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Partitioning and transmutation

Annual report 1999

C Ekberg, Å Enarsson, C Gustavsson, A Landgren,
J O Liljenzin and L Spjuth

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May 2000

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Sammanfattning

Inom separation och transmutionsprojektet vid Institutionen för Kärnkemi, CTH, undersöker vi nya vattenbaserade processer för separation av aktinider. Internationellt pågår även utveckling av andra separationsmetoder, såsom metallurgiska- och salt-smälteprocesser. Utvecklingsarbetet för dessa metoder följer vi främst upp genom litteraturstudier, konferenser och möten.

Separation och transmutation av utbränt kärnbränsle kan användas som ett komplement till ett geologiskt slutförvar och även för att öka energiuttaget ur en given mängd natururan. Tiden som behövs för att avfallets radiologiska "farlighet" ska minska till den naturliga bakgrundsnivån kan drastiskt reduceras om de långlivade radionukliderna, framförallt aktiniderna, kan separeras ut från det utbrända bränslet och transmutteras (omvandlas) till stabila eller kortlivade nuklider. Transmutationen kan ske i en kärnreaktor eller i acceleratordrivna underkritiska system. En effektiv kemisk separation av de långlivade aktiniderna från fissionsprodukterna är nödvändig för att erhålla en effektiv transmutation. Vätske-vätske extraktion anses vara den separationsteknik som är mest aktuell att använda för denna separation före varje transmutionscykel. Internationellt pågår även utveckling av andra separationsmetoder, såsom metallurgiska- och saltsmälteprocesser. Utvecklingsarbetet för dessa metoder följer vi främst upp genom litteraturstudier, konferenser och möten.

Projektet bedrivs som ett grundforskningsprojekt inom vilket i genomsnitt tre forskarstuderande genomför sin forskarutbildning under innevarande period. Forskarutbildningen är inriktad mot att undersöka olika grupper av extraktionsreagens som kan tänkas bli använda i nya separationsprocesser. Det rör sig om ett jonbytesreagens (Aliquat-336), en grupp kelatbildande/jonbytande reagens (malonamider) och solvatiserande reagens (oligo-pyridiner och substituerade triaziner). Undersökningarna inriktar sig på att studera extraktionsegenskaper för diverse intressanta specier, extraktionsmekanismer, kinetik, påverkan av reagensens molekylstruktur etc. Förutom att de studerade reagensen kan uppvisa andra egenskaper vad gäller selektivitet och extraktionsförmåga jämfört med traditionella extraktionsmedel använda inom kärntekniken, så är det en stor fördel att reagensen är fullständigt brännbara (uppbyggda enbart av kol, väte, syre och kväve, CHON-principen), vilket minimerar uppkomsten av sekundärt avfall jämfört med fosfor-baserade extraktions-reagens.

Under perioden har en deltids-forskarstuderande avlagt fil. lic. examen och två aktiva doktorander disputerat. De är Ingela Hagström och Lena Spjuth, som i huvudsak arbetade med malonamider, triaziner och oligopyridiner, samt Anders Landgren, som huvudsakligen studerade Aliquat-336 och oxidationskinetik. Deras resultat ges i korthet nedan.

Malonamider är en grupp extraktionsreagens som har föreslagits för extraktion av både trevärda aktinider och lantanider från hög syrahalt i ett första steg i separationsprocessen. Kvävedonerande extraktionsreagens, såsom oligopyridiner, har i synergistiska system med karboxylsyror potential att i ett andra steg vid låg syrahalt separera de trevärda aktiniderna från lantaniderna. Flertalet av de substituerade malonamiderna och oligopyridinerna som har undersökts inom projektet har baserats på deras extraktionsförmåga och hur denna är relaterad till struktur och basicitet. Alla malonamider som

undersökts har uppvisat en god extraktionsförmåga för trevärda aktinider och lantanider från hög salpetersyrainhalt. Malonamidernas basicitet är starkt beroende av molekylstrukturen och en malonamid med låg basicitet resulterade i en bättre metalextraktion på grund av den svagare konkurrensen mellan protoner och metalljoner om bindningssättet. Malonamider med aromatiska grupper substituerade på kväveatomerna hade den lägsta basiciteten av alla studerade malonamider. Icke-aromatiska malonamider substituerade med en oxyalkylgrupp på den centrala kolatomen hade dessutom lägre basicitet än de som var substituerade med en alkylgrupp. Även oligopyridinernas basicitet är beroende på molekylstrukturen och ett reagens med låg basicitet uppvisar en bättre extraktionsförmåga än ett reagens med högre basicitet. En synergistisk blandning av karboxylsyra och terpyridin (en osubstituerad oligopyridin) visade bra selektivitet för trevärda aktinider relativt lantanider. Ett av problemen med terpyridin är att den löser sig i vattenfasen när den protoniseras, men terpyridinets buffrande effekt i vattenfasen motverkar dock till viss del överföringen av extraktionsreagens till vattenfasen.

Studierna på Aliquat-336 omfattade extraktion av ett antal grundämnen: Sc, Fe, Zr, Nb, Tc, In, La, Ce, Pr, Nd, Pm, Sm, Eu, Th, U, Np, Pu, Am, Cm samt salpetersyra. Aliquat-336 visade sig extrahera fyrvärda metalljoner samt anjoner väl och extraktionen av metalljoner avtar enligt: $M^{4+} > MO_2^{2+} > M^{3+}$. Ett separationsschema baserat på Aliquat-336 för separation av Tc, Np och Pu sammankopplat med en "Reversed Talspeak-process" har tagits fram. Extraktionsbatterierna har dimensionerats med avseende på antal steg och volymflödesförhållanden nödvändiga för att uppnå en separation av 99.9%. Det kritiska steget är plutoniumstrippen.

Kinetiken för oxidationen av uran(IV) till uran(VI) med syre har studerats. Hastigheten för oxidationen är en kombination av en förstaordningens reaktion och en auto-katalytisk reaktion. De reaktiva specierna i det undersökta syraintervallet är det första och det andra hydrolyserade uran(IV)komplexet. Kinetikstudier av redoxreaktioner hos katjoner med icke stabila oxidationstal kan dessutom vara en metod för att bestämma hydrolyskonstanter.

Det goda internationella samarbetet som präglat tidigare år har fortsatt under året och beräknas fördjupas ytterligare i framtiden. Ett EU-projekt har avslutats under våren och en ansökan om ett nytt projekt inom det 5:e ramprogrammet har formulerats.

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1 Introduction

The project concerning partition and transmutation performed at the department of Nuclear Chemistry, CTH, is aimed at the investigation of new processes for separation of different chemical elements. Such element separation is vital for the recovery and purification of the fuel/waste streams in P&T treatment plant. The separation processes selected, within this project, for further investigations are based on liquid-liquid extraction. At present, only aqueous based separation processes are known to be able to achieve the high recovery and separation efficiencies necessary for a useful P&T process. In addition, the engineering and operation experience from wet separation processes by far exceeds those of alternative processes. Internationally several other separation processes, such as molten salt electrolysis and different pyroprocesses are investigated.

However, for the reasons outlined above, it is realistic to believe that aqueous separation techniques will continue to be far ahead of the other methods for yet a long time. This opinion is shared by our European project partners and is the main reason for why research on separation processes is focused, in our case, at aqueous/organic liquid-liquid extraction systems. Unfortunately there is no “supermolecule” known today that can extract all elements intended for transmutation in one single step from high nitric acid concentration. Instead, the actinides and lanthanides are considered to be co-extracted in a first step, from high nitric acid concentration. The extracted elements are thereafter stripped back to an aqueous solution of low nitric acid concentration whereafter the separation of trivalent actinides and lanthanides is performed at this lower nitric acid concentration

The project is at present conducted as fundamental research which is the basis for the work of one research student and three PhD students. During this year one has made her fil. lic. degree and two of them have made their PhD degree on slightly different subject which will be described further in this report. Ingela Hagström finished her fil. lic. thesis on separation of Americium, Anders Landgren has concentrated his work on the investigation of the extracting properties of an ion exchange reagent (Aliquat 336), while Lena Spjuth has mainly worked with chelating/ion exchange reagents (malonamides) and solvating reagents (oligopyridines and substituted triazines). Except the fact that these reagents may show other properties regarding selectivity and extraction ability compared with traditional extracting reagents used in the nuclear technology, they are also completely combustible. Being completely combustible means, in this context, that they consist only of carbon, hydrogen, oxygen and nitrogen (the CHON-principle). Such a composition minimises the amounts of secondary waste, compared with, e.g. phosphor based reagents. This is an important point as such waste is one of the important pathways through which uranium, plutonium and the minor actinides are lost from the reprocessing operation. Being able to burn spent solvent and then recover the actinides from the ash would thus help to reduce losses of these elements.

2 Solvent extraction research

During 1999 two of the three PhD students in this project (Anders Landgren and Lena Spjuth) have finalised their dissertations and thus much of the year has been spent writing theses and reports. Lena has been working with oligopyridines, triazines and malonamides and Anders has been working with Aliquat-336 and redox kinetics. In addition, the third PhD student (Åsa Enarsson) has been on maternity leave combined with sick leave for most of the year. The part-time student, Ingela Hagström, finished her thesis and obtained a fil. lic. degree at the University of Göteborg.

2.1 Oligopyridines, triazines and malonamides

It has been shown that extractants that co-ordinate to the metal ion with a nitrogen atom have a higher selectivity for trivalent actinides over lanthanides than extractants that co-ordinate with an oxygen atom. Several new nitrogen-containing extractants have therefore been studied in order to achieve the best separation between actinides and lanthanides at as high nitric acid concentration as possible. Furthermore, the extractant should be sufficiently stable with regard to degradation by nitric acid and radiation. An optimal molecular structure is still not found so many different structures are being tested to get information about their separation ability, e.g. oligopyridines and substituted triazines. Malonamides have been suggested as the extractant used in the DIAMEX-process for co-extraction of actinides and lanthanides in an advanced reprocessing process prior to transmutation. To be able to understand the extraction mechanism with these extractants, the chemical behaviour must be thoroughly investigated. It has previously been shown that both the structure of the malonamide molecule and the electroinductive effects around the binding site are important factors for the metal extraction.

The malonamides and oligopyridines studied here have all been manufactured at the University of Reading especially for use within this project. Due to this fact the amounts of materials available for studies have been small, thus forcing the work to be done on small volumes and limiting the number of repetitions for each experiment. Extreme care and planning have been utilised to ascertain the correctness of each individual experiment.

All the malonamides studied show a co-extracting capacity for trivalent actinides and lanthanides at high nitric acid concentrations. Multivalent actinides show even better extraction at this acidity. The malonamides with aromatic groups attached on the nitrogen showed the lowest basicity of all malonamides studied, and no decrease in metal extraction was observed at high nitric acid concentrations as compared to the non-aromatic malonamides. Non-aromatic malonamides substituted with alkoxy groups on the central carbon show lower basicity than malonamides with alkyl groups. The malonamides with the lowest basicity also showed the best metal extraction. The relation between basicity and metal extraction for malonamide is opposite to the relation observed for organo-phosphorous extractants and monoamides, at least at low acidities.

Steric hindrance is also an important factor for the metal extraction with malonamides, and it was shown that bulky cyclohexane groups attached to the nitrogen atoms distort the molecule and results in a less favourable angle for co-ordination and thus a lesser strength on the bond.

The slope analysis method used to determine the extracted complex is not an optimal method at higher malonamide concentrations owing to the changes in activity coefficients in the organic phase and the possibility of outer-sphere co-ordination. Spectroscopic methods, such as UV-vis and XAS, might be needed in order to verify the composition of the extracted complex.

Metal extraction from non-acidic media was shown to be similar to that from nitric acid solution, indicating a co-ordinating extraction mechanism opposed to an ion-pair extraction mechanism. UV-vis spectroscopy of extracted uranium complexes also supports a co-ordination mechanism. Protonated malonamide, which is a necessity in an ion-pair extraction, was found in some crystal structures, however, and the large amount of nitric acid extracted to the organic phase might indicate that protonated malonamides are present. Further spectroscopic studies of extracted complexes and adducts formed in the organic phase are needed to verify which mechanism is the dominant one.

Metal extraction with the malonamides from low nitric acid concentration ($<0.05\text{M}$) showed an unexpected increase. This increase must be studied further to verify whether it is a real effect of the extractant or not. The extraction behaviour, with an increase in extraction as the acidity is decreasing, is similar to the chelate extraction with beta-diketones. It is possible that the malonamide can form the enol-tautomer, which might cause the extraction at low acidity. UV-vis (or NMR) studies of the malonamide may verify the presence of keto-enol tautomerisation for malonamides.

The gas-phase basicities for some malonamides were calculated using ab initio methods with the Gaussian software and they show the same relative order as the experimentally determined basicities. However, more gas-phase basicity calculations are needed in order to verify the correlation between calculated and experimental basicity. Gas-phase basicity calculations may also be used for the oligopyridines.

Synergistic mixtures with carboxylic acids and oligopyridines have shown potential for separation of trivalent actinides and lanthanides. In the presence of α -bromodecanoic acid, the unsubstituted terpyridine shows reasonable extraction at low nitric acid concentration ($<0.1\text{M}$) and a separation factor between americium and europium of 7. Terpyridine is, however, easily transferred to the aqueous phase when protonated, which might be troublesome in a continuous counter-current separation process since the extractant concentration in the organic phase will be decreased and terpyridine will instead be present in the aqueous phase. Initial batch-wise process tests show that the terpyridine acts as a kind of buffer in the aqueous phase and as the equilibrium concentration of terpyridine in the aqueous phase is reached, terpyridine will even be transferred back to the organic phase. Real counter-current tests are needed to study the effect of the presence of terpyridine in both phases when extracted from different nitric acid concentrations and with macro amounts of metal. Recovery of the extractant and back-extraction of metals must also be studied further.

Further studies of extraction of cesium, iron, cobalt, silver and uranium with mixtures of terpyridine and α -bromodecanoic acid dissolved in tertbutyl-benzene have been performed by a diploma worker (Charlotta Gustavsson) Preliminary results show that silver could be separated from the other studied metals at 0.1M nitric acid and then cobalt and uranium may be separated from americium, curium, europium and cesium at approximately 0.03M nitric acid. Cobalt and uranium may then be separated using extraction without terpyridine. This work will be finished in the early 2000.

2.2 Use of Aliquat-336 as extractant and redox kinetics of uranium

The quaternary ammonium salt, Aliquat-336, has the potential to be the extractant used in a partitioning and transmutation process. The metal extraction is dependant on the oxidation state of the metal and it was found to decrease in the order: $M^{4+} > MO_2^{2+} > M^{3+}$. Anions, e.g. TcO_4^- , are extracted well with Aliquat-336. It was found that the stoichiometry of the extracted species is two Aliquat-336 molecules per metal atom for hexavalent, tetravalent (except zirconium) and trivalent elements. For zirconium and niobium(V), the ratio 1:1 was found between Aliquat-336 and metal. The extraction of nitric acid was found to decrease the extraction of metals in tracer concentrations by lowering the available free extractant concentration.

The process calculation showed that technecium and the actinide elements, neptunium, plutonium, americium and curium, can be separated in a process based on Aliquat-336 in connection with the Reversed Talspeak process. It was found that one of the critical stages is the stripping of plutonium, which requires a large number of steps and a low volume flow ratio. The other extractants used in the partitioning process, TBP and HDEHP, both contain phosphorous. These reagents should thus be replaced by new extractants containing only carbon, hydrogen, oxygen and nitrogen. The development of an extractant with the capacity of separating the trivalent actinides from the lanthanides at high nitric acid concentration would eliminate the need for the TBP loop. As outlined above, these reagents are under investigation.

Adjustment and control of the oxidation state are important in all chemical separation processes. The reaction rate of the oxidation of uranium(IV) by oxygen to uranium(VI) was found to be a combination of a first-order reaction with respect to uranium(IV) and an autocatalytic effect. Kinetic investigations may be a method for determination of hydrolysis constants for redox unstable elements by making use of the normally undesirable oxidation state instability. It was also found that the extraction experiments with uranium(IV) were carried out under conditions in which the oxidation with oxygen was negligible.

3 Collaborations

Sweden

The Swedish Spallator Network (SSN) is a national network with the objective to inform internally and externally about Swedish and international research concerning accelerator-driven transmutation systems. The group participated in “Energimässan” at Svenska Mässan, Göteborg, in April 1998. The network consists of representatives from different universities and institutes;

- Chalmers University of Technology, Göteborg,
- Royal Institute of Technology, Stockholm,
- Uppsala University,
- Lund University.

Europe

A three-year European contract started in May 1996 concerning new partitioning techniques within the Nuclear Fission Safety program (NEWPART CT FI4I-CT96-0010). There are seven participating institutes from five different countries; Department of Nuclear Chemistry, Chalmers (Sweden), CEA (France), University of Reading (UK), Transuranium Institute (Germany), Forschungszentrum Karlsruhe (Germany), Forschungsanlage Jülich (Germany) and ENEA (Italy). The project has so far been very successful and a proposal for the next Fifth Framework Programme is under preparation. Project meetings are held every 6 months.

England

The University of Reading has an important role in the European contract as a “supplier” of new extractants. The department also perform co-ordination chemistry and molecular modelling of these new ligands. Several new extractants from Reading have been investigated at Chalmers during the year and one Ph.D. student, Lena Spjuth, spent 3 months at the University of Reading to study molecular modelling and synthesis, see Appendix 7.

France

There has been a lot of contacts between the CEA laboratory in Marcoule and Chalmers since the work performed at the two laboratories are closely connected. There is a continuous exchange of new ligands and discussions of new results.

USA

An informal collaboration was initiated in 1992 between the Los Alamos National Laboratory (LANL) and the Department of Nuclear Chemistry, CTH. The collaboration involves exchange of information and results within aqueous based partitioning processes.

Japan

A collaboration was initiated in 1993 between the Department of Nuclear Chemistry, CTH and the Department of Fuel Cycle Safety Research at Japan Atomic Energy Institute (JAERI). It was agreed to exchange information, results and personnel between CTH and JAERI.

4 Meetings and lectures

Since the major part of the year has been spent on writing only a few meetings, conferences and lectures have been attended. In chronological order they are:

- 11/03 Anders Landgren gave a seminar on partition and transmutation at Studsvik.
- 21–23/04 Jan-Olov Liljenzin, Åsa Enarsson and Lena Spjuth attended the last meeting in the NEWPART project within the EU. The meeting was held in Brissanone, Italy.
- 20/5 Åsa Enarsson was at a meeting planning for applications to the 5th framework applications for the EU in Paris.
- 11–16/7 Lena Spjuth and Åsa Enarsson attended the ISEC'99 conference in Barcelona, Spain, and presented two posters.
- 21/7 Jan-Olov Liljenzin was at a meeting preparing for the application of the FEINPUR project for the EU 5th framework program.
- 9/9 Jan-Olov Liljenzin attended a meeting preparing for the application of the IMMOSOLV project for the EU 5th framework program.

5 Publications

The following papers were published during the year. Abstracts are given as appendices with the same numbers as in the list below. The full texts of the papers presented at the International Solvent Extraction Conference, ISEC'99, are given in Appendices 7 and 8.

- 1 **Hagström I, Spjuth L, Enarsson Å, Liljenzin J O, Skålberg M, Hudson M J, Iveson P B, Madic C, Cordier P Y, Hill C, Francois N.** Synergistic solvent extraction of trivalent americium and europium by 2-bromodecanoic acid and neutral nitrogen-containing reagents. *Solv. Extr. and Ion Exchange*, 17, 221, 1999.
- 2 **Hagström I.** Recycling of Americium. Lic. Thesis, Chalmers University of Technology and University of Göteborg, 1999.
- 3 **Karlfeldt K.** Extraction of Americium, Europium and Samarium with Terpyridine and 2-Bromodecanoic Acid in tert-Butylbenzene, 3p project work, Department of Nuclear Chemistry, Chalmers University of Technology, 1999.
- 4 **Landgren A.** The Use of Aliquat-336 in a Partitioning and Transmutation Process and a Kinetic Study of the Oxidation of U(IV) to U(VI). Ph. D. Thesis, Chalmers University of Technology, 1999.
- 5 **Landgren A, Liljenzin J O.** Extraction behaviour of technetium and actinides in the Aliquat-336/nitric acid system. *Solvent Extr. Ion Exch.*, 17(6), 1999.
- 6 **Spjuth L.** Solvent Extraction Studies with Substituted Malonamides and Oligopyridines. Ph. D Thesis, Chalmers University of Technology, 1999.

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Solvent extraction and ion exchange, 17(2), 221–242 (1999)

Synergistic solvent extraction of trivalent americium and europium by 2-bromodecanoic acid and neutral nitrogen-containing reagents

I Hagström, L Spjuth, Å Enarsson, J O Liljenzin, M Skålberg
Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg

M J Hudson, P B Iveson
Department of Chemistry, University of Reading, Whiteknights, Berkshire

C Madic, P Y Cordier, C Hill, N Francois
CEA-Valrhô, Marcoule, Bagnols-sur-Cèze, Cédex

Abstract

The synergistic enhancement in the extraction of trivalent actinides (Am and Cm) and some lanthanides by 2-bromodecanoic acid and different nitrogen-containing extractants was studied. The extraction by mixtures of 2-bromodecanoic acid and 2,2':6',2''-terpyridine or N,N'-dimethyl-N,N'-dicyclohexyltetradecyl malonamide (DMDCHTDMA) respectively, in *tert*-butylbenzene (TBB) or hydrogenated tetrapropene (TPH), was investigated and compared with 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (TPTZ) in synergy with 2-bromodecanoic acid. The synergistic enhancement and the separation factor between americium and europium was higher with the terpyridine mixture compared with the malonamide mixture. The separation factor between americium and europium from nitric acid (0.01 M) with terpyridine (0.02 M), 2-bromodecanoic acid (1 M) in TBB was determined to be 7, while the separation factor for malonamide (0.1 M), 2-bromodecanoic acid (1 M) in TBB was approximately 3. This might indicate a more covalent character in the actinide-terpyridine complex than in the actinide-malonamide complex. The terpyridine was shown to be easily transferred to the aqueous phase when protonated and thus the protonation ability for terpyridine was investigated at different concentrations of terpyridine and 2-bromodecanoic acid. Studies to determine the stoichiometry of the M(III) extracted complex with the synergistic mixtures were also performed.

Recycling of americium*

Ingela Hagström

Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg, 1999

Abstract

Separation of actinides from spent nuclear fuel is a part of the process of recycling fissile material. Extracting agents for partitioning the high level liquid waste (HLLW) from conventional PLTREX reprocessing is studied. The CTH-process is based on three consecutive extraction cycles.

In the first cycle protactinium, uranium, neptunium and plutonium are removed by extraction with di-2-ethylhexyl-phosphoric acid (HDEHP) from a 6 M nitric acid HLLW solution. Distribution ratios for actinides, fission products and corrosion products between HLLW and 1 M HDEHP in an aliphatic diluent have been investigated.

To avoid addition of chemicals the acidity is reduced by a tributylphosphate (TBP) extraction cycle. The distribution ratios of elements present in HLLW have been measured between 50 % TBP in an aliphatic diluent and synthetic HLLW in range 0.1-6 M nitric acid. In the third extraction cycle americium and curium are extracted. To separate trivalent actinides from lanthanides a method based on selective stripping of the actinides from 1 M HDEHP is proposed. The aqueous phase containing ammonia, diethylenetriaminepentaacetic acid (DTPA) and lactic acid is recycled in a closed loop after reextraction of the actinides into a second organic phase also containing 1 M HDEHP. Distribution ratios for americium and neodymium have been measured at varying DTPA and lactic acid concentrations and at varying pH.

Nitrogen-donor reagents have been shown to have a potential to separate trivalent actinides from lanthanides. 2,2':6,2"-terpyridine as extractant follows the CHON-principle and can in synergy with 2-bromodecanoic acid separate americium from europium. Distribution ratios for americium and europium, in the range of 0.02-0.12 M nitric acid, between nitric acid and 0.02 M terpyridine with 1 M 2-bromodecanoic acid in tert-butylbenzene (TBB) was investigated. Comparison with other nitrogen-donor reagents show that increasing lipophilicity of the molecule, by substitution of alkyl-chains to the structure or by changing the position of the nitrogens in the molecule, can be a way to get higher distribution ratios and higher separation factors.

Keywords: Actinides, DTPA, HDEHP, Separation, TBP, Terpyridine.

*Licentiate thesis

Extraction of americium, europium and samarium with terpyridine and 2-bromodecanoic acid in *tert*-butylbenzene

Karin Karlfeldt

Project, 3p, Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg, 1999

Abstract

The separation between trivalent actinides and lanthanides is very important in advanced reprocessing of spent nuclear fuel. The actinides can be transmuted to short-lived or stable nuclides by neutron irradiation, but if there are neutron absorbing species, like the lanthanides, present, the transmutation becomes inefficient. The extraction of americium, europium and samarium with terpyridine and 2-bromodecanoic acid in *tert*-butylbenzene from different HNO_3 concentration and with different metal concentrations was studied.

It was found that the distribution ratio increased when both the metal concentration and the initial HNO_3 concentration decreased. The lower the H^+ concentration in the aqueous phase, the more terpyridine stays in the organic phase which can create extractable complexes with metal ions, terpyridine and 2-bromodecanoic acid. The higher the metal concentration, the less terpyridine stays in the organic phase after the extraction due to the release of protons and subsequent protonation of terpyridine.

The use of Aliquat-336 in a partitioning and transmutation process and a kinetic study of the oxidation of U(IV) to U(VI)*

Anders Landgren

Doktorsavhandlingar vid Chalmers tekniska högskola, Ny serie nr 1529,
ISBN 91-7197-831-3, Department of Nuclear Chemistry, Göteborg, 1999

Abstract

Spent nuclear fuel contains several long-lived radionuclides that must be stored in a safe manner for a long time. Transmutation of these radionuclides into short-lived or stable nuclides reduces the necessary storage time by several orders of magnitude. The nuclides most suitable for transmutation are those of the actinides. The products obtained from partitioning and transmutation are, however, radioactive. Partitioning and transmutation (P&T) should therefore be considered as a complement to a final storage. The connection between partitioning and transmutation, is presented. Generally, it can be concluded that the transmutation efficiency and the separation yield should be high if P&T should be a preferable option.

Liquid-liquid extraction is one separation technique suitable to achieve the necessary separation yield. One group of extractants that can be used is the long-chained quaternary ammonium salts. In this work, the extractant Aliquat-336 has been investigated. The extraction behaviour of several elements, Sc, Fe, Zr, Nb, Tc, In, La, Ce, Pr, Nd, Pm, Sm, Eu, Th, U, Np, Pu, Am, Cm and nitric acid have been investigated. Aliquat-336 shows high extraction of tetravalent elements and anions. The extraction of multivalent cations was found to decrease in the order: $M^{4+} > MO_2^{2+} > M^{3+}$.

A separation process based on Aliquat-336 for separation of technetium, neptunium and plutonium in connection with the Reversed Talspeak process is presented. The process is designed with respect to the number of stages and volume flow ratios needed to achieve at least 99.9% separation. The crucial stage was found to be the stripping of plutonium(IV). Aliquat-336 has potential to achieve the necessary separation of technetium, neptunium and plutonium.

A kinetic study of the oxidation of uranium(IV) to uranium(VI) by oxygen was done. It was found that the oxidation rate is a combination of a first order and an autocatalytic reaction mechanism. The reactive species in the acid interval investigated are the first and second hydrolysed uranium(IV) complexes. A kinetic investigation can be a method for determination of hydrolysis constants for metal cations with unstable oxidation states.

Keywords: transmutation, partitioning, liquid-liquid extraction, quaternary ammonium salts, Aliquat-336, kinetics, oxidation, uranium(IV), hydrolysis.

*PdD thesis

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Extraction behaviour of technetium and actinides in the Aliquat-336/nitric acid system

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Abstract

The extraction behaviour of technetium, thorium, uranium, neptunium, plutonium, americium and curium in the Aliquat-336 (diluted with 1,3-diisopropyl benzene) – nitric acid system have been studied. Aliquat-336 (tricapryl-methyl ammonium nitrate) is a quaternary ammonium salt extracting different species with an anion exchange mechanism. Distribution data obtained are modeled by anion exchange (technetium) and ion-pair formation mechanisms (actinides) with the extraction of nitric acid included to account for the lowering of the free extractant concentration. Reasonably high distribution ratios were obtained for technetium and the tetravalent elements (Th, Np and Pu) and Aliquat-336 can therefore be useful for partitioning of these elements.

Solvent extraction studies with substituted malonamides and oligopyridines*

Influence of structure and chemical Properties on the extraction ability of trivalent actinides and lanthanides

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Doktorsavhandlingar vid Chalmers tekniska högskola, ISBN 91-7197-821-6,
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Abstract

Separation and transmutation of spent nuclear fuel has been considered as a complement to direct disposal in a deep geological repository. The time needed for the waste to decay to natural background levels can be drastically decreased if the long-lived radionuclides, mainly the actinides, in the spent nuclear fuel are separated and transmuted to short-lived or stable nuclides. Critical reactors or subcritical accelerator-driven systems have been considered for the transmutation. An efficient chemical separation of long-lived actinides from fission products is necessary to achieve an efficient transmutation process. Solvent extraction techniques have been suggested as the separation method used prior to each transmutation cycle. Malonamides have been suggested as co-extracting agents for trivalent actinides and lanthanides from high acidity in a first step in such a separation process and nitrogen-donor extractants, such as oligopyridines in synergy with carboxylic acids, have shown potential to be able to separate the trivalent actinides from the lanthanides from low acidity in a second step.

The extractive behaviour and chemical properties of several substituted malonamides and oligopyridines have been studied in this work and have been related to the structure and the basicity of the ligands. It was found that the basicity of the malonamide was strongly related to its molecular structure, and a malonamide with lower basicity was shown to give a better metal extraction, owing to the less severe competition between protons and metal cations for the binding site in the malonamides. Malonamides with aromatic groups attached on the nitrogens were shown to have the lowest basicity of all studied ligands.

The basicity of the oligopyridines was also shown to be dependent on the molecular structure and extractants with low basicity generally resulted in a higher metal extraction. A synergistic mixtures with a carboxylic acid and terpyridine showed good selectivity for trivalent actinides over lanthanides. The main problem with terpyridine is that it is transferred to the aqueous phase when protonated. It was shown, however, that terpyridine present in the aqueous phase has a buffering effect which counteracts the transfer of extractant to the aqueous phase.

Keywords: transmutation, solvent extraction, malonamides, oligopyridines, actinide, lanthanide, separation, synergism, basicity.

*PhD thesis

Extraction studies and *ab initio* calculations of some substituted malonamides*

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Abstract

The extraction ability of four different malonamides is presented together with experimentally determined basicities and calculated gas-phase basicities. The highest metal extraction was achieved with the ligands of lowest basicity. The calculated basicities, using *ab initio* methods, showed to be in good agreement with experimentally determined basicities.

Keywords: Malonamides, Basicity, *Ab Initio* Calculations.

Introduction

Malonamides have been suggested as suitable coextractants for the minor actinides and lanthanides in advanced reprocessing of spent nuclear fuel /1, 2/. The long-lived minor actinides are then to be separated further and transmuted to short-lived isotopes in an advanced reactor or an accelerator-based system. It is therefore important to study the chemistry and extraction behaviour of the malonamides. The extraction efficiency of the malonamides is considered to be related to both electroinductive effects and to steric hindrances around the binding site /1/. The influence of the different malonamide structures on metal- and nitric acid extraction has therefore been studied and the extraction is related to the basicity of the malonamide. Gas-phase basicities have been calculated using *ab initio* methods.

*Paper presented at ISEC'99 in Barcelona

Experimental

Reagents: The different malonamides that have been studied experimentally all have the same general structure, but differ by the nitrogen substituent, R.

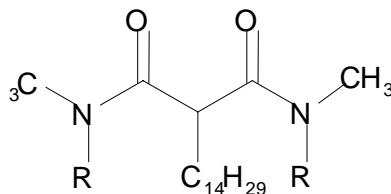


Table A7-1. The different malonamides investigated.

R	Abbreviation
phenyl	DMDPHTDMA
cyclohexyl	DMDCHTDMA
4-chlorophenyl	DMD(pClPH)TDMA
butyl	DMDBTDMA

All the malonamides, except DMDBTDMA, have been synthesised at the University of Reading. Their purity has been checked by $^1\text{H-NMR}$, elemental analysis and melting point /3/. DMDBTDMA, 99% purity, was purchased from Panchim, France.

Procedure: The metal extractions were carried out in 3.5 mL test-tubes by contacting equal volumes of organic and aqueous phase for 5 minutes. The aqueous solutions contained different nitric acid concentrations and 0.1M of the malonamides dissolved in *tert*-butylbenzene (TBB) were used as the organic phase in the extractions. After centrifugation, samples of each phase were taken for analysis. γ -spectrometry was used to determine the ratio of the radioactivity in the two phases (D-value) when metal extraction was considered and for the nitric acid extractions, the samples from each phase after extraction equilibrium were titrated with 0.1M NaOH in ethanolic media.

The basicities of the malonamides were determined by non-aqueous titrations in acetic anhydride media, using 0.1 M HClO_4 in acetic acid as the titrant. The outer salt-bridge in a double junction Ag/AgCl reference electrode was change to 0.1 M LiClO_4 in acetic anhydride.

Results and discussion

The protonation of the malonamide is an important issue when considering the metal extraction from relatively high nitric acid concentrations. During the extraction, the proton and the metal ion are competing for the same binding sites in the malonamide, the carbonyl oxygens. Previous studies have shown that protonation occurs on the carbonyl oxygens rather than on the nitrogens /4/. *Ab initio* calculations performed on protonated malonamides supports this.

As seen in Table A7-2, protonation on the nitrogen results in the highest energy for each species, which is the least stable conformation. The energetically most favourable conformation is when the malonamide is monoprotinated on a carbonyl oxygen and hydrogen bonded to the other carbonyl oxygen. The diprotinated forms are in their most stable conformations when they are not hydrogen-bonded.

Table A7-2. Calculated total energies for different protonation conformations with Gaussian 94 HF/6-31G*.

Structure	C=O-H ⁺ (hydrogen bonded)	C=O-H ⁺	N-H ⁺ (hydrogen bonded)
DMDPHMA H ⁺	-913.296	-913.287	-913.262
DMDPHMA 2H ⁺	-913.519	-913.526	-913.476
DMDCHMA H ⁺	-920.293	-920.280	-920.270
DMDCHMA 2H ⁺	-920.513	-920.520	–

Metal extraction and nitric acid extraction are assumed to be related to the basicity of the molecule. Low basicity of the ligand is considered to give good metal extraction since the competition between proton and metal ion is less severe than with a more basic ligand. The basicity of a few malonamides have therefore been determined experimentally by non-aqueous titrations in acetic anhydride media. The potential at the half-neutralisation point (HNP) was taken as a measure for basicity. Figure A7-1 shows the titration curves for four different malonamides and the HNP's are listed in Table A7-3. The higher the potential at the HNP the less basic the molecule. The 4-chloro-phenyl substituted malonamide is thus the least basic malonamide and the cyclohexyl- and butyl substituted malonamide are the most basic ones.

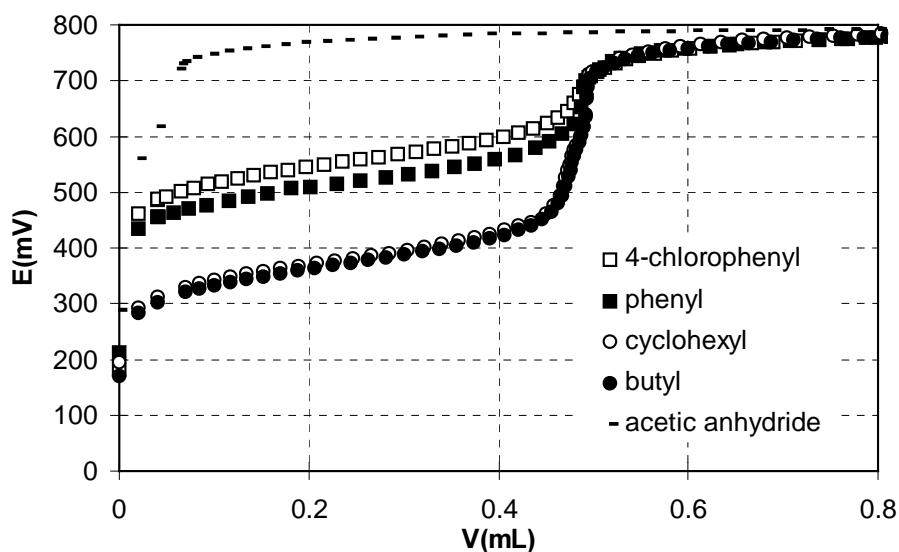


Figure A7-1. Titration with 0.1M HClO₄ in acetic acid, acetic anhydride media of four malonamides, (CH₃-NR-C=O)₂-C-C₁₄H₂₉, with different nitrogen substituents (R_i).

Table A7-3 . Potential at the HNP for the different malonamides studied. The potential is adjusted with an external reference.

R	HNP (mV)
4-Cl-phenyl	557±0.5
phenyl	520±2
butyl	372±6
cyclohexyl	369±5

These basicity data are consistent with earlier extraction studies /3/. The metal extraction shows a decrease in extraction for the cyclohexyl and butyl substituted malonamides at high nitric acid concentration, see Figure A7-2. This could be due to the higher basicity for these ligands and thus the competition between protons and metal for the binding site is more severe than for the less basic molecules. The 4-chloro-phenyl and phenyl derivatives are less basic and don't show this decrease in extraction at high HNO₃ concentration. The nitric acid extraction, Figure A7-3, also shows the same tendency; highest nitric acid extraction for the cyclohexyl substituted malonamide and lowest for the least basic ligand, the 4-chloro-phenyl derivative.

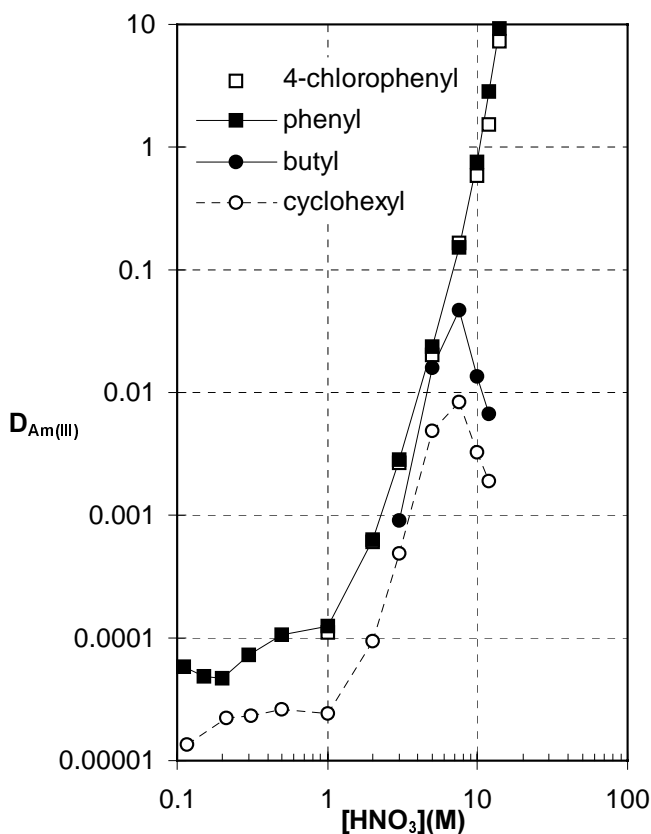


Figure A7-2. Extraction of Am(III) by 0.1M DMDCHTDMA, DMDPHTDMA, DMD(pCIPH)TDMA and DMDBTDMA in TBB (room temperature).

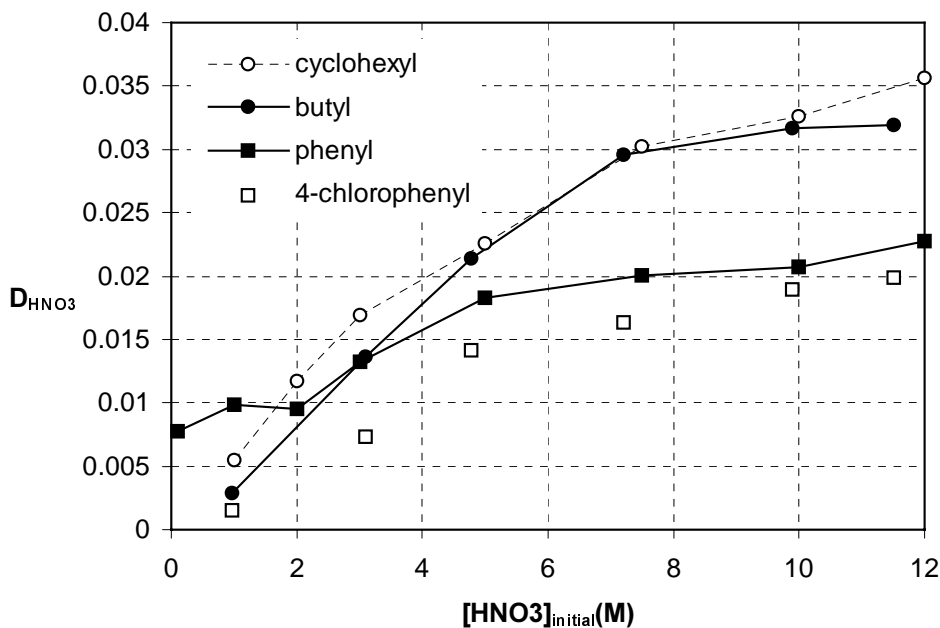


Figure A7-3. Nitric acid extraction with 0.1M of DMDCHTDMA, DMDPHTDMA and DMD(pClPH)TDMA in TBB (room temperature).

Some *ab initio* calculations were carried out in order to investigate if calculated gas-phase basicities could be related to the experimentally determined basicities. Gas-phase basicity is defined as the negative of the Gibbs free energy of the protonation reaction; $L + H^+ \leftrightarrow LH^+$, where L is the ligand. The more negative the ΔG the more basic the molecule.

The Gibbs free energy for the protonation reaction at 25°C is described as;

$$\Delta G_R = \Delta H_R - T\Delta S_R$$

$$\Delta H_R = E(LH^+) - E(L) - E(H^+) + \Delta(PV)$$

$$\text{where } E = E_{\text{elec}} + E_{\text{ZPE}} + (E - E_0)$$

$$-T\Delta S_R = -298.15[S(LH^+) - S(L) - S(H^+)]$$

E_{elec} is the energy of the geometry optimised structure at 0 K, E_{ZPE} is the zero-point energy and $(E - E_0)$ is the energy difference between 0 and 298.15 K. The zero-point energies are adjusted by the correction factor of 0.91 /5-7/. The electronic energy for the proton is zero and the only energy term that contributes to $E(H^+)$ is the translational energy which is equal to $3/2RT$. Since one mol of gas disappears in the reaction the $\Delta(PV)$ term is equal to $-RT$ and the entropy term of a free proton is equal to 7.76 kcal/mol /5-7/.

$$\Delta H_R = E(LH^+) - E(L) - 3/2RT - RT = E(LH^+) - E(L) - 0.889 \text{ kcal/mol}$$

The energies and entropies for the unprotonated (L) and protonated (LH⁺) malonamides can be obtained from frequency calculations preceded by a full geometry optimisation, using the Gaussian 94 software. The basis set 3-21G was used in the geometry calculations and 6-31G* was used for the frequency calculations. All computations were carried out on Silicon Graphics Origin 2000 Supercomputer at Reading University.

The calculated ΔG in Table A7-4 are ordered from the least basic to the most basic structure (the one with most negative ΔG). The long carbon chain at the central carbon (C₁₄H₂₉), which is needed to achieve enough lipophilicity in the extractions, was replaced by a hydrogen to minimise the computation time. Extraction studies with the 2,6-dichlorophenyl derivative is being synthesised and will help to verify the relation between calculated and measured basicity.

Table A7-4. The difference free Gibbs energy for the protonation reaction of some different substituted malonamides (Gaussian94 HF/6-31G*, full geometry optimisation).

R	R ₂	ΔG_r (kcal/mol)
4-Cl-phenyl	H	-215.30
phenyl	H	-228.56
2,6-diCl-phenyl	H	-229.35
cyclohexyl	H	-230.71

These calculated obtained basicity data show the same relative order of basicity as the experimentally determined basicities. More calculations and measurements on new malonamides, e.g. with alkoxy groups on the central carbon, are in progress and are needed to verify the relation between calculated and experimental basicity and the correlation between basicity and extraction. If a property, like basicity, which seems to be related to the metal extraction, could be calculated accurately it might simplify the design of future, optimal extractants.

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Separation of trivalent actinides and lanthanides with some substituted oligopyridines and triazines in synergy with 2-bromodecanoic acid*

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Abstract

The separation of trivalent actinides and lanthanides with some substituted oligopyridines and triazines in synergy with 2-bromodecanoic acid was studied. All ligands, except the quinolinyl-derivatives, showed high metal extraction and good separation factors for trivalent actinides over lanthanides. The substituted di-pyridyltriazines and the quaterpyridine showed the highest distribution ratios and quater- and quinquepyridine the highest separation factors, at low nitric acid concentration. The basicity of the different ligands were determined by non-aqueous titration in acetonitrile media and was related to the metal extraction. The substituted di-pyridyltriazines, which showed the highest metal extraction also showed the lowest basicity.

Keywords: Separation, Actinides, Lanthanides, Non-aqueous titration, Basicity.

Introduction

In future reprocessing of spent nuclear fuel, transmutable actinides are considered to be separated from the fission product /1/. One of the major problems in this reprocessing is the separation of the trivalent actinides from the lanthanides, because of their similar chemical properties /2/. Previous studies on tri-pyridyltriazines (TPTZ) showed that these ligands had potential to separate trivalent actinides and lanthanides /3/. Batch extraction experiments were performed to investigate the possibility of trivalent actinide-lanthanide separation by solvent extraction with a synergistic mixture of substituted oligopyridine or triazine and 2-bromodecanoic acid. Both extraction and separation ability were studied and the basicity of the different ligands was also determined by non-aqueous titration. The extraction and separation was put in relation to the basicity of the ligands.

*Paper presented at ISEC'99 in Barcelona

Experimental

Reagents: The listed oligopyridines and triazines, in Table A8-1, were synthesised at the University of Reading except for Terpy, 98%, which was purchased from Aldrich. The purity of the synthesised ligands were checked by ¹H-NMR, elemental analysis and melting point. *Tert*-butylbenzene (TBB), 99% purity, was used as the diluent in all experiments and was purchased from Acros and 2-bromodecanoic acid (HA), 98% purity, was obtained from Fluka. HPLC-grade acetonitrile from Fischer Scientific, with less than 0.0040% water, was used in the non-aqueous titrations.

Table A8-1. Ligands studied in this work.

Ligand	Name/Abbreviation	Ligand	Name/Abbreviation
	2,2':6',2''-terpyridine Terpy		(4',4'')-di-(4-heptyloxyphenyl)-2,2':6'2'':6''2''':6'''2''''-quinquepyridine Quinque
	4'-tolyl-2,2':6'2''-terpyridine Tolpy		4-octanoyl amino-2,6 di(2-pyridyl) 1,3,5 triazine OADPTZ
	4'-(4-nitrophenyl)-2,2':6'2''-terpyridine Nitrotolpy		4-tetradecanoyl amino-2,6 di(2-pyridyl) 1,3,5 triazine TADPTZ
	4'-(4-dodecyloxyphenyl)-2,2':6'2''-terpyridine Dodoxy		4-tetradecanoyl amino-2,6 di(2-quinoliny) 1,3,5 triazine TADQZT
	(4',4'')-ditolyl-2,2':6'2'':6''2''''-quaterpyridine Quater		4-octanoyl amino-2,6 di(2-quinoliny) 1,3,5 triazine OADQZT

Procedure: The solvent mixture of 2-bromodecanoic acid and the extractant (oligo-pyridine or triazine) in TBB was vigorously shaken with the aqueous phase, containing tracer amounts of ^{241}Am and ^{152}Eu , for five minutes at room temperature. After phase disengagement by centrifugation, aliquots of each phase were taken for radiometric analysis. The γ -activities at 59.6 keV and 122 keV, for ^{241}Am and ^{152}Eu respectively, were measured using a HPGe detector. The distribution ratio D_M was the ratio of the radioactivity of aliquots of organic and aqueous phases, with equal volumes.

The basicities were determined by titration in acetonitrile media, using 0.1M HClO_4 in acetic acid as the titrand /4/. The half-neutralisation potential (HNP) was taken as a value for the basicity after subtraction of the HNP of a imidazole, which was used as an internal reference to be able to adjust for drift of the electrode during the experiment. To facilitate dissolution of the ligands in the titration media, a constant amount of HA was added to the solvent in each experiment. For Quater and Quinque, which are even harder to dissolve, chlorobenzene was also added to the titration media to dissolve the ligands and the ligands were thereafter compared to Terpy in the same media.

Results and discussion

Metal extraction: Extraction studies have been carried out on a number of oligo-pyridines and triazines in synergy with 2 -bromodecanoic acid (HA) in *tert*-butylbenzene (TBB).

A substitution on the terpyridine was expected to increase the distribution ratios because of an increase in lipophilicity of the ligands, but the distribution ratios for the substituted terpyridines are lower than for the unsubstituted Terpy. Other effects, like the basicity of the ligands, seems to be more important for the metal extraction than lipophilicity. The substituted terpyridines in Figure A8-1, i.e. Tolpy, Dodoxy and Nitrotolpy, show similar nitric acid dependency, distribution ratios and separation factors for americium and europium. The different substituents on the central pyridyl groups doesn't seem to effect the extraction considerably.

The substituted triazines, TADPTZ and OADPTZ, showed even better extraction than the oligopyridines, although the separation factor is similar to the oligopyridines, see Figure A8-1 and Table A8-2. On the other hand, the quinoliny derivatives, OADQTZ and TADQTZ, showed almost no contribution to the metal extraction or separation compared to extraction with only HA, see Figure A8-1.

The oligopyridines with four and five pyridyl-groups respectively, Quater and Quinque, both showed larger selectivity for americium over europium than both the substituted terpyridines and the triazines at low nitric acid concentration, Figure A8-2. The number of nitrogens that are coordinated to the metal could be the important factor to achieve good separation of trivalent actinides and lanthanides. However, when the nitric acid concentration is increased the separation factor decreases to a value below the separation factor for the terpyridines, indicating that protonation might hinder the coordination at higher nitric acid concentration.

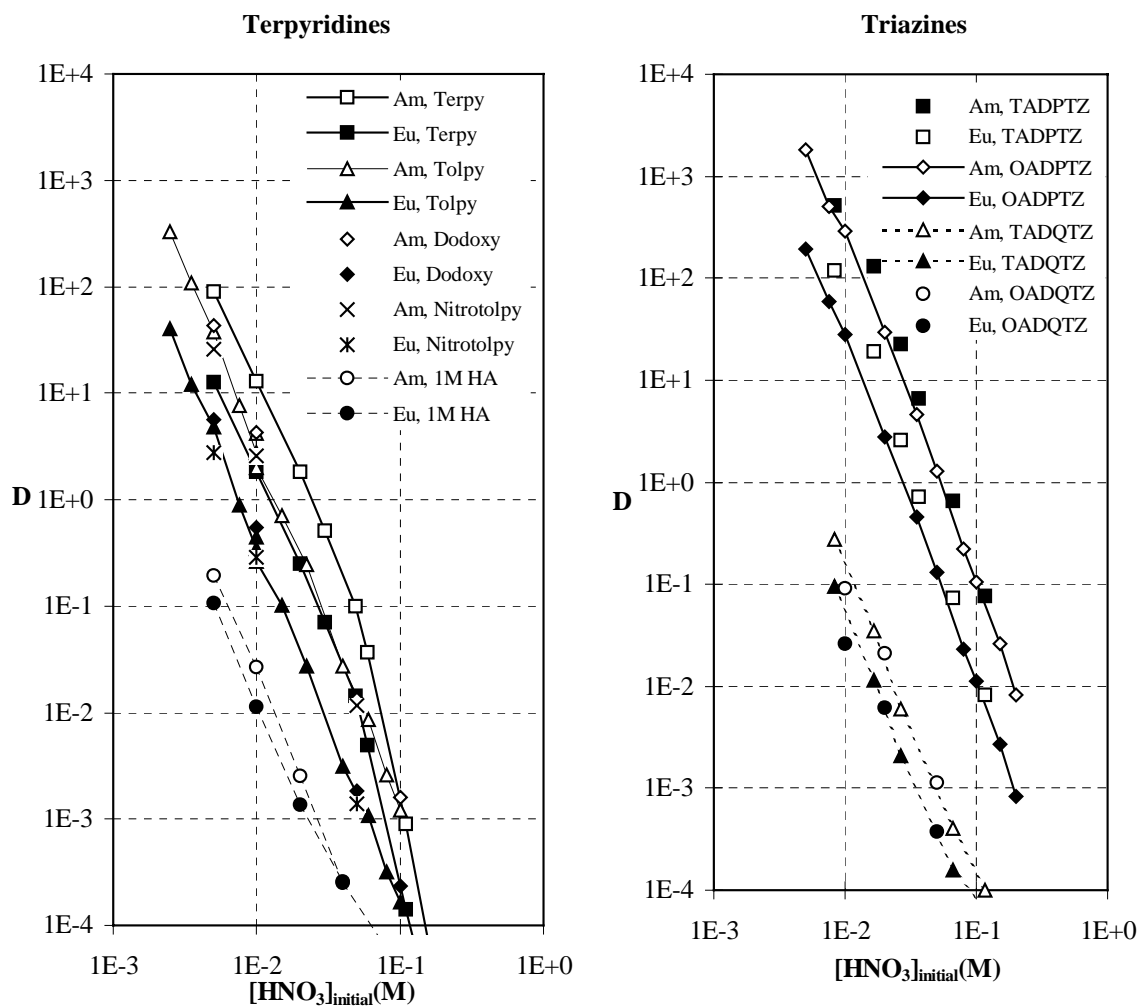


Figure A8-1. Extraction of americium and europium with 0.02M oligopyridine or triazine and 1M 2-bromodecanoic acid (HA) in tert-butylbenzene compared to extraction with only 1M HA.

Table A8-2. Extraction data with 0.02M oligopyridine and 1M HA in TBB at 0.01M HNO₃, Average Δ HNP measured in acetonitrile, addition of 0.25mmol HA. Δ HNP = HNP_{ligand⁻} - HNP_{imidazole} (* interpolated values).

Ligand	Δ HNP(mV)	D _{Am}	SF (D _{Am} /D _{Eu})
Dodoxy	127	4.2	7.7
Tolpy	138	2.8	8.3
Terpy	165	13	7.2
Nitrotolpy	187	2.6	9.0
TADPTZ	187	359	7.5*
OADPTZ	190	287	10
OADQ TZ	215	0.09	3.5
TADQ TZ	232	0.16	3.0*

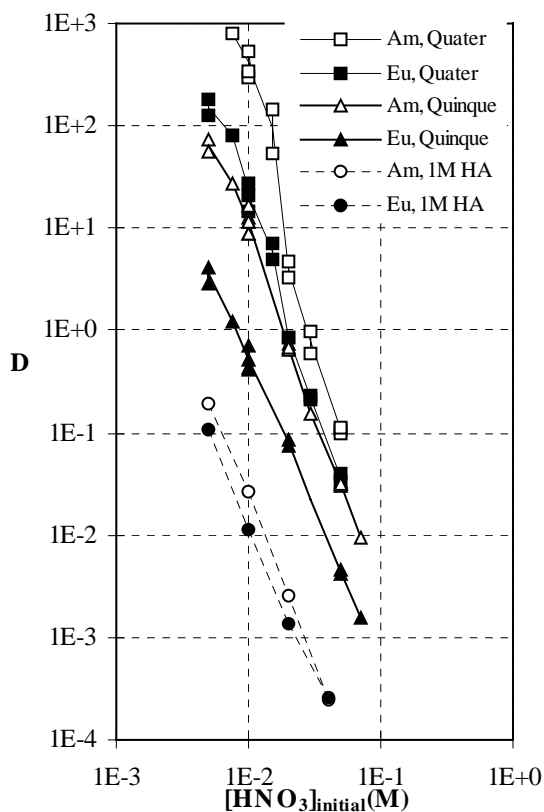


Figure A8-2. Extraction of americium and europium by 0.02M of Quater or Quinque and 1M 2-bromodecanoic acid in tert-butylbenzene from different initial nitric acid concentrations.

Basicity: The basicity of the ligands are assumed to be related to the metal extraction due to competition between protons and metal ions for the binding sites in the molecules, when extracted from acidic media. The basicity was therefore measured for the different ligands, using non-aqueous titration in acetonitrile media. The potential at the half-neutralisation volume (HNP) was used as a measure for the basicity, adjusted with HNP for an internal reference.

The titrations of the different ligands showed lower basicity, higher Δ HNP, for Terpy compared to the substituted terpyridines, Dodoxy and Tolpy, as seen in Table A8-2. The metal extraction is highest for Terpy compared to the other terpyridines which is consistent with the assumption that low basicity gives high metal extraction. However, Nitrotolpy showed the lowest basicity of the terpyridines but also the lowest metal extraction. Low solubility of this ligand in the organic phase might cause the lower extraction. By adding extra lipophilic groups, to increase the solubility, the extraction might increase.

The substituted triazines showed even lower basicity compared to the substituted oligopyridines, see Table A8-2. The di-pyridyltriazines, TADPTZ and OADPTZ, also showed better metal extraction, but the quinolinyl derivatives, TADQTZ and OADQTZ, showed the lowest metal extraction of all studied ligands. The metal extraction seen in Figure A8-1 is mainly due to HA in this system. Molecular modelling shows that there is sterical hindrance in the molecule and this might make a coordination difficult and therefore decrease the extraction.

The separation factor doesn't seem to change much when basicity changes. The best separation factors were achieved by Quater and Quinque at low nitric acid concentration and their basicity was shown to be even higher than Terpy, see Table A8-3. The number of nitrogens that coordinate to the metal during the extraction might be more important for the separation, as mentioned earlier.

Table A8-3. Extraction data with 0.02M oligopyridine and 1M HA in TBB. Average Δ HNP measured in 60% acetonitrile / 40% chlorobenzene with addition of 1mmol HA, Δ HNP = $HNP_{\text{ligand}} - HNP_{\text{imidazole}}$ (* interpolated values).

Name	Δ HNP(mV)	D_{Am}	SF ($D_{\text{Am}}/D_{\text{Eu}}$)
Terpy	127	13	7.2
Quater	112	390	19
Quinque	100	12	22

The relation between metal extraction and basicity is seen in Figure A8-3 where $D_{\text{Am(III)}}$ at 0.01M HNO_3 is plotted versus the Δ HNP for the different ligands. The quinolinyl derivatives were excluded in this graph since they don't contribute to the extraction compared to HA alone. Nitroterpy is also a bit out of range, but solubility problems with this ligand is probably effecting the metal extraction, as discussed earlier.

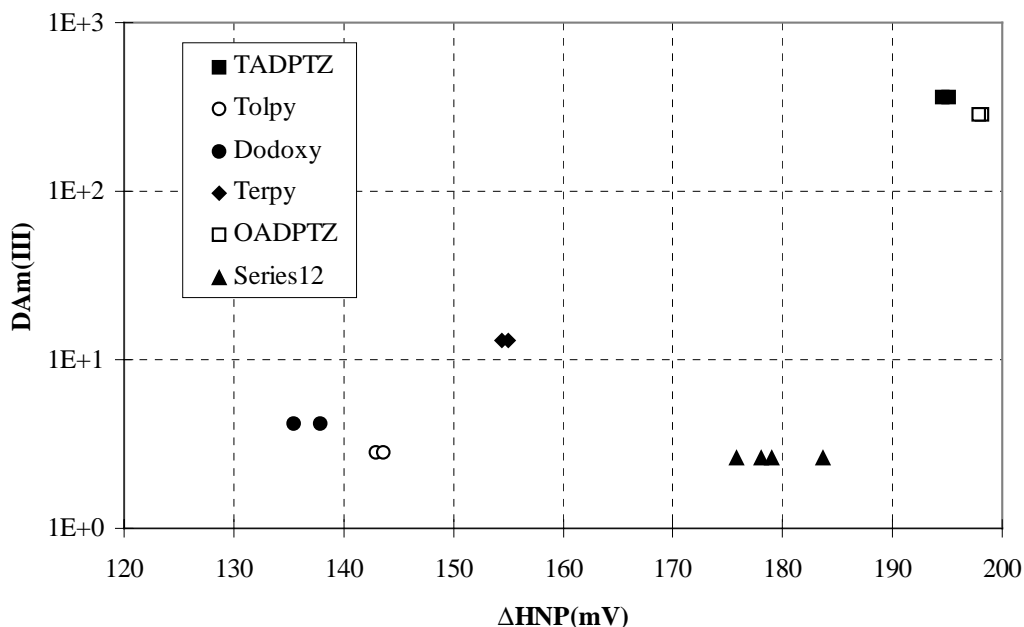


Figure A8-3. Extraction of Am(III) at 0.01M HNO_3 with 0.02M of the ligand, 1M HA in tert-butylbenzene plotted versus basicity (HNP) in acetonitrile.

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