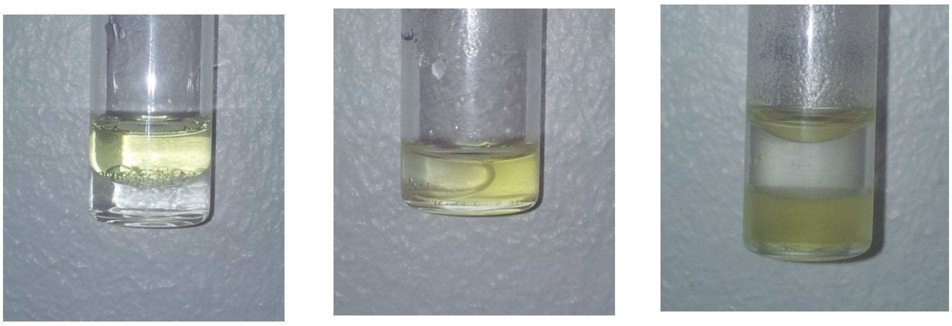


Figure 8. Left: solvent extraction system with different densities. Middle and right: Different appearances of solvent extraction systems where the aqueous and organic phases have similar densities.

3.4.4 Interfacial tension in solvent extraction systems

Interfacial tension can be compared with the more commonly used term surface tension. They both describe the force needed to create a surface of a liquid in a special environment (Hiemenz, 1997). Molecules in the surface of a liquid have higher interaction forces with each other compared to the molecules within the bulk of the liquid, due to the imbalance in energy when not being totally, but only partly, surrounded by neighbors. This creates a stretching-like layer of molecules that allows for example water striders to walk on lakes and (carefully placed) needles to float on water, even though the density of the needle is higher than that of the water. Surface tension mostly refers to a surface in contact with air, while interfacial tension refers to an interface between two liquids, for example between an organic phase and water (Shaw, 1992), though the chemistry and physics in both cases is the same. A low interfacial tension in a solvent extraction system has the advantage that it increases the surface area during the extraction and can therefore speed up the rate of mass transfer in the process (Rydberg 2004A). However, a disadvantage is that a low interfacial tension can make phase separation difficult or slow. If, for example the extraction is performed using centrifuges, having short contact time and precise phase separation, a lower interfacial tension system can be preferred.

The surface or interfacial tension is easily reduced by the addition of surface active agents, surfactants. A surfactant is a molecule that has both a hydrophobic (water hating) and a hydrophilic (water loving) part. The most energetically beneficial way for a surfactant is to dissolve the hydrophobic part in oil (or towards air) while the hydrophilic part is dissolved within the water. Surfactants are therefore usually enriched at interfaces. The addition of a surfactant into a solvent extraction system decreases the interfacial tension in the system (Garner, 1953). However, Garner (1953) shows that the presence of a surface active agent could actually reduce the mass transfer coefficient. This was explained by an interaction between the solute and the surface active agent and by retardation of the diffusion of the solute across the interface. It should, however, be noted that this was a system where the surface active agent did not extract or contributed to the extraction. However, in a system where the extractant is the surface active agent the rate of extraction is assumed to increase with increased extractant concentration (Chaiko, 1989).

Two examples of surfactants are the TBP molecule and a “sibling” molecule to DEHBA, di(2-ethylhexyl)isobutyramide (D2EHIBA) (DEHBA and TBP are both shown earlier in figure 7). A study by Pathak (2009) shows that both D2EHIBA and TBP at ligand concentrations above 0.2 M reduce the interfacial tension in systems consisting of water/*n*-dodecane from 44.3 $mN*m^{-1}$ to less than 30 $mN*m^{-1}$. The effect is explained by ligand enrichment at the interface. However, the addition of TBP is shown to have a higher effect compared with the addition of D2EHIBA. The surface activity of the $CyMe_4$-BTBP is debateable with one study showning that the $CyMe_4$-BTBP is not surface active in an octanol/1 M nitric acid system (Lewis, 2012). However, in another study (Aneheim, 2013B), where the solvent is pure cyclohexanone $CyMe_4$-BTBP is shown to be surface active towards an aqueous phase containing 0.99 M $NaNO_3$, 0,01 M HNO_3. However, when 30 % TBP is added to the solvent, it is not (Aneheim, 2013B). One explanation for this variances is that the surface activity of the ligand varies with the diluent used.

3.4.5 Extraction kinetics

The rate of mass transfer in a solvent extraction system is one of the factors determining which type of equipment can be used in the process (Rydberg, 2004A). The mass transfer rate can either be controlled by one of the chemical reactions involved in the extraction reaction, i.e. kinetic regime, or as the rate of diffusion of various species through the bulk phases and the interfacial film (i.e. diffusional regime) (Rydberg, 2004C).

The rate of for example americium mass transfer from the aqueous into the organic phase can only be compared between different systems when using a set rate of phase contact or mixing, and can easily be estimated by measuring the distribution ratio versus the time of phase contact. Special techniques, such as a Lewis cell **(**Rydberg, 2004C**)** or a Nitsch cell (for example used by Geist et al (1999)) can reveal the rate determining step of the extraction. Different ways to facilitate the phase contact can be applied. Hand shaking or manual agitation of the phases is efficient compared to the standard mechanical devices used in this work. However, in order to achieve a substantial period of phase contact (upto weeks) it is more convenient to use mechanical devices.

3.5 Diluent and Solvent Effects in BTBP based extraction systems

3.5.1 Complex stoichiometry

When forming an extractable complex two CyMe$_4$-BTBP ligands are assumed to bind to one metal in cyclohexanone (SKB, 2009; Retegan, 2009B). However, analyzes in other diluents suggest that the diluent affects the ligand to metal ratio. In anisole and tetrachlorethane for example, the metal to ligand ratio is 1:1.5 (Nilsson, 2006B). These values are statistical mean values of all the complexes present in the system, and a value of 1.5 ligand per metal indicates that the system contains both 1:1 and 1:2 complexes. In the study by Nilsson (2006B), it was proposed that the 1:1 complexes are formed at low ligand concentrations, while at higher concentrations; 1:2 complexes are formed. Sufficient amounts of nitrate ions will contribute to the complex in order to neutralize the charge of the metal. In the case of americium and europium three nitrate ions will join the complex (Retegan, 2009B).

3.5.2 Process development studies

Cyclohexanone has earlier been used as Chalmers GANEX diluent (e.g. Aneheim, 2010; Aneheim 2011; Aneheim, 2012; Aneheim, 2013). Cyclohexanone dissolves CyMe$_4$-BTBP relatively well (16.8 mM at 293 K) (Ekberg, 2010) and offers fairly fast rate of mass transfer; equilibrium is reached after just 5 minutes of manual shaking, which can be compared with 15 minutes in nitrobenzene (Retegan, 2008). C5-BTBP also needs approximately 5 minutes of hand shaking for reaching extraction equilibrium in a cyclohexanone based system (Nilsson, 2006A). Unfortunately, cyclohexanone has a low flash point (44^{o}C) and high solubility in water (Riddick, 1970) and it degrades by for example ring cleavage (Singh, 1964) during radiation. It also degrades in contact with 4 M nitric acid (Aneheim, 2011). A possible oxidation of cyclohexanone has been addressed as another issue with this diluent. Such an oxidation is exothermal and is induced by nitrous acid. That issue in particular can be solved by adding a nitrous acid scavenger, sulfamic acid, to the system (Aneheim, 2012C). Because of the previously mentioned issues two alternative diluents have been screened during this work, hexanoic acid and the more well-known diluent hexanol. Long chained alcohols have traditionally been abandoned as process diluents because of slow extraction kinetics and its slow dissolution of CyMe$_4$-BTBP (45 minutes in an ultra-sound bath was needed to dissolve 10 mM) (Retegan, 2007B). Ultrasound has the disadvantage that it can possibly create over-saturated solutions containing precipitates that are so small that they cannot be seen by the eye, as well as destroy the ligands. It is therefore not used in this work. However, in similar systems based on CyMe$_4$-BTBP, the introduction of a phase transfer catalyst, DMDOHEMA, has been shown to increase the rate of mass transfer in octanol based solvents (Geist, 2006). The effect was explained by the surface active DMDOHEMA complexing the metal cation at the interface and transporting it into the organic phase, where the more thermodynamically favoured complex is formed. A $CyMe_4$-BTBP based extraction systems with an addition of TODGA as phase transfer agent is currently under investigation for a SANEX extraction (Modolo, 2013; Wilden, 2013). As TBP has been shown to be surface active in some solvents (Osseo-Assare, 1991; Pathak, 2009), this work has investigated whether the TBP addition in a GANEX formulation containing TBP and hexanol can decrease the time needed for reaching extraction equilibrium. Hexanoic acid was investigated as GANEX diluent because of its simple degradation chain during radiation; it decomposes into only carbon dioxide and pentane during γ-radiation (Russell, 1959) and it has a higher flash point, boiling point and lower solubility in water compared to cyclohexanone. The figures for the different diluents are listed together with the ones for hexanol in table 3. The flashpoints can be compared to that of kerosene, 38 ^oC (Sciencelab, 2014).

Table 3. Selected physical properties of cyclohexanone, hexanoic acid and hexanol.

	Cyclohexanone	**Hexanoic acid**	**Hexanol**
Flash p. (^{o}C)	64	102	63
Boiling p. (^{o}C)	156	205	148
Solubility in Aq. ($\%_{weight}$)	9.7[a]	0.96	0.666[c]
Aq solubility in ($\%_{weight}$)	5.35[a]	0.268[b]	6.82[c]

a Stephenson, 1992 (19.5 ^{o}C); b Oliveira, 2009 (one of several references) (20 ^{o}C); c Stephenson, 1984 (20 ^{o}C)

3.5.3 Properties of BTBP extraction systems

Several physical parameters of the diluent have been possible to correlate with the extraction of actinides as well as lanthanides in BTBP based extraction systems. These properties include the dipole moment (Retegan, 2007) and the solubility of the ligand in the diluent (Ekberg, 2010). One particular study shows that the extraction of americium using C5-BTBP is higher when using shorter chained alcohols (i.e. hexanol) than longer chained alcohols (i.e. decanol) as diluents. This was explained by the higher alcohol (OH-) group concentration in the shorter chain length alcohol based systems (Nilsson, 2006B) increasing the distribution ratio. The time of phase contact needed for reaching extraction equilibrium has been shown to be different for different diluents i.e. (Retegan, 2007). The chemical reactions at the interface have been reported as being the rate determining step in the extraction of americium by $CyMe_4$-BTBP (Geist, 2012) and by its “sibling extractant” BTP (Weigl, 2006). In order to be able to draw any conclusions concerning the correlation of the distribution ratios and the rate of extraction, the time needed to reach extraction equilibrium for the C5-BTBP ligand in the long chained diluents used by Nilsson (2006B) has been investigated. The $CyMe_4$-BTBP ligand was also investigated in the same diluents and a qualitatively comparision between the two ligands was performed.

It has previously been shown that the extraction of americium and europium in cyclohexanone when using C5-BTBP, is entropically driven (Nilsson 2006). In addition, the distribution ratios of americium and europium when using $CyMe_4$-BTBP in a diluent mixture of cyclohexanone and TBP have been investigated. The latter system has a completely different extraction behaviour; the entropy change in the system during extraction is negative. (Aneheim, 2012C) (table 4), this difference can perhaps be explained by different solvent compositions, with the latter one containing 30 volume % TBP. The thermodynamics of the extractions of americium and europium using CyMe$_4$-BTBP in cyclohexanone have also been studied using an aqueous phase containing 0.5 M NaNO$_3$ and 0.5 M with similar results (SKB, 2005). In order to add new data concerning the americium and europium extraction using the CyMe$_4$-BTBP extractant into different diluents, a study is performed within this work that investigates the thermodynamics of extraction of americium and europium into cyclohexanone, hexanol and nitrobenzene based solvent.

Table 4. Thermodynamic parameters for the extraction of americium(III) and europium(III) by C5-BTBP in cyclohexanone[a] and a by CyMe$_4$-BTBP in mixture of cyclohexanone (70%) and tributylphosphate (30%)[b].

	ΔH [kJ •mol^{-1}]	**±**	**ΔS [J • (K • mol)$^{-1}$]**	**±**	**Diluent**	**Ligand**
Am	-28.8	2.4	36.7	7.7	Cyclohexanone	C5-BTBP
Eu	-19.3	1.9	25.7	6.2	Cyclohexanone	C5-BTBP
Am	-30	1.7	-5.3	5.7	Cyclohexanone+TBP	CyMe$_4$-BTBP
Eu	-19.9	0.6	-9.2	2.1	Cyclohexanone+TBP	CyMe$_4$-BTBP

a Nilsson, 2006A; b Aneheim, 2012C

3.6 Uncertainties

The uncertainties in three or more replicates of an experiment (for example 3 or more distribution ratios) is calculated using the formula for standard deviation

Equation 5

$$s = \sqrt{\frac{\sum (X - M)^2}{n - 1}}$$

where s is the standard deviation, M is the mean value of all samples and n is the number of samples.

Another way of estimating uncertainties in distribution ratios is with a so-called cause and effect diagram, where all the uncertainties are estimated/measured and calculated for the final distribution ratio. Such a diagram is shown in figure 9. The uncertainty in a distribution ratio from this diagram is assumed to be around 3 % (Andersson, 2005). But it should be noted that in some cases the uncertainty can be higher than 3 % why standard deviation calculations are preferable used.

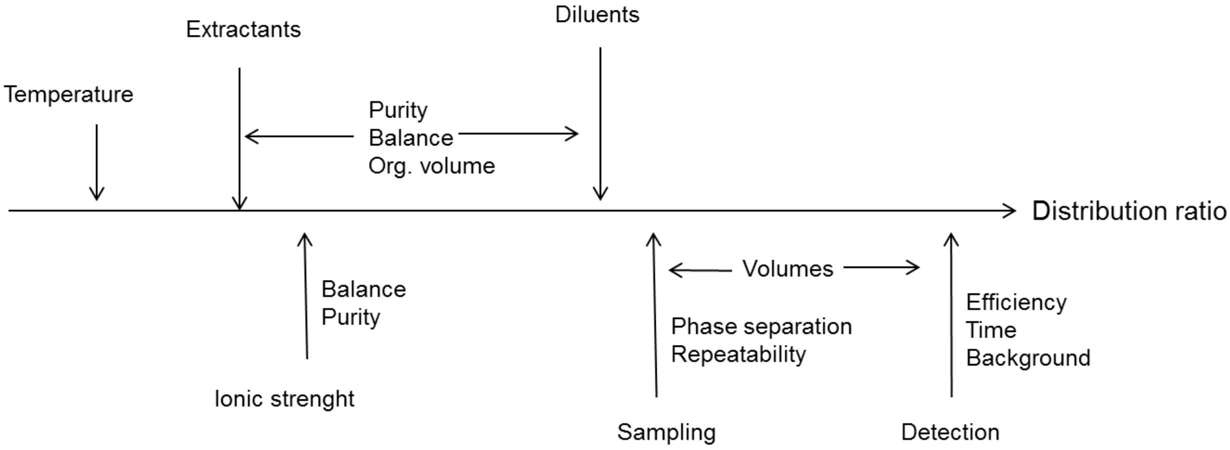


Figure 9. Cause and effect diagram showing the uncertainties in a distribution ratio.

The uncertainty in the measurement of a distribution ratio can be calculated through error propagation of the measurement uncertainty in the respective phases according to

Equation 6

$$\sigma_D = D_M \sqrt{\left(\frac{\sigma_{Rorg}}{R_{org}}\right)^2 + \left(\frac{\sigma_{Raq}}{R_{aq}}\right)^2}$$

where σ_D is the measurement uncertainty in the distribution ratio, D_M is the distribution ratio of the metal, σ_{Rorg} and σ_{Raq} is the uncertainty in the measurement of the respective phases (given by the computer program or calculated from the count rate and the time of the measurements) and R_{org} and R_{aq} are the counts in the respective phases.

3.7 Stability constants

The extraction of americium and europium (denoted as M) using x numbers of $CyMe_4$-BTBP and 3 NO_3^- can be described as

Equation 7

$$\mathrm{M^{3+} + 3NO_3^- + x\overline{BTBP} \rightleftharpoons \overline{M(NO_3)_3BTBP_x}}$$

K_{Ex}, for the extraction is then given by

Equation 8

$$\mathrm{K_{ex} = \frac{\overline{\{M(NO_3)_nBTBP_x\}}}{\{M^{n+}\} * \{NO_3^-\}^3 * \{\overline{BTBP}\}^x}}$$

In cases where the activities of the nitrate as well as ligand species are constant throughout the extraction, for example if the metal concentration is very low compared to that of the nitrate and ligand concentrations a constant can be calculated

Equation 9

$$\mathrm{\{NO_3^-\}^3 * \{\overline{BTBP}\}^x = constant = C}$$

x can thus be found by slope analysis. If it is assumed that the concentrations equals to the activities (which is described by Ekberg (2006)), K_{Ex} can be expressed through the distribution ratio as

Equation 10

$$\mathrm{K_{ex} = \frac{\overline{\{M(NO_3)_nBTBP_2\}}}{\{M^{3+}\} * C} = D_M * \frac{1}{C}}$$

If the enthalpy and entropy of the extraction are constant at the temperature interval used for the experiment, the enthalpy and entropy of extraction can then be obtained by using the Van´t Hoff´s equation

Equation 11

$$\ln \mathrm{K_{ex}} = -\frac{\Delta \mathrm{H_R^0}}{\mathrm{RT}} + \frac{\Delta \mathrm{S_R^0}}{\mathrm{R}}$$

where ln K_{Ex} is the natural logarithm of the extraction constant, $\Delta H^0{}_R$ is the standard enthalpy change, $\Delta S^0{}_R$ is the standard entropy change, R is the molar gas constant and T is the temperature. The enthalpy and entropy may thus be obtained by a linear fit of ln K versus T^{-1}.

3.8 Kinetic comparisons

Since the interfacial area is not known during the batch experiments performed in this work, no calculations of the interfacial flux can be made (such a calculation can be seen for example in Weigl (2006)). However, in order to qualitatively compare the rate of extractions in extraction systems (at constant rate of mixing, volume as well as temperature) the percentage of the equilibrium distribution ratio at time t is given by

Equation 12

$$\% \text{ of } \mathrm{D_{eq}} = \frac{\mathrm{D_t}}{\mathrm{D_{eq}}} * 100$$

4 EXPERIMENTAL

4.1 Preparation of Solutions

All the chemicals (label, purity) used in this work are listed in Appendix B. For dissolving ligands in the organic phase the vials were sometimes put in a warm water bath and then shaken by hand in order to speed up the ligand dissolution. However, the temperature increase was only used in papers V and VI. It should be noted that to dissolving the ligand in a higher temperature than the one used for the extraction experiments can cause oversaturated solutions containing micro precipitations. However, the concentrations used in this work are within the solubility limit at the temperature of extraction, as described by Ekberg et al (2010).

4.2 Extraction Experiments

4.2.1 Extractions

3.5 mL glass vials were used for the extraction experiments. Due to the partly mutual solubility of some solvents, the aqueous and organic phases were pre-equilibrated with the corresponding phase before phase contact was established (this was not needed when the solvent was hexanoic acid, flourobenzene, chlorobenzene or benzene). The phase contact during the extraction was facilitated in a mechanical shaker (IKA, VIBRAX VXR, 1500 rpm) with vials places horizontally and the temperature was controlled using a thermostated circulating water bath. The organic and aqueous phase volumes were always equal. The phases were separated by gravity or by centrifuging. Trace amounts of nuclides, normally volumes of 2-10 µl (^{241}Am: 0.47 M Bq ml^{-1}; ^{152}Eu: 23 k Bq ml^{-1}, not carrier free, total europium concentration is 7.6 ± 4 x 10^{-2} µM; ^{235}U: 84.88 % enrichment, total uranium concentration is 40 mM; ^{238}Pu: 10 M Bq ml^{-1} and ^{244}Cm: 0.23 M Bq ml^{-1}) were added to the extraction systems.

4.2.2 Kinetic studies

For the investigations of extraction kinetics 1 ml of each phase was contacted. Samples were withdrawn after 5, 10, 20, 40 and 60 minutes (sometimes also after 90 and 120 minutes) of phase contact. Two different BTBP ligands (C5-BTBP and CyMe$_4$-BTBP) were used to investigate the ligand side group influence on the rate of extraction of americium. In the side group study, several long-chained alcohol diluents were used as diluents (hexanol, heptanol, octanol, nonanol and decanol), in addition a mixture of 50 % hexanol and 50 % heptanol was investigated and the aqueous phase was 0.99 M $NaNO_3$, 0.01 M HNO_3. For process application studies the same experimental procedure was used, however, the solvents were based on cyclohexanone and TBP or DEHBA and the focus was process application. Inactive europium (0.01 mM, 0. 1 mM and 1 mM) was added to the aqueous phases (4 M HNO_3) in order to reveal it influence on the rate of mass transfer of americium and europium and their separation factor. In order to achieve a deeper understanding concerning the influence of TBP addition, CyMe$_4$-BTBP concentration and acidity on the rate of americium mass transfer, as well as to investigate the possibility of using hexanol as a GANEX diluent, 4 M HNO_3 was used as aqueous phase.

4.2.3 Thermodynamic investigations

In order to continue the thermodynamic work and further explore the diluent effect on the thermodynamic parameters of the extractions, a study of the extraction of americium and europium using $CyMe_4$-BTBP was conducted. The diluents investigated were hexanol, nitrobenzene and cyclohexanone. The temperature was varied using the same thermostatic water bath. The phase contact time was sufficient for reaching extraction equilibrium (over night for hexanol and nitrobenzene and 2 hours for cyclohexanone). This time to reach equilibrium was verified before the experiments were initiated. The aqueous phase was 0.99 M $NaNO_3$, 0.01 M HNO_3 in the case of hexanol and cyclohexanone, but only 0.25 M $NaNO_3$ in the case of nitrobenzene (the lower nitrate concentration was used in order to decrease the otherwise very high distribution ratios).

4.3 Analyzes

4.3.1 Gamma spectroscopy (HPGe)

A high purity germanium detector was used to measure the amounts of americium, europium (Ortec, Gamma Analyst GEM 23195 or Ortec, GEM 15180-S). The europium was analysed using gamma energy of 121.8 keV and the americium using gamma energy of 59.59 keV.

4.3.2 Liquid scintillation counting (LSC)

LSC (Davis 1414 WinSpectral) was used to analyse plutonium, curium, americium and europium content, americium and europium only when separated and in that case only if a high efficiency was needed. Potential quenching was ruled out by standard addition investigations or by control measurements using HPGe (for example with americium). The used scintillation liquids were (or can be) treated according to (Löfström-Engdahl, 2014).

4.3.3 Interfacial tension measurements

The interfacial tension measurements were performed using the du Nouy ring method using a microbalance (SIGMA 701). The ring was lowered into the aqueous phase so that it was totally immersed. The organic solvent was carefully added on top of the aqueous phase. The microbalance then measured the interfacial tension automatically by slowly lowering the sample. Impurities, such as surface active molecules and solutes easily contaminate surfaces and interfaces, and affect the surface/interfacial tension. The presence of impurities was therefore ruled out by measuring the surface tension of the pure solvents or water towards air and comparing it with data from literature. No traces of contaminants were found in any of the constituents. No emulsion was observed during the measurements, probably due to the careful handling of samples. The uncertainties are calculated from duplicates and 3-5 technical replicates/sample. The temperature for the density as well as interfacial tension measurements was 20-22◦C.

For paper I and II, it was assumed that the $CyMe_4$-BTBP or C5-BTBP addition would not influence the interfacial tension, in accordance Lewis et al (2012). It actually might do (Aneheim, 2013B), but during the circumstances used for the experiments in this work, no enrichment was assumed to take place. This assumption could be made since Lewis used an octanol phase and did not observe any surface activity. In the study performed with alcohols in this work, the data from Lewis (2012) was assumed to be more relevant compared to that in cyclohexanone, since long chained alcohols is more chemically similar to octanol than cyclohexanone. In addition to this assumption, the amounts of the ligands held in stock were too small to be used for these, quite voluminous, measurements.

4.3.4 Density measurements

The density measurements were performed using a density probe and a microbalance (SIGMA 701). The probe was calibrated using mq-water and the density at the temperature in the room (20-22◦C).

5 RESULTS & DISCUSSION

5.1 Density measurements

The densities of several extraction systems have been measured in order to investigate their suitability as process alternatives. The densities before and after pre-equilibration in the systems based on cyclohexanone, hexanoic acid and hexanol are listed in table 5. As can be seen, the cyclohexanone based system is the system that is most affected by the saturation with the respective phases. This is not surprising since pure cyclohexanone also has the highest solubility of water (previously shown in table 3). However, hexanoic acid is the diluent that is least influenced by the phase contact, which is beneficial.

In future process development, it should be stressed that the densities must also be checked after metal extraction. A theoretical calculation of the weight of the extracted actinides was made according to the PUREX feed (Appendix A), adjusted for the removal of the bulk uranium described by Miguirditchian (2008). The distribution ratios used for the calculations are retrieved from paper V (hexanol) and VI (hexanoic acid) and from Aneheim et al (2010) for cyclohexanone and are seen in table 6. The whole calculation is seen in Appendix C.

No extraction of fission and corrosion/activation products was taken into account as the greatest influence on the density will be from the extracted actinides, since they are the heaviest elements. Calculating with solely actinides implies that a “worst density scenario” is applied. The concentration of actinides is higher in the feed (13 mM) than the ligand concentration in the organic phase (10 mM), but it was here assumed that no limitation of the extraction due to the low ligand concentration took place. The reason for this was that the only actinide that could be a problem according to ligand concentration is plutonium, as it has a concentration of around 12 mM in the feed, however, as the plutonium is also extracted by the TBP this was not assumed to be a limitation. If, however, it was to be a problem in a future process the feed can easily be diluted. The rest of the actinides (Cm, Am, Np and U) sums up to less than 1 mM. The weights of the extracted actinides are listed in table 7. As can be seen the influence on the density by metal extraction is quite low, the values sums up to 3.2 mg * ml^{-1} (cyclohexanone), 3.1 mg * ml^{-1} (hexanol) and 3.04 mg * ml^{-1} (hexanoic acid).

Comparing the influence on the density of metal extraction with the influence from nitric acid extraction and water dissolution (for example the organic phase: Δ 54 mg * ml^{-1} (cyclohexanone), Δ 13 mg * ml^{-1} (hexanol) and Δ 4 mg * ml^{-1} (hexanoic acid)) clearly shows that the influence on the density is much larger from the pre-equilibration of the two phases compared with that from the metal extraction, except in hexanoic acid. The aqueous phase is only slightly affected by the contact with the hexanol based solvent, the density decreases with 5 mg * ml^{-1}. After being in contact with the cyclohexanone based solvent, the density of the aqueous phase decreases with 28 mg * ml^{-1}. No influence was seen after the contact with the hexanoic acid based solvent.

Table 5. Density data for three GANEX formulations before and after pre-equilibriation. The systems contains 30 % TBP, 70 % of the diluents respectively. The theoretical calculated values are seen in the parenthesis. The aqueous phase is 4 M nitric acid.

	Density (g x ml^{-1})	**Density (g x ml^{-1})**	**Stdev.**	**Density (g x ml^{-1})**	**Stdev.**
	Cyclohexanone	**Hexanoic acid**		**Hexanol**	
Organic phase					
Non pre-equilibrated	0.951	0.940	$5*10^{-4}$	0.861	$3*10^{-3}$
Pre-equilibrated	1.005	0.944	$2*10^{-3}$	0.874	$1*10^{-3}$
Aqueous phase					
Non pre-equilibrated	1.130	1.130	$5*10^{-4}$	1.127	$1*10^{-3}$
Pre-equilibrated	1.102	1.128	$2*10^{-3}$	1.122	$1*10^{-3}$

Table 6. Log D´s for actinides and the lanthanide europium in the three GANEX formulations containing 30 % TBP, the respective diluent and CyMe$_4$-BTBP. The curium data in cyclohexanone is yet unpublished and therefore not collected from Aneheim, 2010.

	Hexanol	**stdav.**	**Cyclohexanone**[a]	**Stdav.**	**Hexanoic acid**	**stdav**
Am	1.50	0.10	2.19	$6*10^{-3}$	0.04	0.01
Pu	1.68	0.08	2.31	$5*10^{-4}$	1.88	0.44
U	0.14	0.01	1.03	$8*10^{-3}$	0.44	0.04
Cm	1.22	0.06	2.03		0.21	0.11

a Aneheim, 2010

Table 7. Calculated amounts (g x L^{-1}) extracted of the respective actinides in the various solvents used in this study.

	Cyclohexanone	**Hexanol**	**Hexanoic acid**
Pu	2.970	2.924	2.946
Am	0.159	0.155	0.084
Cm	0.025	0.024	0.016
Uranium after stage 1	$9.42*10^{-5}$	$5.97*10^{-5}$	$7.57*10^{-5}$
SUM	3.154	3.103	3.046

The densities of the solvent systems containing TBP or DEHBA in cyclohexanone were also investigated but from another angle; in this study the amount of TBP and DEHBA was varied and the influence on the densities was measured after (and before) pre-equilibration with the aqueous phase in order to rule out the influence on the densities of the dissolution of the respective phases in the various systems (paper III). Linear combination of the densities for the pure cyclohexanone and the TBP or DEHBA could have been used. However, three different concentrations were measured in order to rule out if something unexpected, such as a density increase, was taking place when mixing the cyclohexanone with the TBP or DEHBA. As this was performed before subsequent interfacial tension measurements, 1 M nitric acid was used as aqueous phase (the interfacial tension in a system based on cyclohexanone and 4 M nitric acid is too low to measure). The densities of all solvent compositions, except the pure DEHBA, increase through the saturation with the aqueous phase (figure 10). This density increase shows that water and nitric acid are extracted.

It can be concluded from the data in this study that DEHBA does not extract water or nitric acid so much that it affects its density, at least not upto the detection level used here (some g * L^{-1}), but TBP does. For future studies it can be noted that one possible way of decreasing the density of the solvent could be to use DEHBA instead of TBP as extractant for the tetra- and hexavalent actinides.

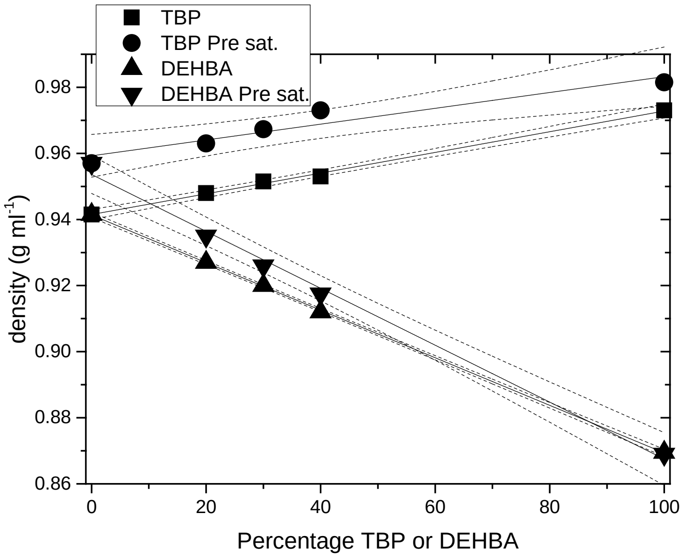


Figure 10. Densities of organic phases consisting of cyclohexanone and the given percentage TBP or DEHBA before and after pre-equilibration with 1 M nitric acid.

5.2 Interfacial tension measurements

Interfacial tension has been measured in several systems in order to reveal its influence on the rate of mass transfer as well as to disclose physical data concerning the systems.

The interfacial tension in long-chained alcohol based extraction systems (hexanol, heptanol, octanol, nonanol, decanol and a mixture of hexanol/heptanol (50 % each)) towards a 1 M nitrate aqueous phase (0.99 M $NaNO_3$, 0.01 M HNO_3) was measured. The interfacial tension clearly increases as the chain length of the alcohol increases (figure 11). This is assumed to be a function of the increasing hydrophobicity of the diluent as the chain length increases. The plateau could perhaps be explained by the fact that the influence of the hydrophilic alcohol-group on the alcohol plays less role when the chain gets longer and the diluents then shows increasingly similar behaviour. This trend could possibly have been predicted from literature data; however, the complete system with this series of diluent and diluent mixture including the aqueous phase has not to the authors knowledge been described earlier and was therefore investigated here as it was going to be used for further solvent extraction experiments.

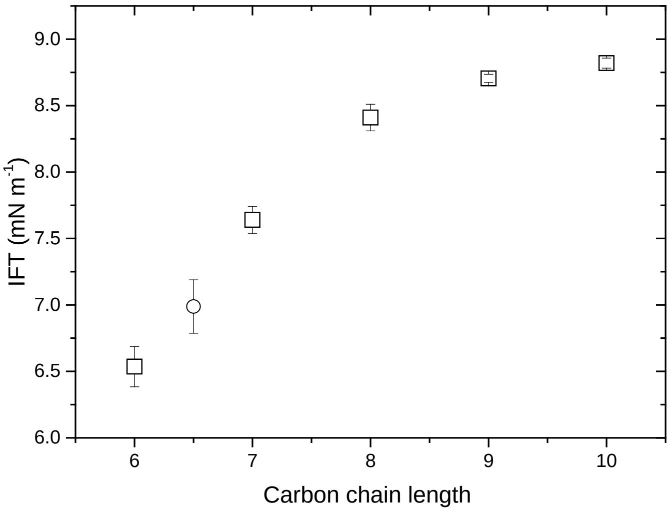


Figure 11. Interfacial tension (IFT) between long chained alcohols (6.5 is the 50/50 % mixture of hexanol and heptanol) and 0.99 M $NaNO_3$, 0.01 M HNO_3. The uncertainties in the IFT are standard deviations based on three samples.

Pure cyclohexanone is completely mixable with 4 M nitric acid. Therefore, in order to be able to do any estimate of the influence of TBP and DEHBA on the interfacial tension in a cyclohexanone based system, the acid concentration was in this case 1 M. Cyclohexanone has a very low interfacial tension (1.90 mN m^{-1}) towards the 1 M nitric acid, and the interfacial tension is increased by the addition of both TBP and DEHBA (figure 12). The interfacial tension at 20 % and 30 % TBP or DEHBA is similar in the two systems. Nevertheless, higher concentrations of TBP and DEHBA show that addition of TBP does not increase the interfacial tension as much as the addition of DEHBA. Compared to Pathak et. Al (2009) the effect here is different. Instead of lowering the interfacial tension, the addition of TBP and DEHBA to cyclohexanone, increase it. This is because of the various features of *n*-dodecane, used in the Pathak study, compared to cyclohexanone. *N*-dodecane is very hydrophobic, while cyclohexanone is not. In the *n*-dodecane system the TBP and D2EHIBA are the more surface active species that are readily adsorbed at the interface, while in the cyclohexanone system, the diluent is more surface active. In the pure TBP and DEHBA systems, DEHBA has significantly higher interfacial tension towards the aqueous phase than the pure TBP has. This is in agreement with the data from Pathak, indicating that TBP is more surface active than DEHBA and D2EHIBA. One possible explanation can be the bulkiness of the branched amides, while the TBP, not as bulky, can easily have its long straight carbon chains dissolved in the organic solvent. Since both these studies are performed at same nitrate concentration they can be compared (it shall be noted that the cyclohexanone study was performed in 1 M nitric acid and the alcohol study in 0.99 M $NaNO_3$, 0.01 HNO_3). It can be seen that pure cyclohexanone has much lower interfacial tension compared to the alcohols, and since earlier studies it has been shown that cyclohexanone has much faster extraction kinetics (Retegan, 2008; Nilsson, 2006A). The study was therefore developed with extraction experiments in the alcohol series in order to investigate whether the interfacial tension difference could explain the difference in extraction rate in a series of diluents

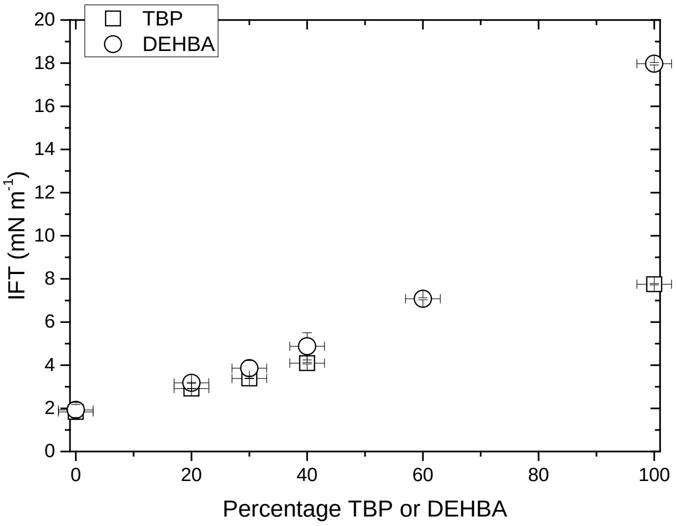


Figure 12. Interfacial tension (IFT) between cyclohexanone based systems containing various percentage of TBP and DEHBA and 1 M nitric acid. The uncertainties in the IFT are standard deviations based on three samples. The uncertainties in the percentage TBP/DEHBA are 5 %.

5.3 Rate of extraction

The time needed to reach extraction equilibrium was investigated in both CyMe$_4$-BTBP and C5-BTBP based extraction system, using long chained alcohols as diluents. The long chained alcohols used were the same as for interfacial tension measurements. A correlation of the interfacial tension versus the time for extraction was made, in order to determine whether the interfacial tension affects the rate of extraction and can explain the differences in rate of extraction when changing the diluent. In the studies, the rate of americium mass transfer from the aqueous into the organic phase is defined as the difference in the distribution ratio per second (paper I) or the number of atoms per second (paper II). However, first the equilibrium distribution rations for the two ligands in the different diluents were measured.

The equilibrium distribution ratios achieved in the long chained alcohols are plotted as a function of the dielectric constant of the diluents in figure 13. The CyMe$_4$-BTBP complexes have a higher distribution ratio in longer chained alcohols (decanol, nonanol and octanol) compared with the C5-BTBP complex. However, in shorter chained diluents (hexanol, “50/50” and heptanol), the complexes seem to be similarily extractable

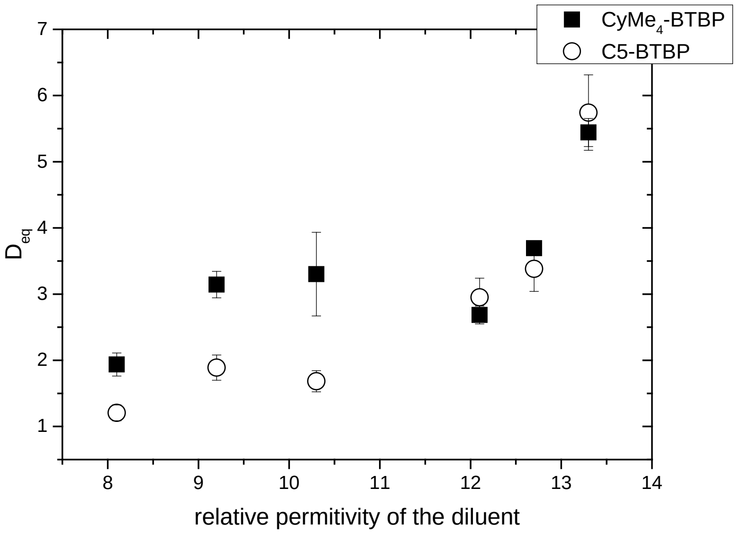


Figure 13. The equilibrium distribution ratios for americium using CyMe$_4$-BTBP and C5-BTBP as ligands in the various alcohols. The uncertainties are standard deviations based on three or more samples. The aqueous phase is 0.99 M, $NaNO_3$, 0.01 M HNO_3, the organic phase is 5 mM ligand in the respective diluents.

The extraction as a function of time in the long chained alcohols is very slow relative to for example, the one in cyclohexanone (Retegan, 2008 (CyMe$_4$-BTBP); Nilsson, 2006A, (C5-BTBP)). Alcohols were therefore chosen as diluents for this. It is not possible to investigate a very fast system, such as the cyclohexanone one, since sampling cannot be made at such short times scales using the, in this work, available techniques. A typical graph of the distribution ratios as a function of time is a smooth curve that initially increases linearly. As the phase contact proceeds the distribution ratios level out until the equilibrium distribution ratio is established. In this work, the linear part of the extraction is used in order to compare the extraction systems. The various distribution curves retrieved from the different systems are seen in figure 14.a (hexanol and “50/50”), figure 14.b (heptanol and octanol) and figure 14.c (nonanol and decanol).

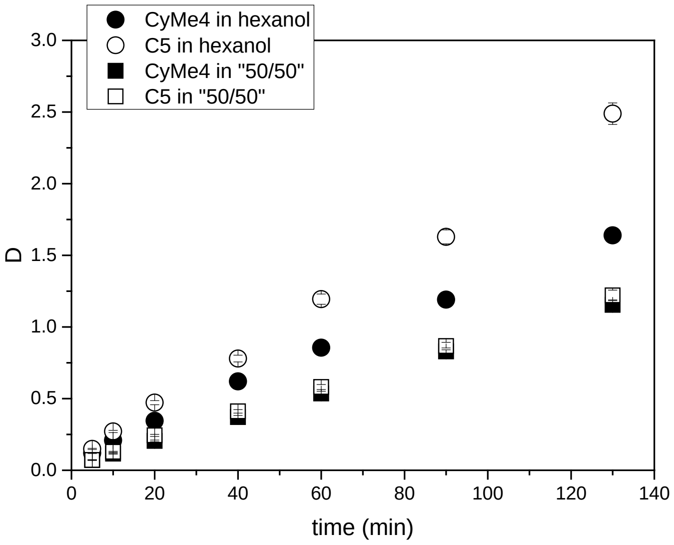


Figure 14.a The distribution ratios for americium using CyMe$_4$-BTBP and C5-BTBP as a function of time in hexanol and "50/50". The uncertainties are standard deviations based on three or more samples (CyMe$_4$-BTBP) or based on counting statistics (C5-BTBP). The aqueous phase is 0.99 M $NaNO_3$, 0.01 M HNO_3, the organic phase is 5 mM ligand in the respective diluents.

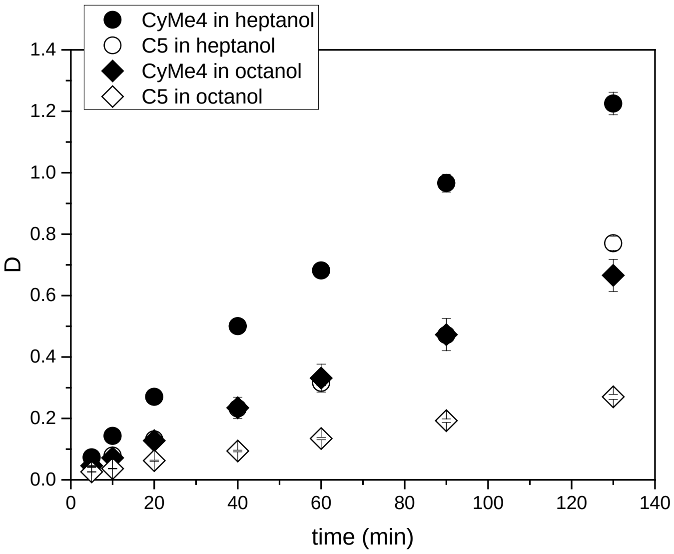


Figure 14.b The distribution ratios for americium using CyMe$_4$-BTBP and C5-BTBP as a function of time in heptanol and octanol. The uncertainties are standard deviations based on three or more samples (CyMe$_4$-BTBP) or based on counting statistics (C5-BTBP). The aqueous phase is 0.99 M $NaNO_3$, 0.01 M HNO_3, the organic phase is 5 mM ligand in the respective diluents.

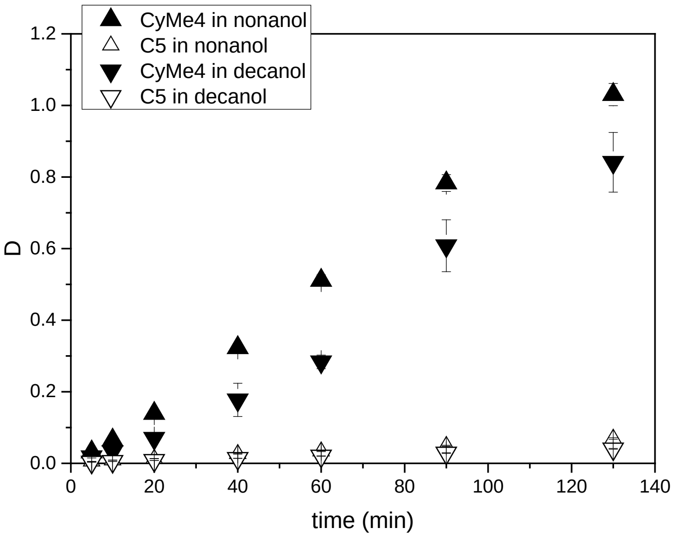


Figure 14.c The distribution ratios for americium using CyMe$_4$-BTBP and C5-BTBP as a function of time in nonanol and decanol. The uncertainties are standard deviations based on three or more samples (CyMe$_4$-BTBP) or based on counting statistics (C5-BTBP). The aqueous phase is 0.99 M $NaNO_3$, 0.01 M HNO_3, the organic phase is 5 mM ligand in the respective diluents.

5.4 Rate of mass transfer versus interfacial tension

The rate of transfer for americium is shown as the dD/dt normalized with respect to the equilibrium distribution ratios in figure 15. As can be seen, the values calculated for the C5-BTBP series decreases as the interfacial tension is increased. However, the CyMe$_4$-BTBP series does not show this behaviour. Instead the data is scattered. In the C5-BTBP system the interfacial tension seems to be a possible way of explaining differences in rate of americium mass transfer in different alcohol diluents. However, that is not the case in the CyMe$_4$-BTBP system.

The study by Geist et al (2012) also shows that an increased specific interfacial area (the area / volume) increased the rate of mass transfer from the aqueous into the organic phase in a CyMe$_4$-BTBP system based on octanol. It is therefore surprising that this CyMe$_4$-BTBP study not shows such trend. This could indicate that the CyMe$_4$-BTBP influences the organic solvent on such a way that the droplets are more monodispersed when going through the alcohol series compared to the C5-BTBP extractant, maybe through being surface active. As seen earlier (in Ekberg, 2010), C5-BTBP is more soluble in the long chained alcohols hexanol and octanol compared to CyMe$_4$-BTBP, maybe the solubility decreases the surface activity of the ligand and hence the effect is not seen in that system. However, that is only a speculation and needs further studies.

In the study by Geist (2012) it was also indicated that an increased nitric acid concentration increased the rate of mass transfer. Benay et. al (2011) proposed that the CyMe$_4$-BTBP was protonated and because of that enriched at the interface, increasing the rate of extraction. Due to this the hexanol system containing CyMe$_4$-BTBP was further investigated, with for example extractions at various nitric acid concentrations. It was also investigated whether hexanol could be a suitable successor to cyclohexanone.

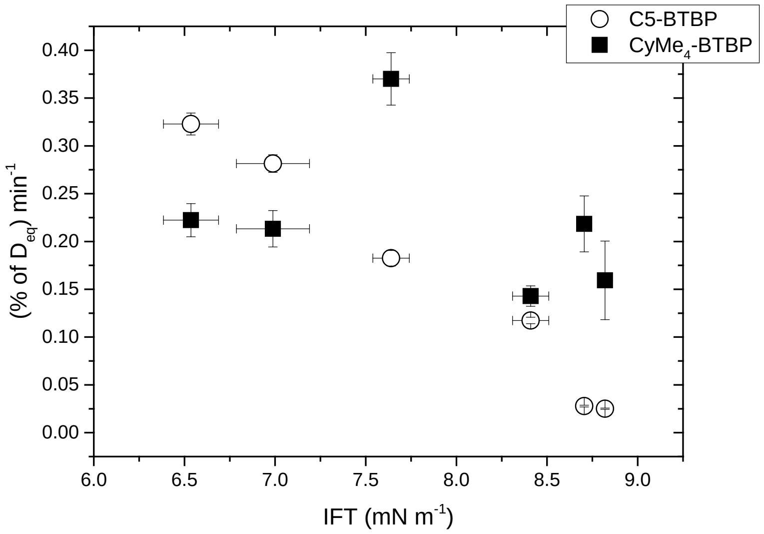


Figure 15. The rate of mass transfer in the $CyMe_4$-BTBP and C5-BTBP systems as afunction of the interfacial tension. The uncertainties are from the linear regressions. The aqueous phase is 0.99 M $NaNO_3$, 0.01 M HNO_3, the organic phase is 5 mM ligand in the respective diluents. For the interfacial tension measurements no ligand was present during the measurements.

5.5 Hexanol as a possible GANEX diluent

A study was performed on hexanol in order to determine whether it could be a possible replacement for cyclohexanone. The aqueous phase used was therefore 4 M nitric acid (in most experiments).

5.5.1 The influence of TBP, CyMe$_4$-BTBP and nitric acid concentrations on the rate of extraction

In order to ascertain whether TBP can influence the rate of mass transfer in a similar way to those phase transfer agents (DMDOHEMA and TODGA) extractions at different TBP concentrations in hexanol were performed (paper V). All the systems reached extraction equilibrium after 40-60 minutes of phase contact and no differences in the rate of extraction could be observed (figure 16). The equilibrium distribution ratios are increased by adding TBP; $D_{Am}=17 \pm 1.8$, in 30 % TBP, $D_{Am}=9.3 \pm 0.6$ in 10 % TBP and $D_{Am}=6.8 \pm 0.05$ in pure hexanol. One possibility is that the TBP coordinates into the complex, making it more hydrophobic, thereby increasing the distribution ratio. A slope analysis of the equilibrium distribution ratios (figure 17) shows that the americium:CyMe$_4$-BTBP complex is a 1:2 complex regardless of the addition of TBP. This could indicate that the TBP coordinates in the outer sphere of the metal. It has actually, been shown in a study by Lundberg et al (2013) that a solvent molecule can bind in the outer sphere of the CyMe$_4$-BTBP europium complex and in the system used here the concentration of TBP is so high that it may be seen as a part of the solvent and not only as a ligand. The alternative is that the TBP does not coordinate at all. No such coordination indicates that the higher distribution ratios in TBP containing solvents are due to solvent effects.

The concentration of CyMe$_4$-BTBP was varied in the next series of experiments. It was clearly observed that the higher the concentration, the faster the extraction equilibrium was reached (figure 18), which is in agreement with Geist (2012), showing that the rate of the extraction of americium is first order with respect to CyMe$_4$-BTBP. The 10 mM CyMe$_4$-BTBP solution reached extraction equilibrium after 40 minutes of phase contact, after 60 minutes the 4.4 mM solution also established equilibrium. The 1.1 mM solution had not reached equilibrium after 60 minutes of phase contact. Finally, the influence of nitric acid on the rate of extraction was tested. The results were inconclusive due to large uncertainties in the measurements (figure 19), but it was revealed that the only system that had reached extraction equilibrium after 60 minutes was the one with the highest concentrated nitric acid (4 M). From this it was concluded that the main constituent in the increased rate of mass transfer in this GANEX solvent was the higher nitric acid concentration, not the TBP addition.

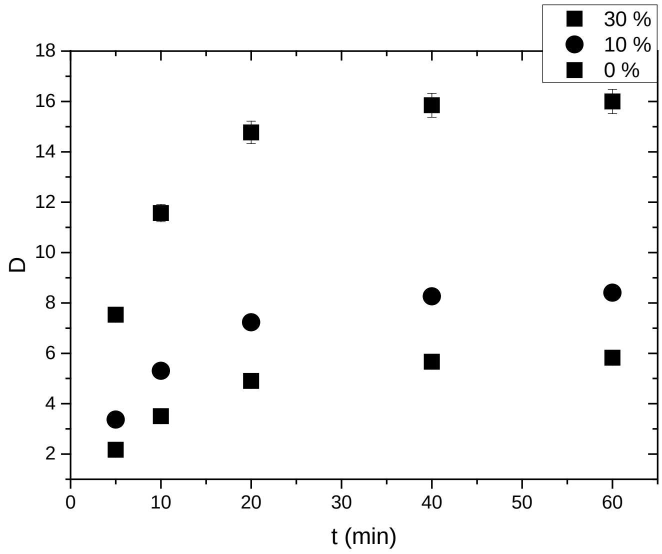


Figure 16. Americium extraction as a function of time into solvents containing various TBP concentrations. The organic phase is hexanol, 10 mM CyMe$_4$-BTBP and various TBP concentrations, the aqueous phase is 4 M nitric acid. The uncertainties are standard deviations and are in some cases smaller than the sample points, hence cannot be seen.

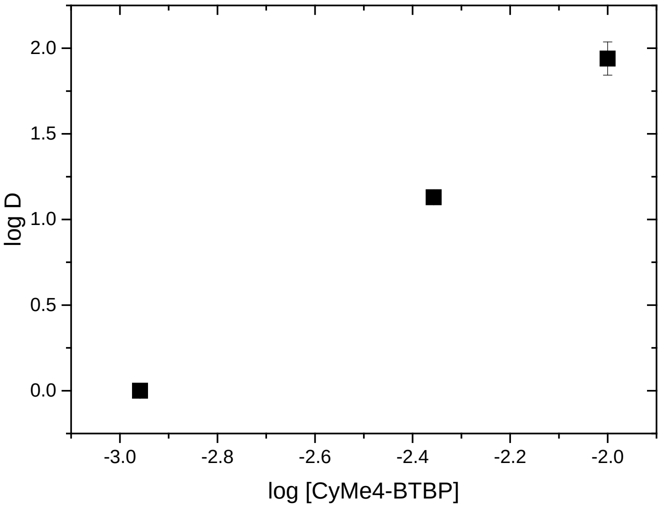


Figure 17. The equilibrium distribution ratios of americium. Uncertainties are standard deviations. The organic phases are hexanol containing 1.1 mM, 4.4. mM and 10 mM CyMe$_4$-BTBP and all solvents contain 30 % TBP. The aqueous phase is 4 M nitric acid. The slope between the data points is 2.

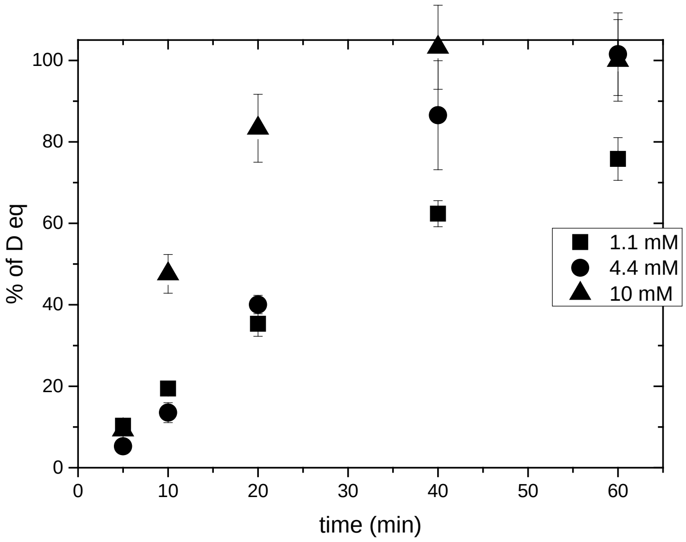


Figure 18. Americium extraction as a function of time into solvents containing various CyMe$_4$-BTBP concentrations. The organic phase is hexanol, 30 % TBP and various CyMe$_4$-BTBP concentrations; the aqueous phase is 4 M nitric acid. The uncertainties are standard deviations.

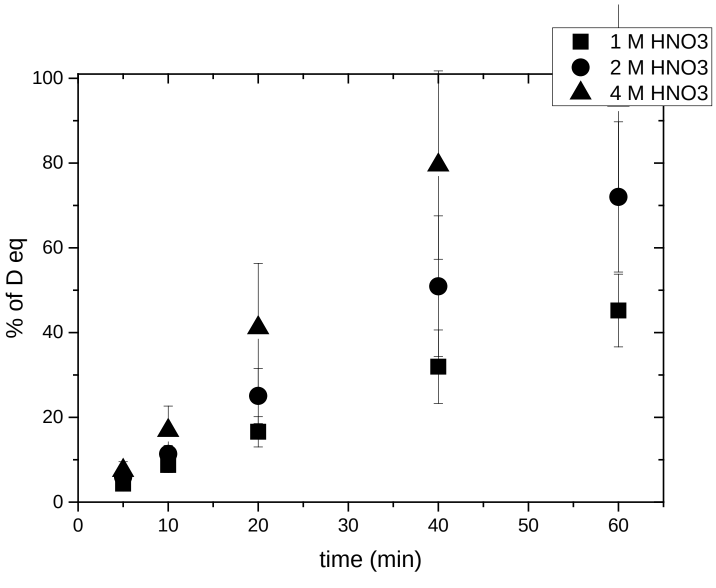


Figure 19. The extraction of americium as a function of phase contact time. Uncertainties are standard deviations and propagated through the normalisation. The organic phases are hexanol and 5 mM CyMe$_4$-BTBP. The aqueous phases are 1, 2 or 4 M nitric acid.

5.6 The influence of metal concentration on the rate of extraction

The system based on $CyMe_4$-BTBP, cyclohexanone and TBP was investigated with respect to time of phase contact and metal concentration in order to see whether the metal concentration influenced the time needed for reaching extraction equilibrium in the system as well as the $SF_{Am/Eu}$ (Paper III and IV). The system contained different concentrations of inactive europium (0.01, 0.1 and 1 mM) and was investigated with respect to the time needed to reach extraction equilibrium for both americium and europium in order to see how much the rate of mass transfer was influenced by the europium concentration.

5.6.1 The influence of metal concentration on the rate of extraction

In the TBP based system there is a difference between the various aqueous phases in the rate of mass transfer of europium, even though the equilibrium distribution ratio is similar (figure 20). The highest europium concentration gives the lowest distribution ratios before reaching the extraction equilibrium (i.e. it is slower). The intermediate concentrated aqueous phase gives the intermediate distribution ratios while the lowest concentration gives the highest (i.e. it is the fastest). This is probably because of the fact that a higher number of europium ions need to be extracted to reach a given distribution ratio when a higher number of metal ions are present in the system. This indicates that the equilibrium distribution ratios are not affected by initial concentrations of europium up to at least 1 mM, even though the rate of mass transfer is affected.

Earlier it has been seen in a cinnamalaldehyde system that europium actually reached extraction equilibrium faster compared to americium, while in a p-anisaldehyde system the rate of mass transfer of europium was slower compared to that of americium. This variation was explained by catalytic effects of the diluent or by differences in the concentration of europium and americium in the spike solution (Retegan, 2007B). The concentration of europium in the standard solution was therefore measured in this study and was seen to be approximately $7 * 10^{-6}$ M. Since this solution is often diluted by at least 100 times the final concentration of europium in the extraction systems is very low and the concentration difference is assumed not to be responsible for the different rates of mass transfer of americum and europium.

The americium extraction also shows a difference in the rate of mass transfer when comparing the different aqueous phases (figure 21). The americium reaches distribution ratios of 30-50 regardless of the metal content in the aqueous phase in less than 5 five minutes after initiating the phase contact. When the phase contact time increases and the americium starts to reach its equilibrium distribution ratio (around D=40) after around 20 minutes of phase contact, there seems to be competition between the ions, where the distribution ratio of americium is slowly suppressed. One exception is in the highest concentrated solution, which shows lower distribution ratios from the beginning of the extraction. This indicates that competitive extractions is taking place, however, the trend is a bit surprising as the europium metal concentration in the lowest concentrated solution is 0.01 mM and the distribution ratio of europium is only around 0.5. This rends a metal concentration in the organic phase of around 0.003 mM. By assuming that 2 ligands bind to every metal it is shown that more than 99.9 % of the ligand is still free. This shows that the finding is explained by something else than competitive extraction.

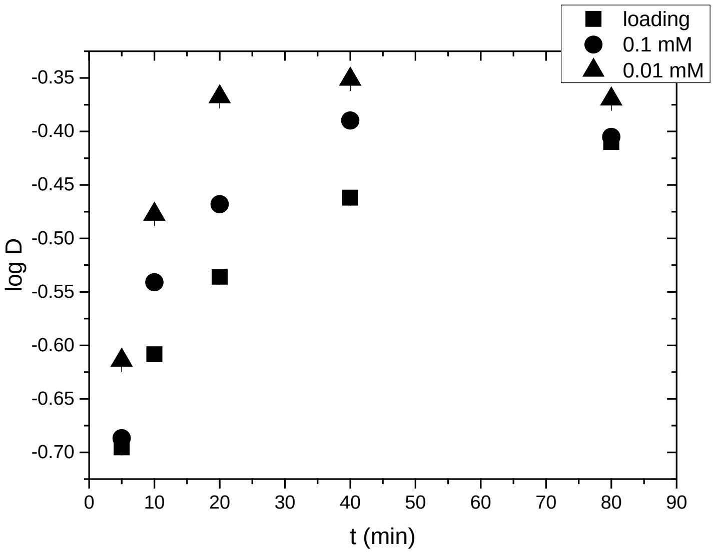


Figure 20. The extraction of europium from 4 M nitric acid by a solvent comprising of 10 mM CyMe$_4$-BTBP, 30 % TBP and 70 % cyclohexanone. The three series correspond to different concentrations of inactive europium in the aqueous phases. The uncertainties in the distribution ratios are 3 % and cannot here be seen behind the sample points

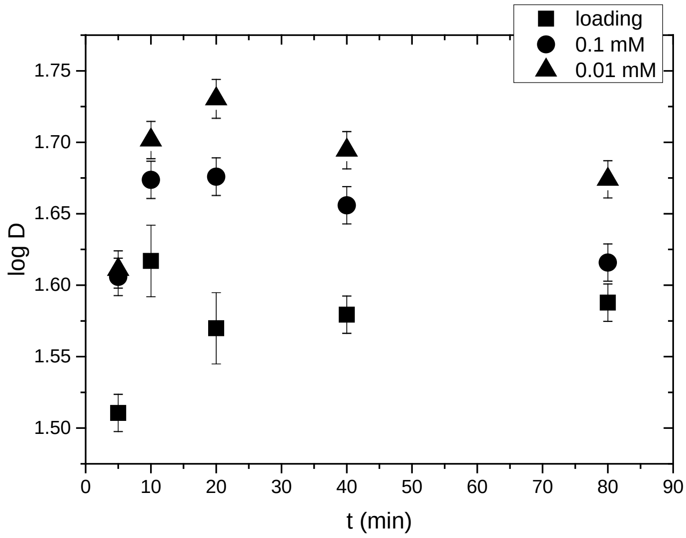


Figure 21. The extraction of americium from 4 M nitric acid by a solvent consisting of 10 mM CyMe$_4$-BTBP, 30 % TBP and 70 % cyclohexanone. The three series correspond to different concentrations of inactive europium in the aqueous phases. The uncertainties in the distribution ratios are 3 %.

5.6.2 The influence of metal concentration on the $SF_{Am/Eu}$

A comparison of the separation factors as a function of time was made between the TBP/DEHBA and cyclohexanone based solvents..

The separation factor ($SF_{Am/Eu}$) in both the solvents containing DEHBA and TBP decreases as the phase contact is prolonged regardless of the metal content in the aqueous phase (figure 22). The separation factors in the TBP based solvents are slightly lower than those achieved in the DEHBA based solvent. The decrease in separation factor as a function of time is due to the fact that americium reaches extraction equilibrium faster than europium. This is an important and new discovery, which shows that it would be beneficial for the separation of americium and europium to use a short phase contact time when designing a plant. A short contact time can be achieved in for example a centrifuge and such equipment could thus be a possible choice of technique for a future GANEX process plant.

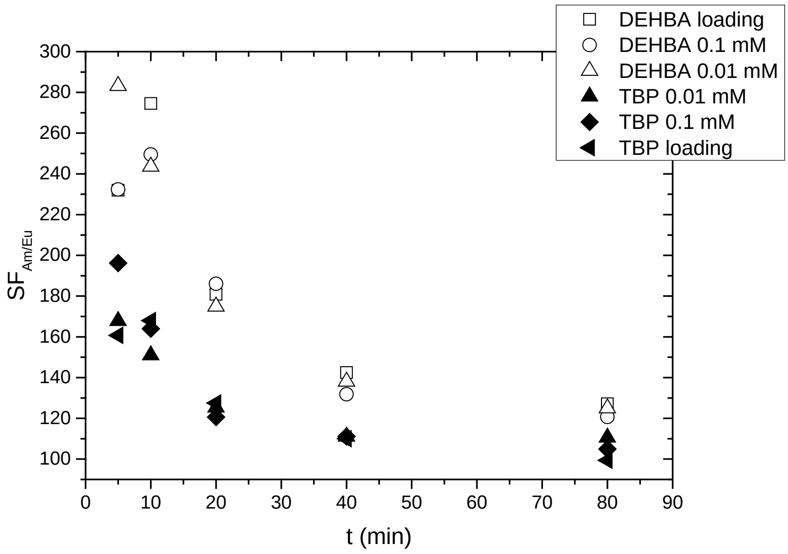


Figure 22. The $SF_{Am/Eu}$ as a function of time in the solvent compositions (10 mM $CyMe_4$-BTBP in 30 % TBP and 70 % cyclohexanone and 10 mM $CyMe_4$-BTBP in 30 % DEHBA and 70 % cyclohexanone) used throughout this study. The various series correspond to various concentrations of inactive europium in the aqueous phase.

5.7 Thermodynamic investigations

5.7.1 Initial experiments

In order to acquire some basic as well as data relevant for the process a study of the thermodynamics of americium and europium extractions was made into three different diluents (cyclohexanone, hexanol and nitrobenzene). Slope analyses were also performed and compared with literature data in order to reveal the complex stoichiometry's in the various diluents.

Analyses of the distribution ratios versus the ligand concentration were made in the three diluents (cyclohexanone, hexanol and nitrobenzene) for americium as well as for europium. Earlier data (SKB, 2005) suggest that two ligands are bound to every metal ion in cyclohexanone, however, the experiment was repeated to verify this claim. In the earlier study, the samples were manually shaken, making a phase contact time longer than 60 minutes hard to achieve. Phase contact was automated in the present study, making it possible to achieve longer phase contact and control the temperature. The equilibrium distribution ratios for americium in hexanol (D_{Am}= 4.70 ± 0.14 (5 mM CyMe$_4$-BTBP)) and cyclohexanone (D_{Am}= 4.61 ± 0.15 (5 mM CyMe$_4$-BTBP)) were found to be similar; except at low ligand concentrations were the extraction is higher into cyclohexanone. In the case of nitrobenzene the equilibrium log D value is orders of magnitude higher compared to the other two diluents. The high distributing ratio in nitrobenzene has been presented previously (Retegan, 2007B), however, no clear explanation for this has been given. Therefore, in order to investigate whether the high distribution ratios obtained in nitrobenzene is due to conjugation between the π-electrons in the diluent molecules and the π-electrons in the ligand, extractions were made using chlorobenzene, fluorobenzene and benzene as diluents. However, the distribution ratios are very low for both nuclides in all the three diluents (table 8). Another possible explanation is that the high relative permittivity of nitrobenzene, also seen in table 8, separates one or several nitrate ions from the rest of the extracted complex. Such a separation would increase the lipophilicity of the complex and thereby increase the distribution ratio through increased solvation of the complex. This theory that has recently been suggested is also strengthened by laboratory result (Ekberg, unpublished work).

Table 8. The extraction of americium and europium using 7 mM CyMe$_4$-BTBP in chlorobenzene, fluorobenzene and benzene. The aqueous phase is 0.99 M NaNO$_3$, 0.01 M HNO$_3$ and the extractions are performed in room temperature (293-295 K). The extractions using nitrobenzene were made at lower CyMe$_4$-BTBP concentration, 5 mM.

Diluent	**Relative permittivity**	**D_{Am}**	**Stdev.**	**D_{Eu}**	**Stdev.**
Benzene	2.275[a]	$15•10^{-3}$	$5•10^{-5}$	No extraction	
Fluorobenzene	5[b]	$10•10^{-2}$	$3•10^{-4}$	$9•10^{-4}$	$3•10^{-5}$
Chlorobenzene	5.62[a]	$13•10^{-2}$	$4•10^{-4}$	$6•10^{-3}$	$3•10^{-4}$
Nitrobenzene	34.82[a]	>100		>1	

a Riddick, 1970; b VCD, 2014

5.7.2 Complex stoichiometry

The slope analysis for the americium as a function of ligand concentration in cyclohexanone gives a slope of 1.9 ± 0.05 while in the case of europium the slope was 1.35 ± 0.07 (figure 23). The difference between the two ions indicates that the stability of the (1:2) complex is stronger in the case of americium than in that of europium where the (1:1) seems to dominate. The trend is similar for hexanol; the slope is lower for europium than for americium. In hexanol the slope was 2.02 ± 0.03 for americium while for europium the slope was 1.67 ± 0.10 (figure 24). This may be explained by the fact that the ligand has a higher affinity for americium compared to europium and therefore favors the two ligand complexation of americium compared to europium. In the case of nitrobenzene, the slopes were respectively 1± 0.10 and 1.1 ± 0.10 for americium and europium (figure 25) and no difference is observed between the elements. When the slope is not an integer the system contains mixtures of several stoichiometrically different complexes, no thermodynamic calculation for the extractions can consequently be made. This is the case for the europium extraction in cyclohexanone and hexanol.

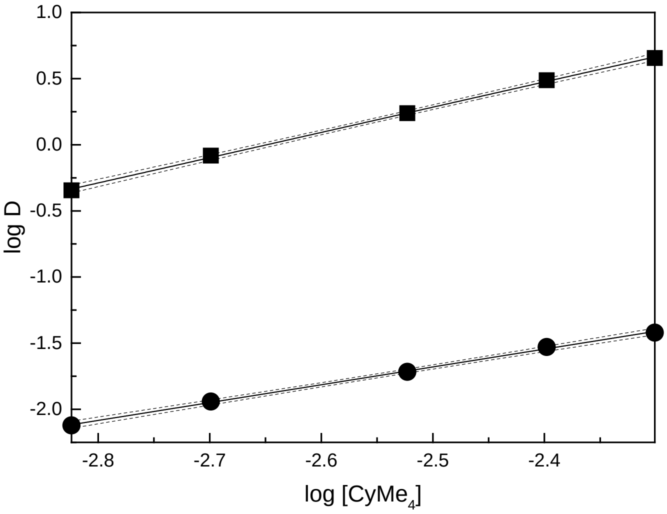


Figure 23. The log D for americium (–■–) and europium(–●–) as a function of the CyMe$_4$-BTBP concentration in the extraction system containing cyclohexanone as diluent. The aqueous phase is 0.01 M HNO_3, 0.99 M $NaNO_3$. The slopes were 1.9 ± 0.05 for americium while in the case of europium the slope was 1.35 ± 0.07. The dotted lines show the 95 % confidence interval of the linear regressions. The R^2 values for the linear regressions are 0.999 for the americium series and 0.999 for the europium series.

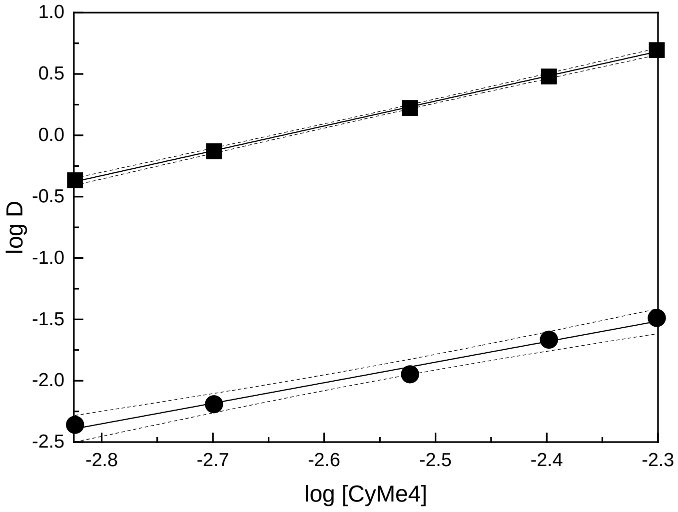


Figure 24. The log D for americium (–■–) and europium(–●–) as a function of the CyMe$_4$-BTBP concentration in the extraction system containing hexanol as diluent. The slope is 2.02 ± 0.03 for americium while for europium the slope is 1.67 ± 0.10. The aqueous phase is 0.01 M HNO_3, 0.99 M $NaNO_3$. The dotted lines show the 95 % confidence interval of the slopes. The R^2 values for the linear regressions are 0.999 for americium and 0.989 for the europium series.

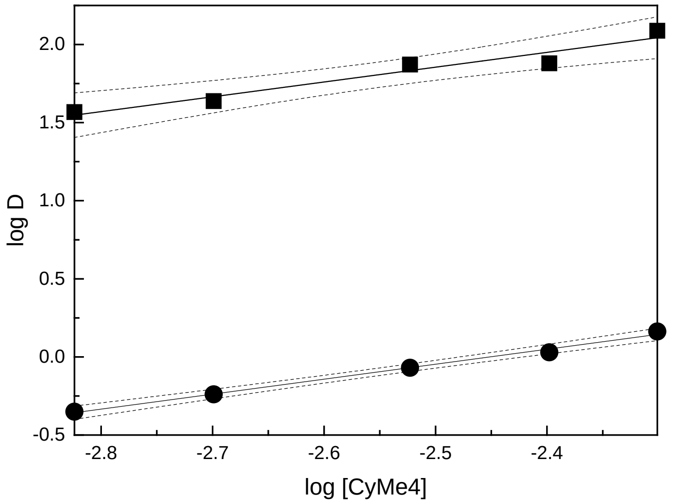


Figure 25. The log D for americium (–■–) and europium(–●–) as a function of the CyMe$_4$-BTBP concentration in the extraction system containing nitrobenzene as diluent. The slopes are 1± 0.10 and 1.1 ± 0.10 for americium and europium, respectively. The aqueous phase is 0.25 M $NaNO_3$. The dotted lines show the 95 % confidence interval of the linear regressions. The R^2 values for the linear regressions are 0.94 for americium and 0.99 for the europium series

5.7.3 Thermodynamic investigations

The distribution ratios for americium as well as for europium in all three diluents (cyclohexanone, hexanol and nitrobenzene) decrease with an increasing temperature. This means that the extraction reaction is exothermal. Literature data suggest that extractions using C5-BTBP in cyclohexanone (Nilsson, 2006A) as well as CyMe$_4$-BTBP into a cyclohexanone based solvent containing TBP (Aneheim, 2012C) also proceeds exothermically. The natural logarithm of the extraction constants for europium in the three diluents plotted as a function of the reciprocal temperature can be seen in figure 26 while the data for americium is seen in figure 27. The thermodynamic parameters calculated for the systems containing pure 1:1 or 1:2 complexes (americium in all diluents and for europium in nitrobenzene) are shown in table 9. The difference of the thermodynamics of the americium extraction using the C5-BTBP (Nilsson, 2006A) or the CyMe$_4$-BTBP into cyclohexanone is not as pronounced; only a slight difference is seen in the enthalpy of the extraction. The entropy in the hexanol and cyclohexanone based systems increase with extraction, while it is decreasing in the nitrobenzene system. In the study by Aneheim (2012C) the entropy change of the system was shown to be around zero or decrease as americium was extracted into a solvent containing cyclohexanone and TBP. In this system the difference in entropy seems to be more prominent when shifting diluent than when changing ligand side group.

Table 9. The thermodynamic parameters; ln K_{ex} (293.15 K), ΔH^0 and ΔS^0 for the extraction of the Am(III) and Eu(III) by 5 mM CyMe$_4$-BTBP from 1 M nitrate solution (0.01 M HNO_3, 0.99M $NaNO_3$) in cyclohexanone (only americium), hexanol (only americium) and nitrobenzene (americium and europium). The uncertainties in ΔH^0 and ΔS^0 are calculated from the linear regression and the 95 % confidence interval of the fitting. The uncertainties in the ln K are calculated by error propagation, using an uncertainty in 3 % of the distribution ratio and a 5 % uncertainty in concentrations of solutions.

		ln K_{Ex}	**ΔH^o**		**ΔS^o**	
Nuclide	**Diluent**	**(at 293 K)**	**[kJ • mol^{-1}]**	**+/-**	**[J x (mol • K)$^{-1}$]**	**+/-**
Am	**Cyclohexanone**	12.2	-21	1.8	30	6.0
	Hexanol	12.2	-19	1.1	40	3.6
	Nitrobenzene	11.2	-44	6.2	-60	20
Eu	**Nitrobenzene**	6.7	-26.2	3.8	-34	13

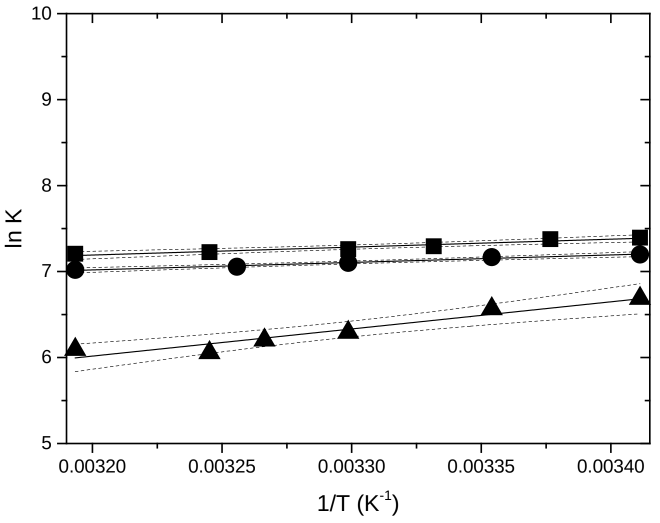


Figure 26. The Ln K_{Ex} for the extraction of europium by $CyMe_4$-BTBP into cyclohexanone (–■–, R^2=0.960), hexanol (–●–, R^2=0.982) and nitrobenzene (–▲– , R^2=0.974) as a function of temperature. The concentration $CyMe_4$-BTBP in all diluents is 5 mM and the aqueous phase is 0.01 M HNO_3, 0.99 M $NaNO_3$. The dotted lines show the 95 % confidence interval of the linear regressions.

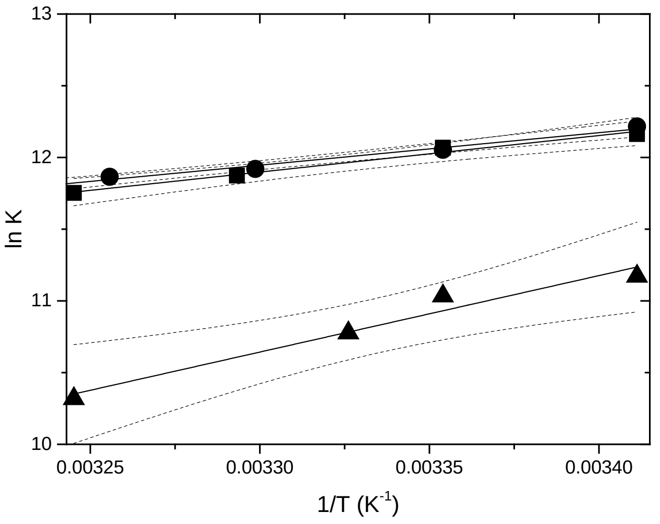


Figure 27. The Ln K_{Ex} for the extraction of americium by $CyMe_4$-BTBP into cyclohexanone (–■–, R^2=0.962), hexanol (–●–, R^2=0.990) and nitrobenzene (–▲–, R^2=0.986) as a function of temperature. The concentration $CyMe_4$-BTBP in all diluents is 5 mM and the aqueous phase is 0.01 M HNO_3, 0.99 M $NaNO_3$ (hexanol and cyclohexanone) and 25 M $NaNO_3$ (nitrobenzene). The dotted lines show the 95 % confidence interval of the linear regressions

5.7.4 The influence of the temperature on the $SF_{Am/Eu}$

Finally, a comparison of the separation factors as a function of temperature was made using the data from the thermodynamic study. The separation factors of americium from europium decrease with an increased temperature in the three diluents (figure 28). This is of importance during process development and indicates that during process development using a solvent containing $CyMe_4$-BTBP ligand, the temperature shall be kept low (around 20^{o}C) in order to favor separation.

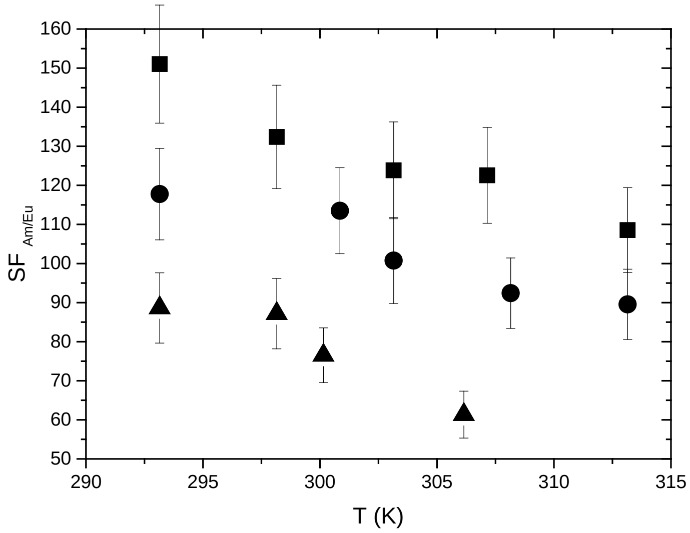


Figure 28. The $SF_{Am/Eu}$ in cyclohexanone (–■), hexanol (–●) and nitrobenzene (–▲–) as a function of temperature. The organic phase is 5 mM $CyMe_4$-BTBP in the various alcohols, aqueous phase is 0.99 M $NaNO_3$, 0.01 M HNO_3. The uncertainties are standard deviations.

6 CONCLUSIONS

“Hen som vill lägga ner kärnkraften får lägga på ett kol”

Different interfacial tension in extraction systems based on C5-BTBP and long chained alcohols as diluents is here suggested as one possible way to explain the differences of the rate of americium mass transfer in the same systems. An interesting observation was that the interfacial tension in the extraction systems is not of such an importance for the rate of americium mass transfer when the systems are based on $CyMe_4$-BTBP.

In this work it has been shown that the Chalmers GANEX solvents based on $CyMe_4$-BTBP, TBP or DEHBA and cyclohexanone can maintain the actinide/lanthanide separation even though the lanthanide concentration is as high as 1 mM. It was also shown that the highest separation factors are achieved at short phase contact times. This discovery is important when designing a process plant as this gives additional insight in which flows and extraction equipment that would be suitable for an upscaling of the selected process.

Concerning novel diluents for a Chalmers GANEX solvent based on TBP and $CyMe_4$-BTBP, both the investigated diluents, hexanol and hexanoic acid display a lower influence from the aqueous phase with respect to density compared to cyclohexanone. However, hexanoic acid did not work as a process diluent, since the extraction of americium and curium was much lower compared to that of plutonium. Hexanol would be a better choice, however, it does not either render as high extraction of actinides as the cyclohexanone based solvent does. This work stresses the importance of the density of a these Chamers GANEX solvents and in that respect, it is here pointed out that DEHBA can be preferred over TBP in a GANEX solvent that requires a decreased density, for example one based on FS-13.

It was shown that conjugation between the diluent and complexes did not explain the high extraction of americium into $CyMe_4$-BTBP systems based on nitrobenzene. One possible explanation suggested was that the high relative permittivity of nitrobenzene separates one or two or all nitrate ions from the rest of the extracted complex. Such a separation would increase the lipophilicity of the complex and thereby increase the distribution ratio through increased solvation of the complex. Thermodynamic parameters for the extraction of americium using $CyMe_4$-BTBP into three various diluents (cyclohexanone, hexanol and nitrobenzene) have been presented. It was not possible to calculate the parameters for europium in cyclohexanone and hexanol due to a mixture of 1:1 and 1:2 complexes in the systems. Concerning all these three diluents the extractions proceed exothermal. It was shown that best separation of americium from europium was achieved at low temperatures in all three diluents, which have completely different diluent properties. It can be summarized that for $CyMe_4$-BTBP systems it can probably be generalized for mostly diluents that it is important to keep the temperature constant in order to get comparable data as well as to use the actual process temperature also for batch experiments, as the extraction probably will be reduced when increasing the temperature and that a lower temperature of the process favors americium/europium separation.

7 FUTURE WORK

Work on optimizing the GANEX solvent should continue by searching for a more suitable diluent. As of today, phenyl trifluoromethyl sulfone is being screened and seems promising. It is important to then also carry out the investigations of temperature variations as well as metal loading and phase contact time. Enrichment of the CyMe$_4$-BTBP ligand as well as the C5-BTBP at the liquid-liquid interface can be investigated using interfacial tension measurements and compared to the data presented in this study.

The presence of separated complexes in nitrobenzene systems have already been investigated and confirmed (Ekberg, unpublished work). More in-depth investigations into the diluent effects when comparing cyclohexanone and hexanol remain as a future project. One recommendation would be to investigate the thermodynamics of the complexation (for example by using time resolved laser induced fluorescence spectroscopy) in order to split up the overall thermodynamics of extraction into smaller parts.

Finally, a thorough investigation of CyMe$_4$-BTBP systems and the rate of mass transfer of americium and europium in various diluents and TBP concentrations should be performed using for example Nitsch cells in order to rule out the differences between the different diluents. It would also be beneficial to understand why americium and europium have different rate of extraction.

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9 LIST OF ABBREVIATIONS

ACSEPT	Actinides recycling by SEParation and Transmutation (European project within the 7th Framework Programme)
ADS	Accelerator Driven Systems
BIMET	2S,2S)-4,4-(ethane-1,2-diylbis(sulfanediyl)) bis(2-aminobutanoic acid
BTBP	6,6´-bis(5,6-dialkyl-[1,2,3]triazine-3-yl)2,2´bipyridine
BTP	2,6-Di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine
C5-BTBP	6,6’-bis(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2’]-bipyridine
CHON	Carbon, hydrogen, Oxygen, Nitrogen
$CyMe_4$-BTBP	6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridine
D	Distribution ratio
DEHBA	N,N-di-2-ethylhexyl-butyramide
DEHiBA	N,N-di-(ethyl-2-hexyl)isobutyramide
DIAMEX	DIAMide EXtraction
DMDOHEMA	N,N´-dimethyl-N,N´-dioctylhexylethoxymalonamide
GANEX	Grouped ActiNide EXtraction
HPGe	High Purity Germanium detector
HTP	Hydrogenated TetraPropylen
HSAB theory	Hard and soft acid and bases
IAEA	International Atomic Energy Agency
ICRP	International Commission for Radiological Protection
IT/IFT	Interfacial Tension/InterFacial Tension
MOX	Mixed Oxide Fuel
OECD	Organization for Economic Co-operation and Development
P&T, S&T	Partitioning/Separation and Transmutation
PUREX	Plutonium Uranium Redox EXtraction
SACSESS	Safety on ACtinide SEparation ProceSeS (European project within the 7th Framework Programme)

SANEX	Selective ActiNide EXtraction
$SF_{A/B}$	Separation between species A/B
SKB	Swedish Nuclear Fuel and Waste Management Co.
TALSPEAK	Trivalent Actinide-Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TBP	Tri butyl phosphate
TODGA	N,N,N′,N′-Tetraoctyl Diglycolamide

10 LITERATURE

Adnet, Miguirditchian, Hill, Heres, Lecomte, Masson, Brossard, Baron, Development of new hydrometallurgical processes for actinide recovery: GANEX concept, proceedings of GLOBAL 2005, Tsukuba Japan, Paper No. 119, 2005

Alcock, Grimley, Healy, Kennedy, The extraction of nitrates by tri-n-butyl phosphate (TBP). Part 1.-The system TBP+ Diluent+ H_2O+ HNO_3, Transactions of the Faraday Society, 52, 1956

Anderson, Newton, Mass, Aspre, Richmond, Calif, Solvent Extraction Process for Plutonium, US Patent 2,924,506, 1960

Andersson, Extraction properties of some nitrogen-containing extractants and determination of nitrate complex formation for lanthanides and selected actinide using solvent extraction, thesis for the degree of doctor, Chalmers University of Technology, Chalmers Reproservice, Gothenburg, 2005

Aneheim, Ekberg, Fermvik, Foreman, Retegan,, Skarnemark, A TBP/BTBP-based GANEX Separation Process – Part 1: Feasibility, Solvent Extraction and Ion Exchange, 28, 2010

Aneheim, Ekberg, Fermvik, Foreman, Gruner, Hajkova, Kvivalova, A TBP/BTBP-based GANEX Separation Process - Part 2: Ageing, Hydrolytic and Radiolytic Stability, Solvent Extraction and Ion Exchange, 29, 2011

Aneheim, Ekberg, Foreman, Löfström-Engdahl, Mabile, Studies of a Solvent for GANEX Applications Containing $CyMe_4$-BTBP and DEHBA in Cyclohexanone, Separation Science and Technology, 47, 2012

Aneheim, Ekberg, Foreman, Aqueous complexation of palladium to prevent precipitation and extraction in a group actinide extraction system, Hydrometallurgy, 115–116, 2012B

Aneheim, Ekberg, Foreman, A TBP/BTBP-Based GANEX Separation Process Part 3: Fission Product Handling, Solvent Extraction and Ion Exchange, 31, 2013

Aneheim, Ekberg, Littley, Löfström-Engdahl, Skarnemark, Technetium chemistry in a novel group actinide extraction process, Journal of Radioanalytical and Nuclear Chemistry, 296, 2013B

Aneheim, Development of a Solvent Extraction Process for Group Actinide Recovery from Used Nuclear Fuel, thesis for the degree of doctor, Chalmers University of Technology, Chalmers Reproservice, Gothenburg, 2012C

Aoki, Research and development in Japan on long-lived nuclide partitioning and transmutation technology, Progress in Nuclear Energy, 40, 2002

Baron, Lecomte, Heres, Mauborgne, Cyclic method for separating chemical elements present in an aqueous solution, US Patent US: 2004/0124141 A1, 2004

Bell, Carpentier, Carrott, Geist, Gregson, Hérès, Magnusson, Malmbeck, McLachlan, Modolo, Müllich, Sypula, Taylor, Wilden, Progress towards the development of a new GANEX process, Procedia Chemistry, 7, 2012

Benay, Schurhammer, Wipff, Basicity, complexation ability and interfacial behavior of BTBPs: a simulation study, Physical Chemistry Chemical Physics, 13, 2011

Bond, Leuze, Removal of Actinides from High-Level Wastes Generated in the Reprocessing of Commercial Fuels, Transplutonium 1975 : proceedings of the Symposium at Baden Baden, September 13-17, 1975 / 4th International Transplutonium Symposium, Editors, W. Muller, R. Lindner, assisted by Hj. Matzke, J. Richter, M. L. Bradbury, 1975

Bruggink, van der Zwaan, The role of nuclear energy in establishing sustainable energy paths, International Journal of Global Energy Issues, 18, 2002

Brundtland,, Our Common Future, Report of the World Commission on Environment and Development, Oxford University Press, Oxford, 1987

Chaiko, Osseo-Asare, Monolayer Behavior Of Surface Active Metal Extractants, Surfactants in Solution, p 297-310, 1989

Choppin, Liljenzin, Rydberg, Ekberg, Radio chemistry and nuclear chemistry, 4rd edition, Elsevier, chapter 21, 2013A

Choppin, Liljenzin, Rydberg, Ekberg, Radio chemistry and nuclear chemistry, 4rd edition, Elsevier, chapter 11, 2013B

Condamines, Musikas, The extraction by n,n-dialkylamides I. HNO3 and other inorganic acids, Solvent extraction and Ion Exchange, 6, 1988

Davis, Thermodynaimcs of extraction of nitric acid by tri-n-butyl phosphate-hydrocarbon solutions, Oak Ridge, National Laboratory, US, Atomic energy commission, 1961

Ekberg, Uncertainties in Actinides Solubility Calculations Illustrated using the Th-OH-PO4 System, thesis for the degree of doctor, Chalmers University of Technology, Chalmers Reproservice, Gothenburg, reprinted 2006

Ekberg, Dubois, Fermvik, Retegan, Skarnemark, Drew, Foreman, Hudson, Extraction behavior of nickel(II) using some of the BTBP-class ligands. Solvent Extraction and Ion Exchange, 25, 2007

Ekberg, Aneheim, Fermvik, Foreman, Löfström-Engdahl, Retegan, Spendlikova, Thermodynamics of Dissolution for BTBP-Class Ligands in Different Diluents and Its Reflection on Extraction, Journal of Chemical and Engineering Data, 55, 2010

Fermvik, Berthon, Ekberg, Englund, Retegan, Zorz, Radiolysis of solvents containing C5-BTBP: identification of degradation products and their dependence on absorbed dose and dose rate, Dalton Transactions, 32, 2009

Fermvik, Aneheim, Gruner, Hajkova, Kvicalova, Ekberg, Radiolysis of C5-BTBP in cyclohexanone irradiated in the absence and presence of an aqueous phase, Radiochimica acta, 100, 2012

Foreman, Hudson, Geist, Madic, Weigl, An Investigation into the Extraction of Americium(III), Lanthanides and D-Block Metals by 6,6’-Bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2’]bipyridinyl (C5-BTBP), Solvent Extraction and Ion Exchange, 23, 2005

Foreman, Hudson, Drew, Hill, Madic, Complexes formed between the quadridentate, heterocyclic molecules 6,6_-bis-(5,6-dialkyl- 1,2,4-triazin-3-yl)-2,2_-bipyridine (BTBP) and lanthanides(III): Implications for the partitioning of actinides(III) and lanthanides(III). Dalton Transactions, 13, 2006

Garner, Hale, The effect of surface active agents in liquid extraction processes, Chemical Engineering Science, 2, 1953

Geist, Nitsch, Kim, On the kinetics of rare-earth extraction into D2EHPA, Engineering Science, 54, 1999

Geist.' Hill, Modolo, Foreman, Weigl, Gompper, Hudson, 6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl) [2,2′]bipyridine, an Effective Extracting Agent for the Separation of Americium(III) and Curium(III) from the Lanthanides, Solvent Extr Ion Exc, 24, 2006

Geist, Magnusson, Mullich, Modolo, A kinetic study on the extraction of americium (III) into CyMe$_4$-BTBP, Actinide and Fission Product Partitioning and Transmutation12th Information Exchange Meeting, Prague http://www.oecdnea.org/pt/iempt12/documents/posters/5/geist-full.pdf, 2012, accessed 13th of May 2014.

Hiemenz, Rajagopalan, Colloid and Surface chemistry, 3rd revised and expanded. Marcel Dekker, Inc., New York, 1997

Holm, Thesis for the degree of masters: RadTox, A computer program for assessing radiotoxicity curves for spent nuclear fuel Chalmers University of Technology, Göteborg, Sweden, 2012

IAEA, 2007, TECDOC-1529, Management of Reprocessed Uranium Current Status and Future Prospects, 2007

IAEA, 2011, Nuclear Technology Review, 2011, International Atomic Energy Agency, Vienna, 2011

IAEA, 2013, Nuclear Technology Review 2013, GC(57)/INF/2, Vienna, 2013

Ionova, Ionov, Rabbe, Hill, Madic, Guillaumont, Krupa, Mechanism of trivalent actinide/lanthanide separation using bis(2,4,4-trimethylpentyl)dithiophosphonic acid (CYANEX 301) and neutral O-bearing co-extractant synergistic mixtures, Solvent Extraction and Ion Exchange, 19, 2001

Ionova, Ionov, Rabbe, Hill, Madic, Guillaumont, Modolo, Krupa, Mechanism of trivalent actinide/lanthanide separation using synergistic mixtures of di (chlorophenyl) dithiophosphinic acid and neutral o-bearing co-extractants, New Journal of Chemistry, 25, 2001

Lewis, Harwood, Hudson, Drew, Wilden, Sypula, Modolo, Vu, Simonin, Vidick, Bouslimani, Desreux, From BTBPs to BTPhens: the effect of ligand pre-organization on the extraction properties of quadridentate bis-triazine ligands, Procedia Chemistry 7, 2012

Liljenzin, Persson, Svantesson, Wingefors, The CTH-process for HLLW treatment, Part I–General description and process design, Radiochimica Acta, 35, 1984

Lundberg, Persson, Ekberg, Crystal structure of [Eu(CyMe4-BTBP)2 κ 2 O,O’-(NO3)]-(NO3)2·n-C8H17OH and its structure in 1-octanol Solution, Dalton Transactions, 42, 2013

Löfström-Engdahl, Skarnemark, Tayara, Eriksson, Halldin, Halleröd, Malmberg, Mattiasson Bjugren Purification of used Scintillation Liquids containing the alpha emitters americium and plutonium, in press, Journal of Radioanalytical and Nuclear Chemistry, 2014

Madic, Hudson, High Level Waste Partition by means of Completely Incinerable Extractants, Final Report, European Commission Contract No. FI2W-CT91-0112, EUR 18038, 1998

Madic, Hudson, Liljenzin, Glatz, Nannicini, Facchini, Kolarik, Odoj, New partitioning techniques for minor actinides, Final Report, NEWPART. EUR 19149, European Commission, Luxembourg, 2000

Madic, Overview of the hydrometallurgical and pyro-metallurgical processes studied worldwide for the partitioning of high active nuclear wastes, 6th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Madrid, Spain (11-13 December 2000), 2001

Madic, Testard, Hudson, Liljenzin, Christiansen, Ferrando, Facchini, Geist, Modolo, Gonzalez-Espartero, Mendoza, PARTNEW New Solvent Extraction Processes for Minor Actinides, Final Report CEA-R-6066, 2004

Magnusson, Christiansen, Malmbeck, Glatz, Investigation of the radiolytic stability of a CyMe4-BTBP based SANEX solvent, Radiochimica Acta, 97, 2009

Malmbeck, Carrott, Geist, Heres, Magnusson, Miguirditchian, Modolo, Sorel, Taylor, Wilden, The hydrometallurgical co-separation of Neptunium, Plutonium, Americium and Curium by the EURO-GANEX process, Proceedings of ISEC (International Solvent Extraction conference), 2014

Miguirditchian, Guillaneux, Guillaumont, Moisy, Madic, Jensen, Nash, Thermodynamic Study of the Complexation of Trivalent Actinide and Lanthanide Cations by ADPTZ, a Tridentate N-Donor Ligand, Inorganic Chemistry, 44, 2005

Miguirditchian, Chareyre, Heres, Hill, Baron, Masson, GANEX: Adaptation of the DIAMEX-SANEX Process for the Group Actinide Separation, Proceedings of GLOBAL 2007, Conference on advanced nuclear fuel, Boise Idaho (United States), 2007

Miguirditchian, Sorel, Camès, Bisel, Baron, Extraction of uranium (VI) by DEHiBA from the batch experimental data to the counter current process, fundamentals to industrial applications. Proceedings of ISEC (International Solvent Extraction conference), 2008

Modolo, Wilden, Daniels, Geist, Magnusson, Malmbeck, Development and demonstration of a new SANEX Partitioning Process for selective actinide(III)/lanthanide(III) separation using a mixture of CyMe$_4$-BTBP and TODGA, Radiochimica Acta, 101, 2013

Nair, Mahajan, Prabhu, Extraction of uranium(VI) and plutonium(IV) with some high molecular weight aliphatic monoamides from nitric acid medium, Journal of Radioanalytical and Nuclear Chemistry, 191, 1995

Nilsson, Ekberg, Foreman, Hudson, Liljenzin, Modolo, Skarnemark, Separation of Actinides(III) from Lanthanides(III) in Simulated Nuclear Waste Streams using 6,6’-Bis-(5,6-

dipentyl-[1,2,4]triazin-3-yl)-[2,2’]bipyridinyl (C5-BTBP) in Cyclohexanone, Solvent Extraction and Ion Exchange, 24, 2006A

Nilsson, Andersson, Drouet, Ekberg, Foreman, Hudson, Liljenzin, Magnusson, Skarnemark , Extraction Properties of 6,6′-Bis-(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridinyl(C5-BTBP), Solvent Extraction and Ion Exchange, 24, 2006B

Nilsson, Nash, Review Article, A Review of the Development and Operational Characteristics of the TALSPEAK Process, Solvent Extraction and Ion Exchange, 25, 2007

Nilsson, Nash, Trans-Lanthanide Extraction Studies in the TALSPEAK System: Investigating the Effect of Acidity and Temperature, Solvent Extraction and Ion Exchange, 27, 2009

OECD-NEA, Nuclear Energy Agency database, general facts 2012, accessed august 12th, 2014 (http://www.oecd-nea.org/general/facts/)

Oliveira, Pratas, Marrucho, Queimada, Coutinho, Description of the mutual solubilities of fatty acids and water with the CPA EoS, Alche journal, 55, 2009

Osseo-Asare, Aggregation, Reversed micelles, and Microemulsions in Liquid-Liquid Extraction: The TRI-n-butyl phosphate-Diluent-Water-Electrolyte System, Advances in Colloid and Interface Science, 37, 1991

Pathak , Kanekar , Prabh, Manchanda, Comparison of Hydrometallurgical Parameters of N,N-Dialkylamides and of Tri-n-Butylphosphate, Solvent Extraction and Ion Exchange, 27, 2009

Pearson, Hard and soft acids and bases, HSAB, Part II, Journal of Chemical Education, 45, 1968

Persson, Wingefors, Liljenzin, Svantesson, The CTH-Process for HLLW Treatment, Part II - Hot Test, Radiochimica Acta, 35, 1984.

Prabhu, Mahajan, Nair, Di(2-ethyl hexyl) butyramide and di(2-ethyl hexyl)isobutyramide as extractants for uranium(VI) and plutonium(IV), Journal of Radioanalytical and Nuclear Chemistry, 224, 1997

Retegan, The Influence of Diluents and Side Groups of the Ligands on Liquid-Liquid Extraction of Actinides and Lanthanides, Thesis for the degree of licentiate, Chalmers University of Technology, Gothenburg, Sweden, 2007

Retegan, Dubois, Ekberg, Fermvik, Johnson, Wass, Skarnemark, Extraction of Actinides with Different 6,6'-bis-(5,6-Dialkyl-[1,2,4]-Triazin-3-yl)-[2,2']-Bipyridines (BTBPs), Solvent Extraction and Ion Exchange, 25, 2007A

Retegan, Ekberg, Fermvik, Skarnemark, The Effect of Diluents on Extraction of Actinides and Lanthanides, in Scientific Basis for Nuclear Waste Management XXX, edited by D.S. Dunn, C. Poinssot, B. Begg (Mater. Res. Soc. Symp. Proc. 985, Warrendale, PA), 0985-NN14-05, 2007B

Retegan, Ekberg, Englund, Fermvik, Foreman, Skarnemark, The behaviour of organic solvents containing C5-BTBP and CyMe$_4$-BTBP at low irradiation doses, Radiochimica Acta, 95, 2007C

Retegan, Ekberg, Fermvik, Foreman, Skarnemark, A comparative study of some BTP and BTBP class ligands, Solvent Extraction: Fundamentals to Industrial Applications, Proceedings of ISEC 2008, Tucson, Arizona, US, 1, 545-550, 2008

Retegan, Investigations of solvent systems based on bis-triazine-bipyridine (BTBP)-class Ligands for the Separation of Actinides from Lanthanides, thesis for the degree of doctor, Chalmers University of Technology, Chalmers Reproservice, Gothenburg, 2009

Retegan, Berthon, Ekberg, Fermvik, Skarnemark, Zorz, Electrospray Ionization Mass Spectrometry Investigation of BTBP – Lanthanide(III) and Actinide(III) Complexes, Solvent Extraction and Ion Exchange, 27, 2009B

Rice, Irving, Leonard, Nomenclature for liquid-liquid distribution (solvent extraction), Pure & Applied Chemistry, 65, 1993

Riddick, Bunger, Techniques of organic solvents, vol 2, 3rd edn. Wiley, New York, 1970

Royal society 2009, exhibition, https://royalsociety.org/exhibitions/2009/rutherford/ernest-rutherford/, accessed the 2nd of October, 2014

Russell, Johnsen, Some Aspects of the Radiation Chemistry of Liquid Aliphatic Carboxylic Acids, Journal of Physical Chemistry, 63, 1959

Rydberg, Cox, Musikas, Choppin (eds.) Solvent extraction principles and practice, 2nd edn, Marcel Dekker Inc., chapter 7, 2004A

Rydberg, Cox, Musikas, Choppin (eds.) Solvent extraction principles and practice, 2nd edn, Marcel Dekker Inc., chapter 2, 2004B

Rydberg, Cox, Musikas, Choppin (eds.) Solvent extraction principles and practice, 2nd edn, Marcel Dekker Inc., chapter 5, 2004C

Sailor, Bodansky, Brau, Fetter, van der Zwaan, Nuclear power: A Nuclear Solution to Climate Change?, Science, 288, 2000

Salvatores, Slessarev, Ritter, Fougeras, Tchistiakov, Youinou, Zaetta, Long-lived radioactive waste transmutation and the role of accelerator driven (hybrid) systems, Nuclear Instruments and Methods in Physics Research A, 414, 1998

Schulz, Navratil (Eds.), Science and Technology of Tributyl Phosphate, 1CRC Press, Boca Raton, FL, 1984

Sciencelab.com, 2014, http://www.sciencelab.com/msds.php?msdsId=9924436, accessed the 14th of May, 2014

Shaw, Introduction to colloid and surface chemistry, 4th ed. Chapter 4, Butterworths, London, 1992

Shevchenko, Smelov, The effect of mono- and dibutyl phosphates on the extraction of plutonium with tributyl phosphate. Atomic Energy, 5, 1958

Singh, Freeman, Radiolysis of cyclohexanone, I, Pure liquid, Canadian Journal of Chemistry, 42, 1964

SKB, Andersson, Drouet, Ekberg, Liljenzin, Magnusson, Nilsson, Retegan, Skarnemark, Partitioning and Transmutation Annual report 2004, (R-05-13), page 18-19, Swedish Nuclear Fuel and Waste Management Co, Sweden, 2005

SKB, Aneheim, Ekberg, Fermvik, Foreman, Nästrén, Retegan, Skarnemark, Partitioning and Transmutation Annual report 2008, (R-09-03), page 46 Swedish Nuclear Fuel and Waste Management Co, Sweden, 2009

SKB, Webpage by SKB, http://www.skb.se/templates/standard____24109.aspx, accessed the 7th of august, 2014A

SKB, Webpage by SKB; http://www.skb.se/Templates/Standard____33926.aspx, accessed the 7th of august, 2014B

Stephenson, Stuart, Tabak, Mutual Solubility of Water and Aliphatic Alcohols, Journal of Chemical and Engineering Data, 29, 1984

Stephenson, Mutual Solubilities: Water-Ketones, Water-Ethers, and Water-Gasoline-Alcohols, Journal of Chemical and Engineering Data, 37, 1992

Thiolet, Musicas, Synthesis and uses of the amides extractants, Solvent Extraction and Ion Exchange, 7, 1989

Thomas, Silver, Spring, Process of securing plutonium in nitric acid solution in its trivalent oxidation state, US Patent 2,849,277, 1949

Virtual chemistry database, VCD 2014 (<http://www.virtualchemistry.org/molecules/462-06-6/index.php#refs> accessed 12.08.2014), 2014

Warf, Extraction of cerium(IV) nitrate by butyl phosphate, Journal of American Chemical Society, 71, 1949

Weaver, Kappelmann, Talspeak: a new method of separating americium and curium from the lanthanides by extraction from an aqueous solution of an aminopolyacetic acid complex with a monoacidic organophosphate or phosphonate, Report from U.S. Atomic Energy Commission, 1964

Weigl, Geist, Mullich, Gompper, Kinetics of Americium(III) Extraction and Back Extraction with BTP, Solvent Extraction and Ion Exchange, 24, 2006

Wilden, Modolo, Schreinemachers, Sadowski, Lange, Sypula, Magnusson, Geist, Lewis, Harwood, Hudson, Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe4BTBP and TODGA as 1-cycle SANEX Solvent Part III: Demonstration of a Laboratory-Scale Counter-Current Centrifugal Contactor Process, Solvent Extraction and Ion Exchange, 31, 2013

Zwaan Van der, The role of nuclear power in mitigating emissions from electricity generation, Energy Strategy Reviews, 1, 2013

APPENDIX A

The content of a typical PUREX feed is seen in table X. The table is collected from specifications from Europart, the 6th European framework program; Charter for accessing the extraction properties of newly synthesized ligands within Europart.

Table X. Charter for accessing the extraction properties of newly synthesized ligands within Europart.

Elements	PUREX feed (mg/L)
Se	20
Rb	120
Sr	280
Y	155
Zr	1 245
Mo	1 185
Tc	255
Ru	400
Rh	80
Pd	520
Ag	30
Cd	35
Sn	20
Sb	5
Te	170
Cs	1 265
Ba	595
La	425
Ce	830
Pr	390
Nd	1 420
Pm	20
Sm	280
Eu	55
Gd	40
U	247 015
Np	160
Pu	2 985
Am	160
Cm	25

The chemicals and their labels and purity together with the number of the paper where they were used are seen in table Y. The ligands CyMe$_4$-BTBP (Paper II-VII) and DEHBA (paper III and IV) were synthesized in house according to Foreman (2006) (CyMe$_4$-BTBP) and Thiolet (1989) (DEHBA). C5-BTBP (paper I) was kindly supplied (long time ago) from the University of Reading, UK. The synthesis of the ^{14}C labeled CyMe$_4$-BTBP was made in house and is described in paper V. The water used in all experiments is purified using a Milli-Q system (>18 MΩ).

Table Y. The chemicals and their label and purity used in the papers.

Chemical	**Label**	**Purity**	**Used in paper**
Nitric acid	Sigma aldrich	68%	All papers
$NaNO_3$	Riedel-de HAEN AG	p.a.	I, II, VII
Hexanol	Sigma aldrich	98%	I,II, V, VII
Heptanol	Merck Schuchardt	98%	I, II
Octanol	Acros organics	99%	I, II
Nonanol	Fluka	>99 %	I, II
Decanol	Sigma aldrich	99%	I, II
Cyclohexanone	Acros organics	99.8 %	III, IV, VII
TBP	Fluka (Sigma aldrich)	>97% (95 %)	III, IV, (V), VI
$Eu(NO_3)_3$	Sigma aldrich	99.9 %	III
Hexanoic acid	Sigma aldrich	99.5 %	VI
Nitrobenzene	Sigma aldrich	>99.0 %	VII
Chlorobenzene	Aldrich	99%	VII
Fluorobenzene	Fluka	>97 %	VII
Benzene	Merck	p.a.	VII

APPENDIX C

For the calculations of the extracted amount of metal the distribution ratios was used to calculated % extracted together with the concentration in the PUREX feed. The molar weights used for calculating molar concentration (in order to control for loading) was 238 g * mol^{-1} (U), 244 g * mol^{-1} (Pu), 243 g * mol^{-1} (Am) and 247 g * mol^{-1} (Cm). As can be seen high molar weights were chosen in order to not underestimate the influence. The concentrations of the elements in the feed are seen in table Z. The percentages extracted of every element in the three diluents are seen in table AA.

Table Z. The calculated concentrations and percentage extracted of the elements into the three solvents.

	g * L^{-1} in feed	**concentration (M)**
Pu	2.985	0.012
Am	0.16	$6.6 * 10^{-4}$
Cm	0.025	$1.0 * 10^{-4}$
Uranium after stage 1	$1.03 * 10^{-4}$	$4.32 * 10^{-7}$

Table AA. Percentage extracted of the actinides into the different GANEX solvents.

	Percentage extracted		
	Cyclohexanone	**Hexanol**	**Hexanoic acid**
Pu	99.5	98.0	98.7
Am	99.4	96.9	52.4
Cm	99.1	94.3	62.1
Uranium after stage 1	91.5	58.0	73.5