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Partitioning and transmutation
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Ingela Hagström, Anders Landgren, Jan-Olov Liljenzin,
Mats Skålberg, Lena Spjuth

Department of Nuclear Chemistry,
Chalmers University of Technology, Göteborg

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

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1. INTRODUCTION

The current research project on Partitioning and Transmutation (P&T) at the Department of Nuclear Chemistry, CTH, has the primary objective to investigate separation processes useful in connection with transmutation of longlived radionuclides in high level nuclear waste. Partitioning is necessary in order to recover and purify the elements before and after each irradiation in a P&T treatment. In order to achieve a high transmutation efficiency the chemical separation process used must have small losses to various waste streams.

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. The engineering and operation experience from wet separation processes by far exceeds those of alternative processes based on melt refining, molten salt electrolysis, pyroprocessing, and volatility. It is realistic to believe that aqueous separation techniques will continue to be far ahead of the other possibilities for a long time to come. This belief is shared by our European project partners and is the main reason why research on separation processes at the department is concentrated on aqueous/organic liquid-liquid extraction systems.

2. SOLVENT EXTRACTION RESEARCH

New extraction reagents should be selective, have a high loading capacity and be burnable without solid residues. This limits the possible elements in the extractant molecules to hydrogen, carbon, nitrogen and oxygen, the so called CHON-principle. However, the CHON-principle has also a wider meaning. Addition of chemicals to the process solution should be limited to those already present in large amounts in high level waste from conventional PUREX reprocessing of spent fuel, i.e. water and nitric acid.

Long chained amines and quaternary ammonium salts constitute one group of possible CHON-reagents. Other useful reagent classes are derivatives of malonamides, of tri-pyridyl-triazine, of picolinamides, and various oligopyridines, e.g. terpyridin and is derivatives. In order to comply with the requirements of high loading capacity, reasonable viscosity and high solubility in suitable organic diluents, the molecular weight of the reagent must not be too high. Furthermore, part of the reagent structure should have some similarity to the diluent molecules in order to maximize solubility at a given molecular weight. On the other hand, the molecular weight of the reagent should be high enough to make the reagent little soluble in the aqueous phase.

Due to the similarity in chemical behavior of lanthanides and the trivalent actinides (americium and curium) various routes can be envisaged, e.g., (i) coextraction of both element groups followed by stripping and separation of the element groups (or single elements) by a second reagent having sufficient separation power, (ii) extraction of trivalent actinides only by using a very selective reagent. The main strategy in our research follows route (i) above.

2.1 Long chain quaternary amines

Aliquat-336 (tricapryl-methylammonium nitrate) is a quaternary ammonium salt that extracts neutral or negatively charged species with an anion exchange mechanism. The diluent used is a dialkyl substituted aromatic compound, 1,3-diisopropylbenzene. In the experiments done, the distribution of elements between the two phases is measured and expressed in terms of the distribution ratio, D.
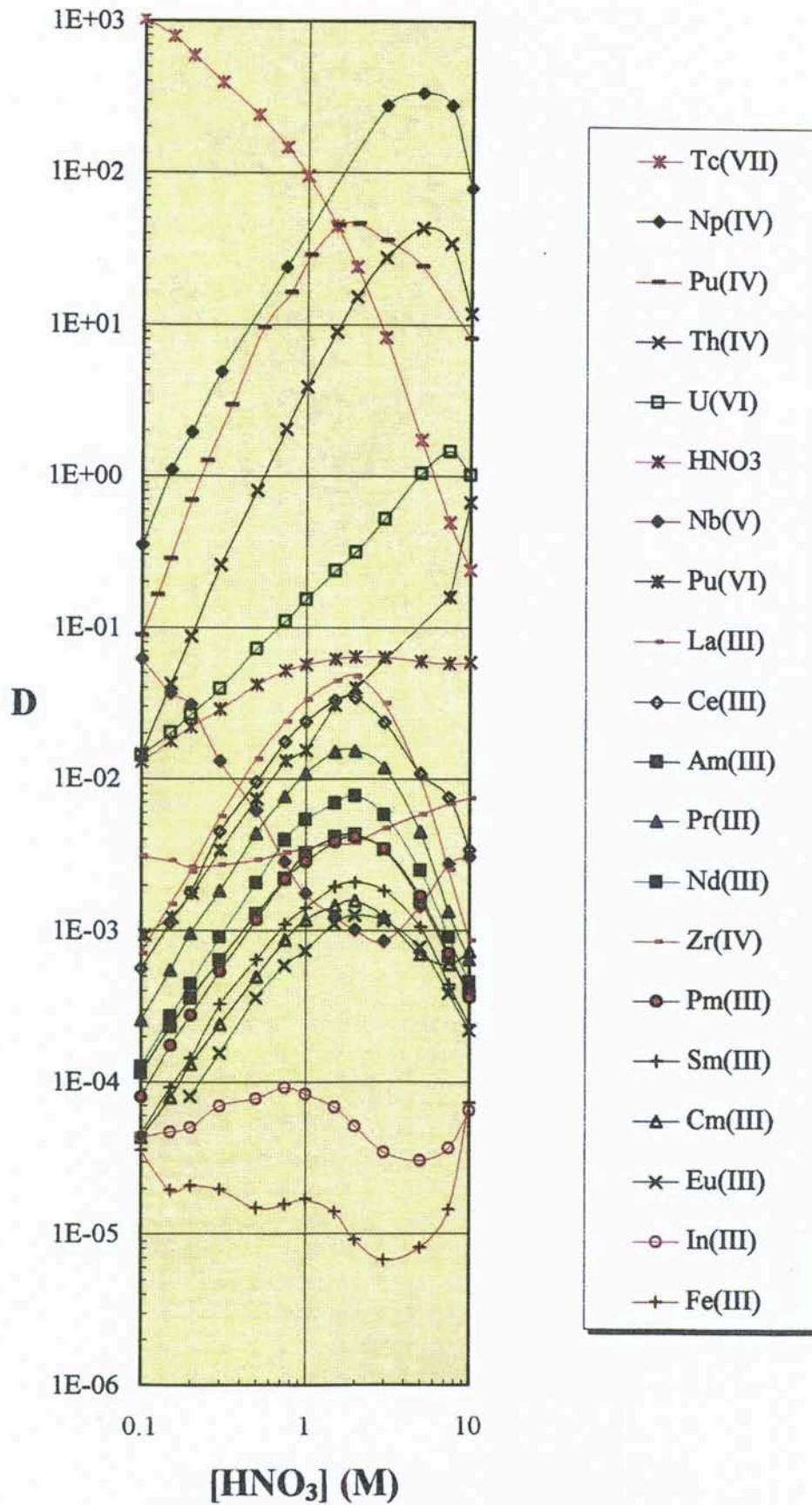
$$D_M = [M]_{org,tot}/[M]_{aq,tot}$$

Figure 1. *Distribution ratios for some elements as a function of the nitric acid concentration.*

The distribution ratio for M is defined as the ratio of the total concentration of M in the organic phase, $[M]_{org,tot}$, to the total concentration of M in the aqueous phase, $[M]_{aq,tot}$. A distribution ratio greater than unity means that M is enriched in the organic phase whereas a distribution ratio less than unity means that M is enriched in the aqueous phase.

The extraction of metal cations with Aliquat-336 will depend on the charge and radius of the metal ion, i.e., the ability to form complexes with the ligand, the ligand concentration and the extractant concentration. By varying the oxidation state of the metal and the ligand concentration it is possible to separate different elements from each other.

Some distribution ratios as a function of the nitric acid concentration are shown in Figure 1 [1, 2]. The results are given at 0.20 molar Aliquat-336 in the organic phase, except for plutonium which is given at 0.05 molar. The tetravalent elements, Th^{4+}, Np^{4+} and Pu^{4+}, all have distribution ratios above unity. These highly charged elements easily form complexes with nitrate and can therefore be separated from lower charged cations. The trivalent elements, Ln^{3+} (lanthanides), Am^{3+}, Cm^{3+}, In^{3+} and Fe^{3+}, all have distribution ratios below unity. Since the charge is lower for these elements they do not form nitrate complexes as easily as the tetravalent elements. Distribution ratios for the hexavalent elements, uranium and plutonium, as uranyl and plutonyl ions are between those of the tetravalent and trivalent elements. This is due to the fact that the charge of the metal atom in MO_2^{2+} is higher than the effective charge of the ion. Technetium as pertechnetate, i.e. an anion, shows very high distribution ratios at low nitric acid concentration. In this case pertechnetate ions can extract directly in to the organic phase without forming nitrate complexes. Nitrate ions will compete with pertechnetate ions for extractant molecules and therefore the distribution ratio is decreasing with increasing nitric acid concentration. Nitric acid is also extracted with Aliquat-336. Although the distribution ratio is low, the nitric acid consumes a large amount of extractant molecules since the nitric acid concentration is high. This is the reason why the distribution ratios for the tri- and tetravalent elements show a maximum when the nitric acid concentration is increased. The extraction of zirconium and niobium is difficult to explain.
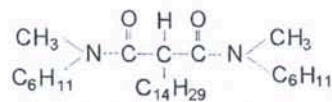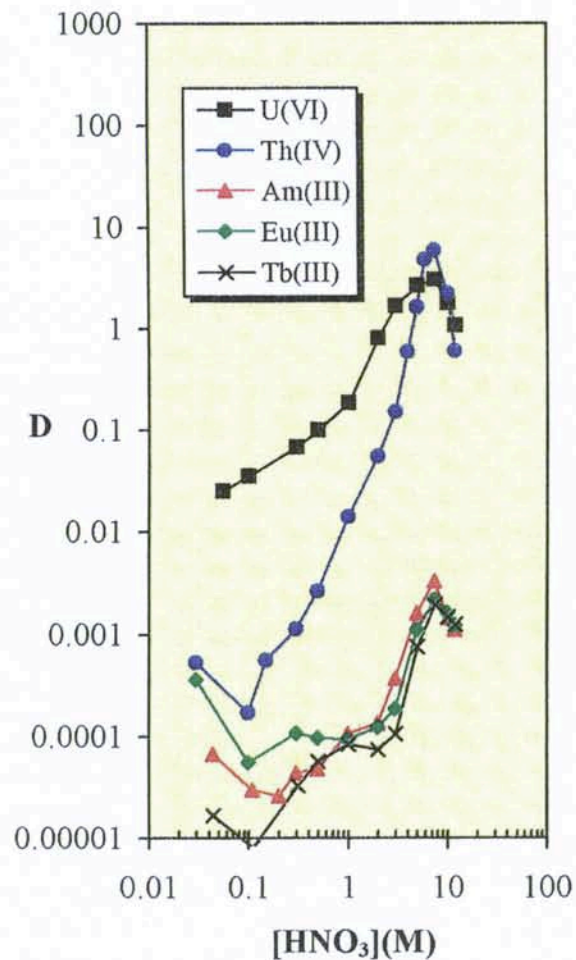
2.2 Malonamides

Coextraction of trivalent actinides (Am^{3+}, Cm^{3+}) and lanthanides are considered as an interesting separation route in a partitioning process with a following step for separation of trivalent actinides and lanthanides. Malonamides have shown potential as a possible coextractant for actinides and lanthanides in such a process. In France, a separation process called the DIAMEX process, based on a malonamide is under development.

Molecular structure and electro-inductive effects are important factors when extraction by malonamides is considered. The studies at Chalmers are concentrated on structural and electronic influences on metal extraction by three different malonamides. The synthesis of these malonamides is performed in collaboration with the University of Reading. Extraction data for some actinides, lanthanides and nitric acid has been determined [3], see Figure 2. When the nitric acid concentration is increased the phenyl substituted malonamide shows a constant increase in metal extraction. The other two malonamides do not behave in this way. Steric effects in the malonamides were evaluated by molecular modelling and it could be concluded that the phenyl groups in DMDPHTD minimize the steric hindrance in the molecule and that this might be one of the reasons for the increase in metal extraction for DMDPHTD [4]. The electro-inductive effects by the phenyl groups is probably also involved. By mixing the neutral malonamides with 2-bromodecanoic acid (a carboxylic acid with relatively low pK_a) a synergistic effect in the extraction is observed and a separation between Am and Eu is observed [5]. Because this acid violates the CHON-principle we are searching for other
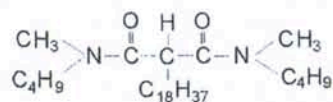
N,N′-dimethyl-N,N′-dibutyloctadecyl malonamide (DMDBOD)

N,N′-dimethyl-N,N′-dicyclohexyltetradecyl malonamide (DMDCHTD)
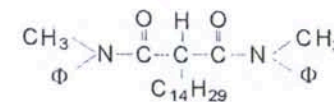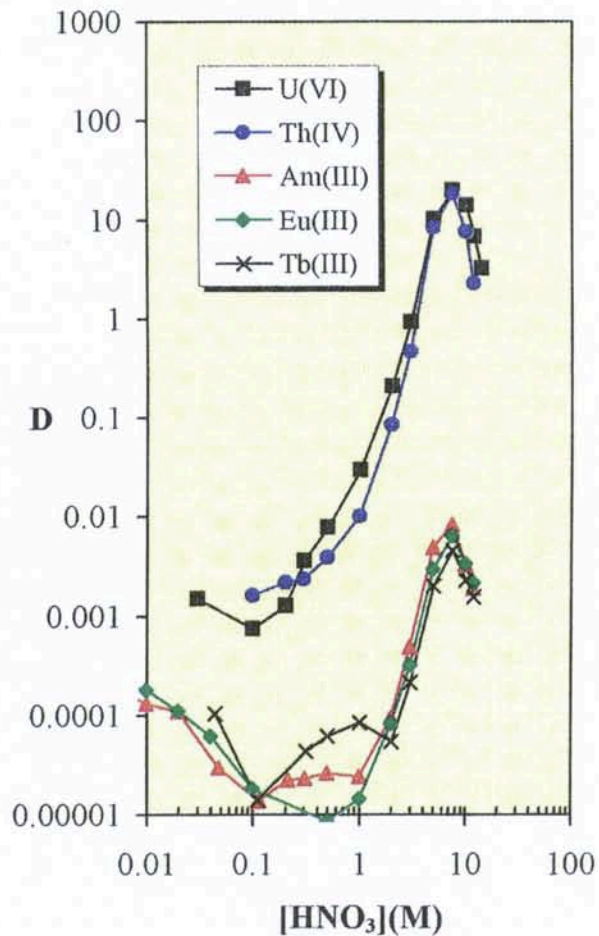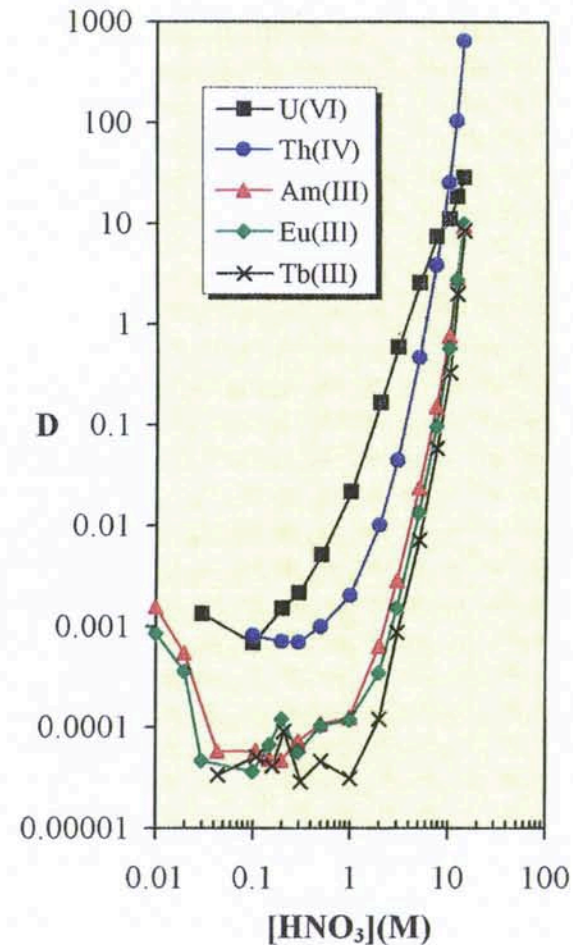
N,N′-dimethyl-N,N′-diphenyltetradecyl malonamide (DMDPHTD)

Figure 18-2. Extraction data for some elements by 0.1 M malonamide in **tert**-*butylbenzene.*

organic acids which could replace 2-bromodecanoic acid.

In March 1996, one graduate student (Lars Ekengren) finished his diploma work regarding extraction by malonamides. Two different extraction mechanisms were evaluated and a minimization program was used to fit the suggested extraction mechanism to the experimentally achieved extraction data [6].

2.3 Oligopyridines

Nitrogen-donor reagents have been shown to have a potential to separate trivalent actinides from lanthanides, probably because of the more covalent character of the nitrogen-actinide bond compared to the nitrogen-lanthanide bond. TPTZ (2,4,6-tri-(2-pyridyl)-1,3,5-triazine) and oligopyridines are suggested as interesting basic structures for this purpose. Because of the hydrophilicity of the reagents, a lipophilic carboxylic acid has to be added. The carboxylic acid should have a low pK_a since it has to be dissociated to some degree in the pH range of interest (<3). 2-bromodecanoic acid has been used for this purpose. The presence of 2-bromodecanoic causes a synergistic effect in the metal extraction and at the same time a separation factor between lanthanides and trivalent actinides of about 10 is achieved [5].

3. COLLABORATION

Sweden
The swedish coordination-group in partitioning and transmutation, initiated in 1993, consisting of representatives from universities and industries was involved in arranging the Second International Conference on Accelerator-Driven Transmutation Technologies and Applications (ADTT) in Kalmar, Sweden, June 3-7, 1996. The participating universities and industries in the coordination group are;

* Chalmers University of Technology, Göteborg, J.O. Liljenzin, M. Skålberg, A. Landgren, L. Spjuth, and Ingela Hagström.
* Royal Institute of Technology, Stockholm, T. Thedéen, W. Gudowski, and E. Möller.
* Uppsala University and The Svedberg Laboratory, H. Condé, S. Carius, E. Traneus, A. Bäcklin, and J. Thun.
* Manne Siegbahn Laboratory, Stockholm, M. af Ugglas.
* Scanditronix Medical Systems AB, Uppsala, B. Anderberg, and J. Modeer.
* Experts on reactor technology, Västerås, K. Hannertz, C. Sundkvist, C. Pind, and E. Tenerz.
* The Industrial Group, C. Mileikowsky.

EC
A collaboration with France, England, Germany, Italy and Sweden officially started on the 1 st of May 1996. The project is funded by the EC (NEWPART CT FI4I-CT96-0010). A project meeting was held on July 1 in Brussels and the first progress meeting, where all participants presented their work, was held in Marcoule, November 13-15. The next progress meeting will be held in Göteborg, Sweden, May 1997, and will be arranged by the Department of Nuclear Chemistry.

UK
Within the EC-contract there is a close collaboration between Chalmers and the University of Reading, UK, concerning synthesis and investigations of new nitrogen containing extractants. The malonamides used in the investigations at Chalmers were synthesized in Reading.

Investigations of new alkylated terpyridines, which are being synthesized in Reading, are planned to begin early in 1997.

Germany

Professor Heino Nitsche from Forschungszentrum Rossendorf in Dresden, visited our department in June and discussions about future collaboration were held. A collaboration with the Transuranium Institute was initiated. Calculations on Rubbia's Fast Energy Amplifier was performed comprising of core calculations and reprocessing losses. The work resulted in a paper which was presented at the ADTT conference.

France

The close collaboration with CEA in France was continued. Present and future work has been discussed with Charles Madic and coworkers at several occasions. Experiences with the AKUFVE system were also exchanged.

USA

An informal collaboration was initiated in 1992 between 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 Research Institute (JAERI). It was agreed to exchange information, results and personnel between CTH and JAERI.

4. TRAVELLING

Several conferences were attended during 1996, see the travelling reports (appendix VI- VIII).

5. LECTURES

Prof. Jan-Olov Liljenzin has given the following invited lectures:

1996-02-02   at KTH/MSL, Stockholm, Separation for transmutation

1996-02-12   at a meeting of The Royal Society of Art and Languages, Göteborg, Slutlagring av radioaktivt avfall. Var ligger problemen? (Final storage of radioactive waste. Where are the problems?)

1996-05-15   at the Departments of Inorganic Chemistry of CTH and of GU, Göteborg, Varför har vi grundämnen? Stjärnans vardagsliv på huvudserien i Hertzprung-Russel diagrammet (Why do we have chemical elements? The daily life of a star on the main sequence in the Hetzprung-Russel diagram)

1996-05-22   at the symposium "Den internationella utvecklingen av kärnkrafttekniken" (The international development of nuclear power technology), Stockholm, Hur utvecklas upparbetning av använt kärnbränsle och separation av aktinider (How is the development of reprocessing of spent fuel and separation of actinides proceeding)

1996-10-31   at Föreläsningar i kemi (public lectures in chemistry in cooperation with; Akzo Nobel, EKA Chemicals, Mölnlycke, Astra Hässle, Volvo and Norsk Hydro) CTH/GU, Göteborg, Kärnkraftteknik. Igår - Idag - Imorgon. (Nuclear Energy Technology. Yesterday - Today - Tomorrow.)

1996-11-11   at the Symposium on Radiochemistry in Memory of Marie Curie, University of Helsinki, History and Present Status of Teaching and Research in Radiochemistry and Nuclear Chemistry at Chalmers University of Technology.

Dr. Mats Skålberg has given the following invited lecture:

1996-04-20   at Svenska Kemistsamfundets undervisningssektions studiedagar i Stenungsund, Stenungsund, Transmutation och Separation (Transmutation and Separation)

All the scientists involved in the Transmutation and Partitioning project at Chalmers presented their work at SKB in October 1996.

Lena Spjuth gave an invited lecture about spent nuclear fuel, waste management and recycling of fuel for SKR (Sveriges Kemiingenjörers Riksförening) in February 1996.

6. REFERENCES

[1]   Landgren, A., Liljenzin, J.O., and Skålberg, M., The extraction of Some Trivalent Elements with Aliquat-336, *Proceedings of the International Conference on Accelerator-Driven Transmutation Technologies and Applications (ADTT)*, Las Vegas, USA, July 25-29, (1994) 646-652.

[2]   Landgren, A., Liljenzin, J.O., and Skålberg, M., A Separation Process Based on Aliquat-336, TBP and HDEHP, *Proceedings of the International Solvent Extraction Conference - ISEC'96*, Melbourne, March 19-23, (1996) 1315-1320. See appendix I.

[3]   Spjuth, L., Liljenzin, J.O., Skålberg, M., Hudson, M.J., Chan, G.Y.S., Drew, M.G.B., Feaviour,M., and Madic, C., Coextraction of Actinides and Lanthanides from Nitric Acid Solution by Malonamides, Submitted to *Radiochimica Acta* (1996).

[4]   Chan, G.Y.S., Drew, M.G.B., Hudson, M.J., Iveson, P.B., Liljenzin, J.O., Skålberg, M., Spjuth, L., Madic, C., Solvent extraction of metal ions from nitric acid solution using N,N'-substituted malonamides. Experimental and crystallographic evidence for two mechanisms of extraction, metal complexation and ion-pair formation, Accepted for publication by *J. Chem. Soc. Dalton Trans.* (1996).

[5]   Hagström, I., Spjuth, L., Liljenzin, J.O., Skålberg, M., Synergistic Extraction of Americium and Europium by 2-Bromodecanoic Acid and Nitrogen-Containing Neutral Ligands, Manuscript in preparation (1996).

[6]   Ekengren, L., *Extraction studies with N,N'-substituted malonamides*, Diploma Thesis, Department of Nuclear Chemistry, Chalmers University of Technology, March 8, (1996). See appendix V.

[7]   Magill, J., Peerani, P., van Geel, J., Landgren, A., and Liljenzin, J.O., Inherent Limitations In Toxicity Reduction Associated with Fast Energy Amplifiers, *Proceedings of the International Conference on Accelerator-Driven Transmutation Technologies and Applications*, Kalmar, June 3-7, (1996). See appendix III.

Appendix
I

A Separation Process Based on Aliquat-336, TBP and HDEHP

A. Landgren, J.-O. Liljenzin and M. Skålberg

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

ABSTRACT

A baseline flow sheet for separation of elements intended for transmutation is presented. In the first part of the process Aliquat-336 dissolved in 1,3-diisopropyl benzene is used as extractant. Since little data is available for the Aliquat-336 system the extraction of some elements and nitric acid with Aliquat-336 dissolved in 1,3-diisopropyl benzene has been studied. The extraction data obtained were then used in a code for process calculations where the number of steps and volume flow ratios needed in each extraction battery were determined.

INTRODUCTION

Transmutation of long lived radionuclides in nuclear waste into short lived or stable nuclides requires a partitioning stage, where untransmuted material is separated from transmuted and recycled for further neutron irradiations. One way of achieving a sufficient separation yield, quantitatively as well as qualitatively, is by using solvent extraction. The Los Alamos National Laboratory (LANL) - Jarvinen (1992) - has suggested a separation process based on Aliquat-336 (tricaprylmethyl-ammonium nitrate) and HDEHP (bis-2-ethylhexyl phosphoric acid). However, it was found that some stages in the suggested process would not work as proposed and therefore some modifications of the process flow sheet were made. In the process (see Figure 1) neptunium and plutonium in their tetravalent state, technetium as pertechnetate and iodine are extracted from a 2 molar nitric acid solution to an organic phase consisting of 0.2 molar Aliquat-336 in DIPB (1,3-diisopropyl benzene). After a scrubbing stage, neptunium and plutonium are stripped from the organic phase to 0.1 molar nitric acid. In the next stage, technetium is stripped with 10 molar nitric acid whereafter the organic phase is washed to prevent buildup of remaining elements. The outgoing raffinate contains about 2 molar nitric acid. Before this stream is fed to a Reversed Talspeak process, the nitric acid concentration must be lowered to about 0.1 molar. This is done in the next stage, where nitric acid, ruthenium and palladium are extracted with 50 % TBP (tributyl phosphate) in Nysolvin 75A (an aliphatic kerosene) whereafter ruthenium and palladium are stripped with 9 molar nitric acid. Nitric acid is recovered in the next stage where it is stripped by water giving a 3 molar solution. In the Reversed Talspeak process americium, curium and the lanthanides are extracted with 1 molar HDEHP (bis-2-ethylhexyl phosphoric acid) in Nysolvin 75A. The actinides, americium and curium, are stripped with 0.05 molar DTPA (diethylene triamine pentaacetic acid), and 1.5 molar lactic acid whereafter the lanthanides are stripped with 6 molar nitric acid. Finally, the organic phase is washed with 0.5 molar ammonium carbonate and recycled to the first extraction battery in the Reversed Talspeak process. The separated neptunium, plutonium, americium, curium, technetium and iodine are then recycled to the transmuter for further neutron irradiations. Of the three parts described, it was found that little extraction data is available for the Aliquat-336 system and therefore the Aliquat-336 - nitric acid system has been investigated experimentally.
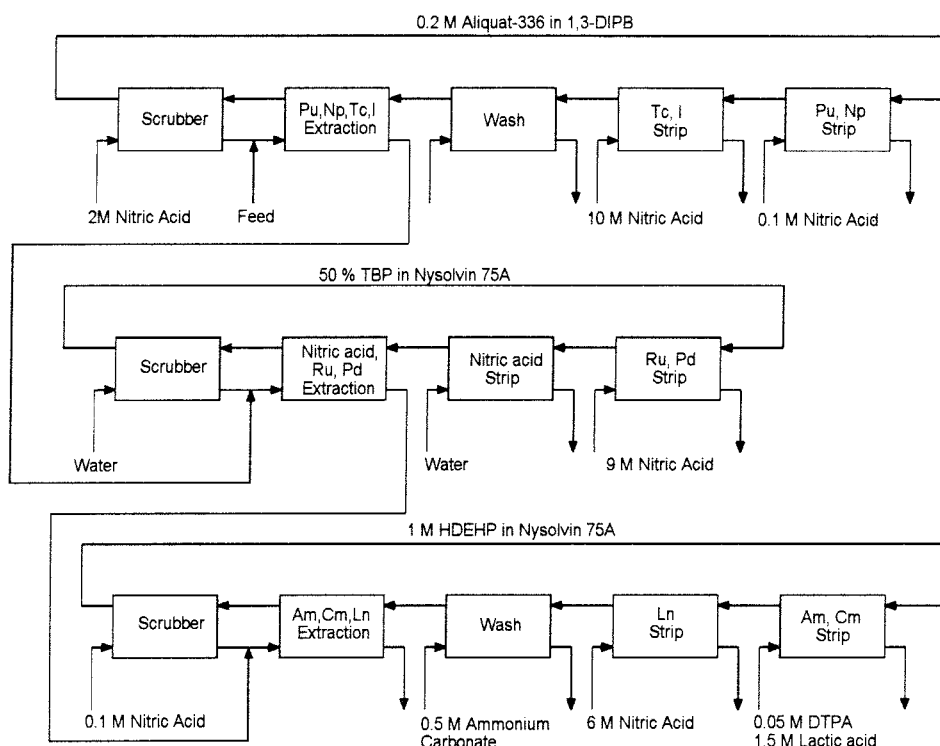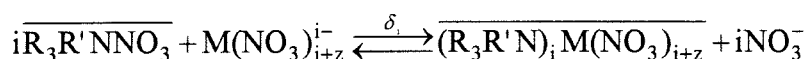
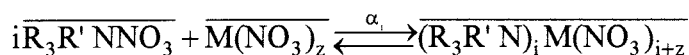**Figure 1. Flow sheet for the separation process.**

THEORY

Extraction of Metal Ions

Aliquat-336 is a quaternary ammonium salt extracting negatively charged species with an anion exchange mechanism or neutral species with an adduct formation mechanism. Therefore, positively charged species must form a negatively charged or neutral complex in the aqueous phase to be extracted with Aliquat-336. If it is assumed that no polynuclear complexes are formed the complex formation in nitric acid solution can be written

$$M^{z+} + iNO_3^- \xrightleftharpoons{\beta_i} M(NO_3)_i^{z-i}$$
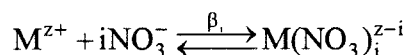
where z is the charge of species M, i is an integer $z \leq i \leq N$ where N is the maximum number of nitrate ions coordinated to M and β_i is the overall stability constant for the formation of the i:th nitrate complex. The extraction can take place either in the organic phase or at the interface according to

$$i\overline{R_3R'\,NNO_3} + \overline{M(NO_3)_z} \xrightleftharpoons{\alpha_i} \overline{(R_3R'\,N)_i\,M(NO_3)_{i+z}}$$

$$i\overline{R_3R'NNO_3} + M(NO_3)_{i+z}^{i-} \xrightleftharpoons{\delta_i} \overline{(R_3R'N)_i\,M(NO_3)_{i+z}} + iNO_3^-$$

respectively. Species in the organic phase are written with a line above their formulas. Since the metal nitrate complexes are weak a high nitrate concentration is needed for the extraction. The solution is thus far from ideal and activities should be used instead of concentrations in the

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equilibrium equations. However, activity factors are mostly unknown in the system used and difficult to determine. Therefore it is assumed that all activity factors are unity. The distribution ratio of M for the two cases can then be expressed as

$$D_{M^{z+}} = \sum_{i=0}^{P} \alpha_i \left[\overline{R_3R'NNO_3}\right]^i / \sum_{i=0}^{N} \frac{\beta_i}{\lambda_z\beta_z} \left[NO_3^-\right]^{i-z} = \sum_{i=0}^{P} \beta_{i+z}\delta_i \left[\overline{R_3R'NNO_3}\right]^i / \sum_{i=0}^{N} \beta_i \left[NO_3^-\right]^{i-z}$$

where P is the maximum number of Aliquat-336 molecules in the extracted species and λ_z is the distribution constant for the uncharged metal nitrate complex, between the organic and aqueous phases.

Extraction of Anions

Since Aliquat-336 is a liquid anion exchanger, negatively charged species can be extracted without formation of nitrate complexes. The anion A^{a-} is thus extracted according to

$$a\overline{R_3R'NNO_3} + A^{a-} \xrightarrow{\varepsilon_a} \overline{(R_3R'N)_a A} + aNO_3^-$$
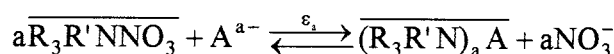
and therefore the distribution ratio for the anion A^{a-} can be expessed as

$$D_{A^{a-}} = \varepsilon_a \left[\overline{R_3R'NNO_3}\right]^a / \left[NO_3^-\right]^a$$

The extraction of nitric acid with Aliquat-336, lowers the concentration of free extractant in the organic phase. Since high nitrate concentrations are needed for extraction of positively charged species, the nitric acid will compete with the extractable metal nitrate complexes for extractant molecules.

EXPERIMENTAL

Nitric acid solutions were prepared from concentrated nitric acid of analytical grade (J.T. Baker). The organic solutions were prepared by dissolving Aliquat-336 in the nitrate form (Fluka) with 96 % 1,3-diisopropyl benzene (Acros). 5 % by volume 1-dodecanol (Merck) was added to the organic solutions as a third phase inhibitor. 3.98 ml of the aqueous phase and 20 µl of the radionuclide stock solution were added to a test tube which always gave a metal concentration less than 0.006 molar. The aqueous phase was allowed to "equilibrate" for one hour, whereafter 4.0 ml of the organic phase was added to the test tube. After shaking the tube vigorously for five minutes the phases were separated in a centrifuge at about 4000 rpm. A sample of suitable volume was withdrawn from each phase and transferred to a measuring vial. ^{95}Zr(IV), ^{95}Nb(V), and ^{235}U(VI) were determined by γ-spectrometry using a HPGe-detector, ^{234}Th(IV) was measured by liquid scintillation counting using a LKB WALLAC 1219 RACKBETA and ^{99m}Tc(VII) by a NaI(Tl) scintillation detector, Intertechnique model CG-4000. The extraction of nitric acid was investigated by potentiometric titration of hydrogen ions in both the aqueous and organic phases with sodium hydroxide using a Mettler DL20 titration equipment. The organic phase was titrated in 95 % ethanol (Kemetyl).

SIMULATION

The measured distribution ratios were expressed as a function of the initial nitric acid concentration in the aqueous phase and these functions were then inserted in a code for process calculations -

Liljenzin (1981). For the extraction of neptunium and plutonium with Aliquat-336, extraction data determined by - Shabana (1977) - has been used as an approximation. For ruthenium and palladium no extraction data is available for the Aliquat-336 system and therefore no calculation has been performed for these elements in this part. Data for the TBP - Svantesson (1979) - and HDEHP - Svantesson (1980) - systems are available in the code. The simulation was performed in order to calculate the number of stages and volume flow ratios needed in each mixer-settler battery to separate at least 99.9 % of the elements intended for separation in that battery.

RESULTS

The results from the simulation are given as percent extracted of the total incoming amount of each element to every battery. Also the number of stages and volume flow ratios needed are calculated. The results are given in Tables 1 and 2. A value of 100 % in the tables means that the extraction is higher than 99.9995 % and a value of 0.000 means that it is lower than 0.0005 %. In the part of the process where TBP is used, the volume change of the organic and aqueous phases is taken into account. The volume flow ratio is not constant through the extraction battery. In Tables 1 and 2 the volume flow ratio is given as the ratio between the flow rates of the incoming organic and aqueou streams.

TABLE 1
Percent in the organic phase leaving each battery. *Extraction part/Scrubber part

Element	Pu, Np, Tc, I Extraction	Pu, Np Strip	Tc, I Strip	HNO₃, Ru, Pd Extraction	Ru, Pd Strip
Fe	0.000	†	†	0.000	0.000
Zr	0.000	0.000	†	0.000	87.6
Nb	0.000	†	†	0.000	0.000
Tc	100	99.9	0.026	100	0.000
Ru	-	-	-	79.5	0.000
Pd	-	-	-	100	0.000
In	0.000	†	†	0.000	†
La	0.000	0.000	0.000	0.001	0.000
Ce	0.000	0.000	0.000	0.001	0.000
Pr	0.000	0.000	0.000	0.000	0.000
Nd	0.000	0.000	†	0.000	0.000
Pm	0.000	0.000	†	0.001	0.000
Sm	0.000	†	†	0.024	0.000
Eu	0.000	0.000	†	0.030	0.000
Th	100	66.7	93.9	0.000	†
U	0.001	0.002	0.000	100	98.9
Np	99.9	0.100	95.1	0.000	100.0
Pu	100	98.5	99.3	55.0	99.6
Am	0.000	0.000	†	0.000	0.000
Cm	0.000	†	†	0.000	0.000
HNO₃	3.37	1.57	5.62	89.7	37.5
volume flow ratio	*0.5/1.0	3.3	1.0	*3.5/7	1.76
number of stages	*12/5	5	5	*11/9	10

TABLE 2
Percent in the organic phase leaving each battery. *Extraction part/Scrubber part

Element	HNO$_3$ Strip	Am, Cm, Ln Extraction	Am, Cm Strip	Ln Strip	Wash
Fe	†	100	0.000	88.2	0.568
Zr	0.000	100	0.000	100.0	0.171
Nb	†	14.4	0.000	†	†
Tc	0.196	0.000	†	†	†
Ru	0.000	0.000	0.000	†	†
Pd	0.296	0.000	0.000	†	†
In	†	0.000	†	†	†
La	0.000	100	98.9	0.000	0.000
Ce	0.000	100	96.9	0.000	0.000
Pr	0.000	100	92.8	0.000	0.000
Nd	0.000	100.0	90.0	0.000	0.000
Pm	0.000	100	90.9	0.003	0.000
Sm	0.000	100	91.8	0.003	0.000
Eu	0.000	100	95.3	0.024	0.000
Th	†	0.000	†	†	†
U	0.000	100	0.000	†	†
Np	0.000	0.000	†	†	†
Pu	0.000	100	0.000	99.9	0.055
Am	0.000	100	0.010	0.000	0.000
Cm	0.000	100	0.045	0.000	0.000
HNO$_3$	0.000	0.040	0.000	0.440	0.000
volume flow ratio	1.9	*0.4/0.5	0.5	4.0	4.0
number of stages	14	*6/10	8	5	4

The sign † means that the concentration is zero in the incoming streams.
Distribution ratios for some elements and nitric acid as a function of the initial nitric acid concentration are given in figure 2. Data for some trivalent elements are given in - Landgren (1994).
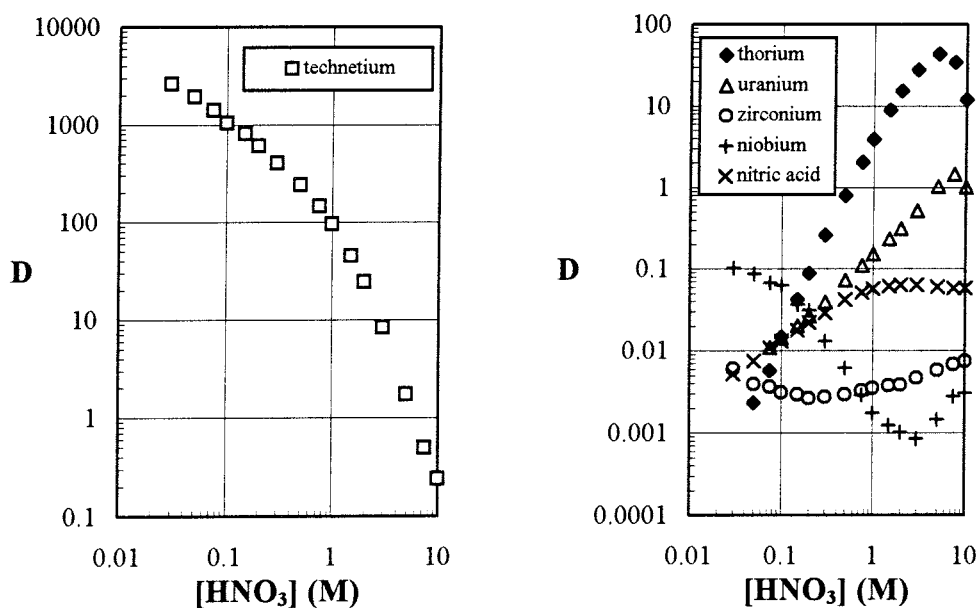

Figure 2. Distribution ratios for some elements and nitric acid as a function of the initial nitric acid concentration using 0.20 molar Aliquat-336 dissolved in 1,3-diisopropyl benzene.

DISCUSSION

In Figure 2 it is seen that the distribution ratio for technetium(VII) decreases with increasing concentration of nitric acid in the aqueous phase. At first, the slope is about -1 and then decreases to about -3. This change of the slope is due to the fact that extraction of nitric acid becomes important, thus lowering the amount of free Aliquat-336 in the organic phase. For thorium(IV) and uranium(VI) the distribution ratios increase with increasing nitric acid concentration because the concentration of extractable metal nitrate complexes increases. However, again the extraction of nitric acid becomes important at higher nitric acid concentrations and therefore the distribution ratios start to decrease.

The extraction of nitric acid increases with increasing nitric acid concentration until a constant distribution ratio of about 0.06 is reached at about 2 molar nitric acid. This behaviour indicates that the extractant is fully loaded with nitric acid from about 2 molar and above.

From Table 1 it is seen that thorium and plutonium will cause serious trouble in the first part of the separation process. All incoming thorium is extracted in the first battery and more than 50 % remains in the organic phase after the two backextractions, which means that unless thorium is not backextracted in the following washing stage, thorium will accumulate in the process and load the organic phase. The same is true for plutonium, but it must be considered that the plutonium data used is given for another solvent - Shabana (1977) - than 1,3-diisopropyl benzene and is not well investigated at nitric acid concentrations below 0.5 molar. The nitric acid concentration in the outgoing raffinate is lowered from 1.9 molar to 0.1 molar before the stream is fed to the Reversed Talspeak process. In Table 1 it is seen that only 79.5 % of the ruthenium is separated. The remaining 20.5 % will end up as waste in the outgoing raffinate from the Reversed Talspeak process. This due to the fact that the nitric acid concentration is not allowed to decrease below 0.1 molar in the outgoing raffinate. Since ruthenium is not intended for transmutation this will not affect the separation process negatively. In the reversed Talspeak process, it is seen in Table 2 that americium and curium will be contaminated with zirconium, niobium, the lanthanides and uranium. However, the amounts of niobium and uranium are negligible compared with zirconium and lanthanides.

Another drawback of the process is that two of the extractants, TBP and HDEHP do not follow the CHON principle, i.e. contain only carbon, hydrogen, oxygen and nitrogen. They will therefore produce secondary waste which is not completely incinerable.

ACKNOWLEDGEMENTS

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Appendix
II

Extraction of Some Metal Cations from Nitric Acid Solution by N,N'-Substituted Malonamides

L. Spjuth[1], M. Skålberg[1], J.-O. Liljenzin[1], M.J. Hudson[2],
G.Y.S. Chan[2], M.G.B. Drew[2], M. Feaviour[2] and C. Madic[3]

[1] Dept. of Nuclear Chem., Chalmers Uni. of Technology, Göteborg, Sweden
[2] Department of Chemistry, Uni. of Reading, Whiteknights, Berkshire, G.B.
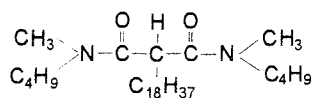[3] Centre d'Etudes Nucléaires de Fontenay-aux Roses, France

ABSTRACT

The extraction of Am(III), Cm(III) and some trivalent lanthanides by two newly synthesised malonamides; N,N'-dimethyl-diphenyltetradecyl malonamide (DMDPHTD) and N,N'-dimethyl-dicyclohexyltetradecyl malonamide (DMDCHTD) has been investigated. A comparison of the extraction data for these malonamides for U(VI), Th(IV) and some trivalent elements by N,N'-dimethyl-dibutyloctadecyl malonamide (DMDBOD) was also performed. The dependence on nitric acid concentration, diamide concentration and molecular structure of the extraction from nitric acid solution has been considered. It is possible that for nitric acid solutions (0.1M to 1M), a coordinative mechanism dominates for the extraction of metal cations but at higher acid concentrations an ion-pair mechanism involving the mono- or diprotonated diamide and a metal nitrate anion appears to be more important.
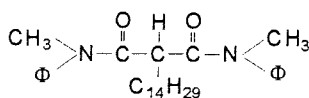
INTRODUCTION

In a transmutation process, the long-lived radioactive waste may be converted to short-lived or stable nuclides by neutron irradiation. Unfortunately, the stable lanthanide nuclei are also efficient neutron absorbers. In the first part of the process, an efficient solvent extraction system is needed to coextract the transmutable elements, e.g. Am, Cm, Np and the stable nuclides such as the lanthanides from the remaining waste. Malonamides have been suggested as possible coextractants and thus have been previously investigated -Musikas et al. (1987). The chemical properties of the malonamides depend on the nature of the substituents on the nitrogen and on the groups attached to the central carbon atom. It has been shown that the molecular structure of the malonamides has a great influence on the metal extraction -Cuillerdier et al. (1991). Enhanced extraction into the organic phase was observed when the carbon chain on the methylene carbon was lengthened in order to increase the hydrophobic nature of the extractant. The malonamides are suitable, completely incinerable extractants for both actinides and lanthanides, which may form ion-pairs or coordination compounds with the metal-containing species. In the case of the coordination complexes, the two carbonyl amide groups are bound to the metal - Hudson et al. (1994). With respect to the ion-pairs, a mono- or diprotonated malonamide may form an ion-pair with a nitrato anion of the metal - Hudson et al. (1995). In order to study the effect of substituents attached to the nitrogen atom, two new malonamides were investigated and compared with the reference malonamide DMDBOD. In all of the molecules there was a N-methyl group plus one other group. For both the N-butyl derivative, DMDBOD, and the cyclohexyl derivative, DMDCHTD, the other N-alkyl groups are rather bulky, non-planar groups but in DMDPHTD, the planar phenyl group is less bulky and, as discussed briefly later, is able to lie close to the long hydrophobic alkyl chain. It is possible that the bulky N-butyl and cyclohexyl groups sterically hinder the chelation of the diamide to the metal and the formation of ion-pairs. Alternatively, they could change the O=C...C=O torsion angle and change the O...O distance
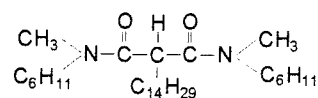
between the carbonyl oxygen atoms. Such differences in conformation will be briefly related to observed extraction properties in this study.

$$CH_3, C_4H_9 \searrow N-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{C_{18}H_{37}}{\overset{\|}{C}}}-\overset{O}{\overset{\|}{C}}-N\diagdown^{CH_3}_{C_4H_9}$$

N,N′-dimethyl-dibutyloctadecyl malonamide (DMDBOD)

$$CH_3, \Phi \searrow N-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{C_{14}H_{29}}{\overset{\|}{C}}}-\overset{O}{\overset{\|}{C}}-N\diagdown^{CH_3}_{\Phi}$$

N,N′-dimethyl-diphenyl tetradecyl malonamide (DMDPHTD)

$$CH_3, C_6H_{11} \searrow N-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{C_{14}H_{29}}{\overset{\|}{C}}}-\overset{O}{\overset{\|}{C}}-N\diagdown^{CH_3}_{C_6H_{11}}$$

N,N′-dimethyl-dicyclohexyl tetradecyl malonamide (DMDCHTD)

EXPERIMENTAL

Materials

N,N′-dimethyl-dibutyloctadecyl malonamide (DMDBOD) was provided by Synthelec AB, Sweden and the two other N,N′-pentaalkylmalonamides were synthesised and purified at the University of Reading, UK. The diluents used, tert-butylbenzene and n-dodecane, were obtained from Aldrich and the purity was 99%. The purities of the reference and the new malonamides, as determined by high resolution electron impact -mass spectroscopy, 400 Mhz ^{1}H-NMR and elemental analyse were over 99.9%.

Procedure and Apparatus

The nitric acid solutions were pre-equilibrated with the tracer solution before distribution rati determination. The malonamides were vigorously shaken with the aqueous phase for five minutes, a time which enables equilibrium to be reached, and after phase disengagement by centrifugation, aliquots of each phase were taken for radiometric analysis. The γ-energies at 59.6 keV, 122 keV, 185 keV and 879 keV for ^{241}Am, ^{152}Eu, ^{235}U and ^{160}Tb respectively were measured using a HPGe detector. For the α- and β-emitters (^{244}Cm and ^{234}Th) a LKB Wallac 1219 Rackbeta liquid scintillation counter was used. All experiments were performed with tert-butylbenzene as diluent. The distributions of nitric acid between the aqueous and organic phases were determined by potentiometric titration using a Mettler DL20 Compact Titrator. The titrations were performed in ethanolic media to facilitate the mixing of the solutions.

RESULTS AND DISCUSSION

Metal Extraction

Extraction data for some trivalent elements were determined with the two new extractants and compared with the extraction data for uranium(VI), thorium(IV) and the same trivalent metals extracted by DMDBOD. The extraction behaviour of DMDPHTD was considerably different from the other two. The metal extraction at high nitric acid concentration (above 7M HNO$_3$) by DMDPHTD showed a constant increase which was not seen with DMDBOD or DMDCHTD (Figure 1) for which there were maxima at ca 7M HNO$_3$.

There is evidence to indicate that below nitric acid concentrations of 1M the main species of the malonamide (E) is the unprotonated form, the dominant species in 5M nitric acid is the mono-protonated species $EH^+NO_3^-$, whereas above 7M nitric acid the diprotonated form $EH_2^{2+}(NO_3^-)_2^{2-}$ predominates -Byers (1995). These observations will be supported later, Figure 2, by the data for the extraction of nitric acid.
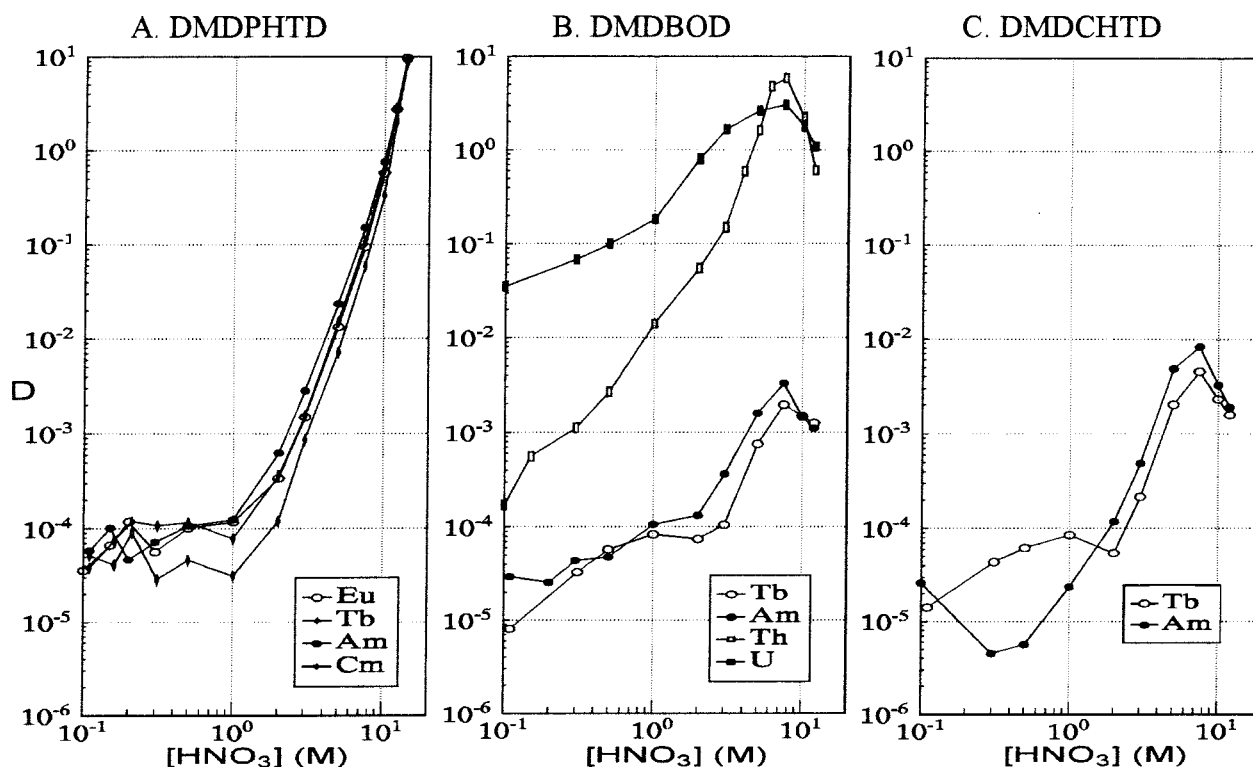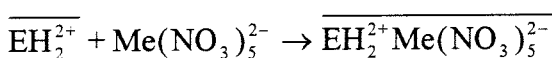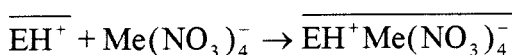
Figure 1.   A. Extraction of some trivalent elements by DMDPHTD (0.1M) in *tert*-butylbenzene.
   B. Extraction of some trivalent elements and uranium(VI) and thorium(IV) by DMDBOD (0.1M) in *tert*-butylbenzene.
   C. Extraction of some trivalent elements by DMDCHTD (0.1M) in *tert*-butylbenzene.

Examination of the data in Figure 1 shows a point of inflection at *ca* 1M HNO_3 suggesting a change in mechanism, which may be related to the diamide species. For trivalent metal ions, from 1 to 5M nitric acid concentration, the dominating extracted species could be $EH^+Me(NO_3)_4^-$. Above 5M nitric acid concentrations, the extracting species becomes the diprotonated species EH_2^{2+}. The anion extracted could be two $Me(NO_3)_4^-$ anions or one $Me(NO_3)_5^{2-}$ dianion. Clearly, in order to extrac these anions, the protonated carbonyl groups must be available and they appear to be more available for the diprotonated form of the diphenyl derivative than for the other two diamides. For a coordination mechanism, the trivalent metal ion extraction by malonamides may be described as:

$$Me^{3+} + 3NO_3^- + n\overline{E} \rightarrow \overline{Me(NO_3)_3 E_n}$$
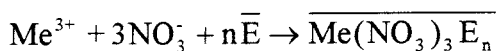
For the ion-pair mechanism, the equations are of the type:

$$\overline{EH^+} + Me(NO_3)_4^- \rightarrow \overline{EH^+Me(NO_3)_4^-}$$

$$\overline{EH_2^{2+}} + Me(NO_3)_5^{2-} \rightarrow \overline{EH_2^{2+}Me(NO_3)_5^{2-}}$$

where E is the malonamide.

Estimation of the Number of Malonamide Molecules

There is interest in establishing the number of malonamide molecules in the extracted species. When the distribution ratio for the metal extraction is plotted as a function of malonamide concentration, the slope should approximate to the number of malonamide molecules present in the extracted complex. From the data in Table 1, it can be seen that there are between two and three malonamide molecules per metal ion, which is consistent with a coordination mechanism but not with an ion-pair mechanism. However, it has often been shown that conventional slope analysis results in non-integral slopes for amide extractants. This has been attributed to the non-ideality of the organic solution or explained by extra amide molecules in the second coordination sphere -Nigond et al. (1994). This can reflect also an aggregation of the E/HNO$_3$ solvates in the organic phase (micelles formation) - Nigond et al. (1995).

TABLE 1
Results of slope analysis for Am at 0.2M-1M malonamide.

Malonamide	[HNO$_3$](M)	Slope	r	[HNO$_3$](M)	Slope	r
DMDBOD	0.3	2.5	0.9940	3	2.3	0.9937
DMDPHTD	0.5	2.6	0.9835	2	2.7	0.9992
DMDCHTD	1	3.6	0.9916	7.5	2.2	0.9979

Nitric Acid Extraction

As is seen in Figure 2, the extents of nitric acid extraction do not differ significantly for the two extractants, DMDPHTD and DMDBOD. The number of HNO$_3$ molecules extracted per diamide molecule increases uniformly with nitric acid concentration. At 5M HNO$_3$ the ratio between HNO$_3$ and diamide molecules is close to one for both malonamides, whilst in 7M HNO$_3$ the ratio is between one and two. These values suggest that, at 5M nitric acid, the dominating species is EH$^+$NO$_3^-$ but around 7M nitric acid EH$_2^{2+}$(NO$_3$)$_2^{2-}$ dominates. These observations are consistent with an ion-pair mechanism.
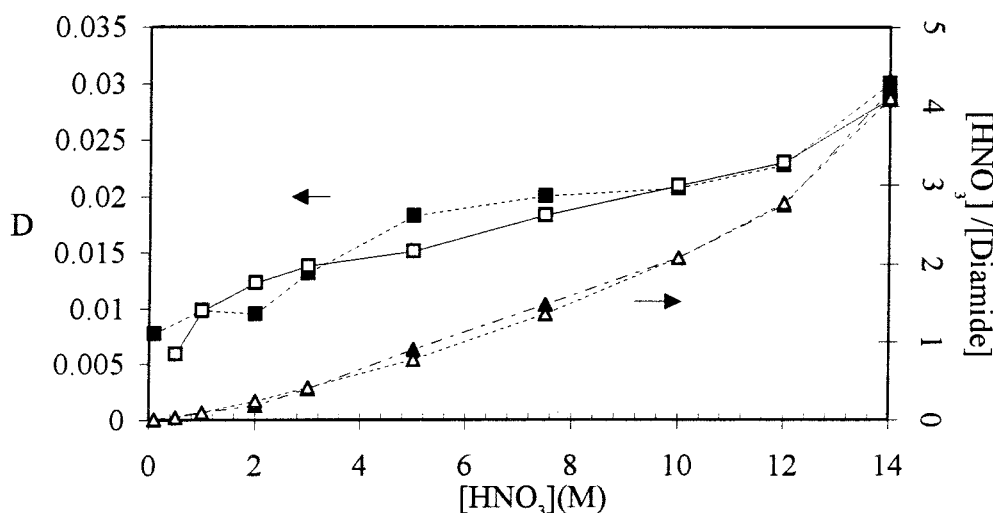

Figure 2. Extraction of nitric acid by 0.1M DMDBOD in tert-butylbenzene (unfilled symbols), by 0.1M DMDPHTD in tert-butylbenzene (filled symbols) and the average number of HNO$_3$ molecules extracted per diamide molecule (right scale).

Molecular Modelling

We have studied the conformations of above malonamides by molecular mechanics using the Dreiding force field within the CERIUS2 package (Molecular Simulations Inc., Cambridge, U.K., 1995). Crystal data for malonamides are sparse as only six structures have been determined. The conformation can be characterised best by the O=C...C=O torsion angle and values obtained in these structures are either in the range 66 to 93 or 116 to 126°. We have carried out conformational searches on both DMDCHTD and DMDPHTD and structures obtained by molecular mechanics are shown in Figure 3.
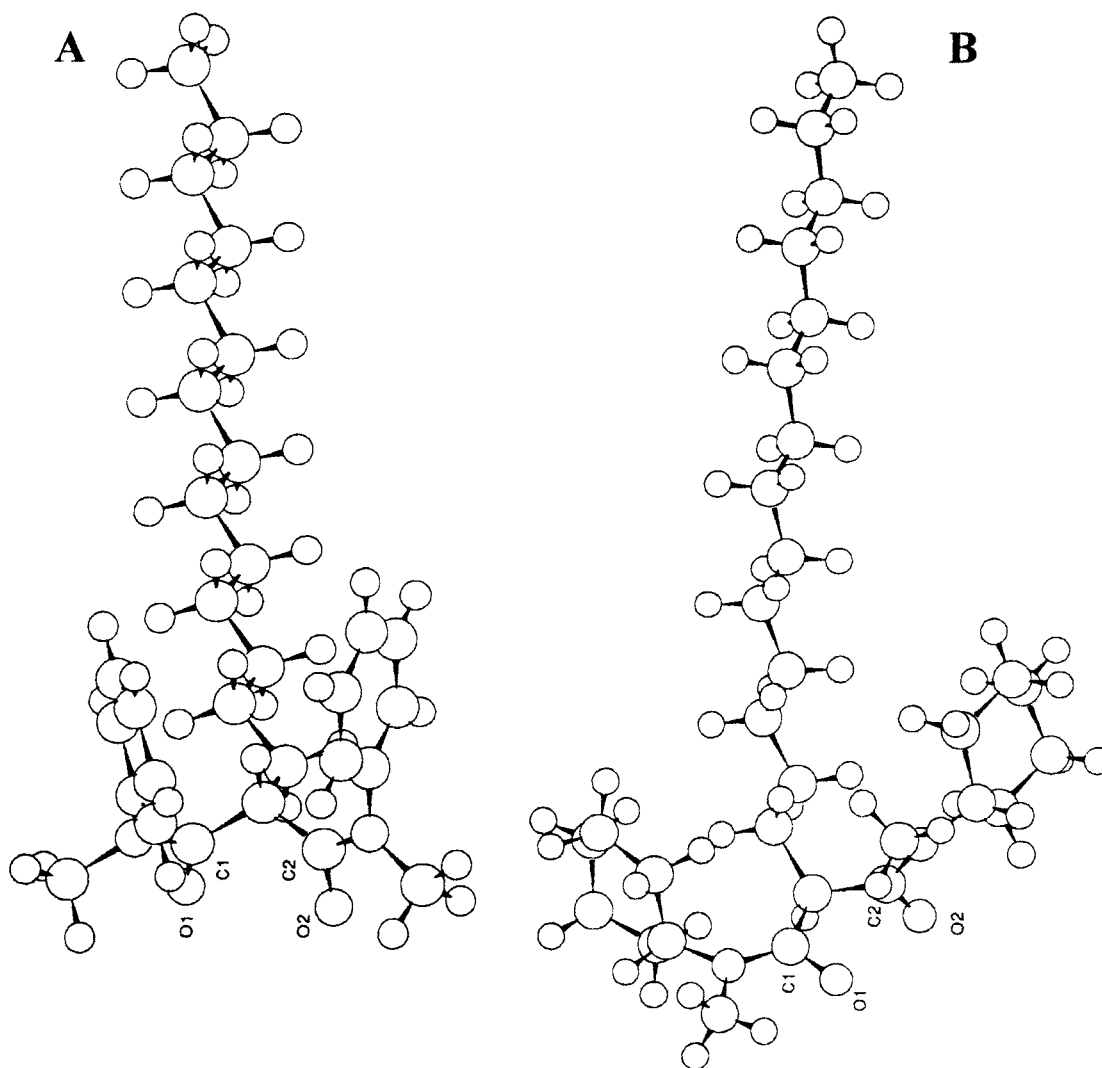
Figure 3.   A. Model structure of DMDPHTD showing the O(1)=C(1)...C(2)=O(2) torsion angle is only 19° with an O(1)=O(2) distance of 2.87Å which is suitable for coordination or for protonation. The phenyl groups are adjacent to the n-alkane chain thus enabling the carbonyl groups to be involved in chemical reaction.

B. Comparable model of DMDCHTD . The O(1)=C(1)...C(2)=O(2) torsion angle is 66° and the O(1)=O(2) distance of 3.06Å which combined values render the molecule less suitable for coordination or for intramolecular protonation.

Interestingly enough, the torsion angle obtained in DMDCHTD is 66°, a value comparable with those found experimentally, while that for DMDPHTD is only 19°, a value close to that obtained when the ligand is coordinated in a bidentate fashion to a metal or when there is intramolecular protonation. This could confirm that in DMDPHTD the carbonyl amide groups are more available than in the other malonamides to coordinate or to form ion pairs with a metal-containing anion. In the cases of DMDBOD and DMDCHTD, the methyl, butyl or cyclohexyl groups do not restrict the relative carbonyl positions and the torsion angle of ca 60° does not facilitate the approach of the carbonyl amide group at the interfacial surface.

CONCLUSIONS

The points of inflection observed for the distribution ratios seen as a function of nitric acid concentrations, have been related to changes in the mechanisms of extraction. At low acidities a coordination mechanism dominates but at higher values the ion-pair mechanism(s) are important.
The diphenyl derivative DMDPHTD is able to extract metal species even at the highest acid concentrations used probably because steric hindrances are minimised.

ACKNOWLEDGEMENTS

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Appendix
III

Inherent Limitations In Toxicity Reduction Associated with Fast Energy Amplifiers

J. Magill, P. Peerani, J. van Geel
European Commission, Joint Research Centre, Institute for Transuranium Elements,
Postfach 2340, D-76125 Karlsruhe, Germany

A. Landgren, J.-O. Liljenzin
Department of Nuclear Chemistry, Chalmers University of Technology,
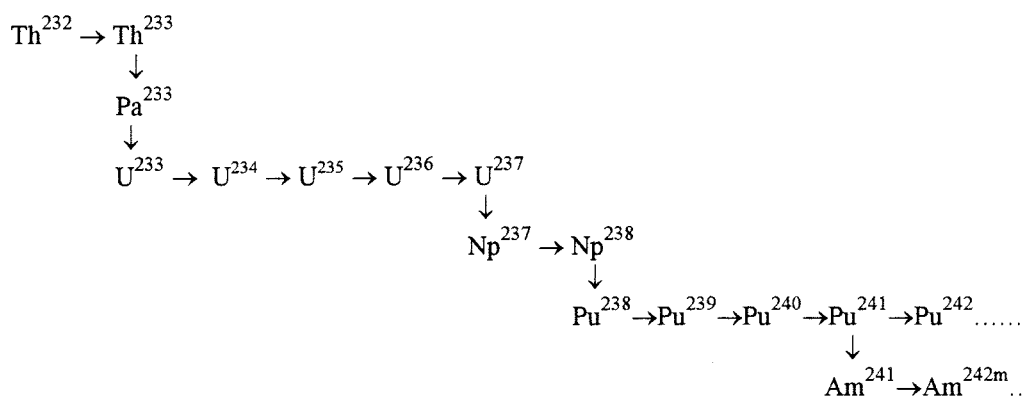S-412 96 Göteborg, Sweden

Abstract

In the recently proposed Fast Energy Amplifier (F-EA) closed cycle concept [1], the spent fuel with burnup > 100MWd/kg initial heavy metal, IHM, is removed, reprocessed to remove fission products, and returned to the sub-critical unit together with natural thorium to compensate for burnt fuel. Potentially, actinide toxicity is reduced to zero in this scheme. In reality, of course, the actinide toxicity is reduced to the "small" fraction lost to the waste through reprocessing and refabrication.

In this paper we present the results of calculations on the irradiation of thorium in a fast flux to a burnup of 100MWd/kg to estimate the amounts of U, Pa, Th etc. in the spent fuel. A model for the reprocessing and refabrication of this waste is developed with particular emphasis on processing losses. This procedure of irradiation to a burnup of 100MWd/kg, removal from the unit, reprocessing of the waste and refabrication of fresh fuel is then repeated to monitor the build-up of actinides over many such cycles. Using typical values for processing losses, the resulting actinide toxicity in the waste is calculated.

Equilibrium Core Configuration

The main reaction path associated with the neutron irradiation of Th^{232} is:

$$Th^{232} \rightarrow Th^{233}$$
$$\downarrow$$
$$Pa^{233}$$
$$\downarrow$$
$$U^{233} \rightarrow U^{234} \rightarrow U^{235} \rightarrow U^{236} \rightarrow U^{237}$$
$$\downarrow$$
$$Np^{237} \rightarrow Np^{238}$$
$$\downarrow$$
$$Pu^{238} \rightarrow Pu^{239} \rightarrow Pu^{240} \rightarrow Pu^{241} \rightarrow Pu^{242} \ldots\ldots$$
$$\downarrow$$
$$Am^{241} \rightarrow Am^{242m} \ldots$$

Important subsidiary reaction paths are through (n,2n) reactions. The most important of these reactions is with Th^{232} and leads to the formation of Pa^{231} and U^{232} i.e.

$$Th^{232} (n,2n) \rightarrow Th^{231} (\beta^{-}) \rightarrow Pa^{231} (n,\gamma) \rightarrow Pa^{232} (\beta^{-}) \rightarrow U^{232}$$
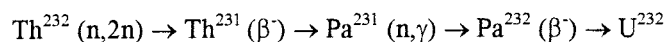
This latter reaction shows clearly the connection between proliferation resistance (through U^{232}) and toxicity (through Pa^{231}) of the irradiated fuel and is an example of

the so-called proliferation-toxicity dilemma of the thorium based fuel cycle [2]. For the evaluation of the isotope fractions in the main and subsidiary reaction paths above, the Rubbia cross section data from table 1 was used [3]. For isotopes not shown in table 1, the default values from the ORIGEN2 [4] library AMO0TTTC were used.

Table 1. Averaged Cross Sections (barn) of Actinides Relevant to the F-EA (from [3])

Isotope	(Rubbia et al., [3])			(present work)		
	n,γ	n,2n	n,f	n,γ	n,2n	n,f
Th^{230}	0.1678	1.4e-3	0.02570			
Th^{232}	0.3088	1.4e-3	0.00857	0.3544	8.5e-4	0.0069
Pa^{231}	2.9570	9.8e-4	0.2253	1.4300	3.9e-4	0.1422
Pa^{233}	0.9760	4.1e-4	0.0555	0.4653	3.9e-4	0.1422
U^{232}	0.6525	7.5e-4	2.0680			
U^{233}	0.2573	7.5e-4	2.6845	0.2796	3.8e-4	2.9120
U^{234}	0.5595	1.5e-4	0.3105	0.4063	1.3e-4	0.2689
U^{235}	0.5073	9.7e-4	1.8138	0.5585	4.5e-4	1.9420
U^{236}	0.4101	7.3e-4	0.0888	0.3759	3.9e-4	0.0706
U^{237}	0.4175	2.0e-3	0.6181			
U^{238}	0.3086	1.1e-3	0.03668			
Np^{237}	1.4708	2.3e-4*	0.2965	0.6302	5.3e-4*	0.2739
Np^{238}	0.4000	7.3e-4	2.0912			
Np^{239}	1.8275	3.2e-4	0.4309			
Pu^{236}	0.3564	3.0e-4	1.4241			
Pu^{238}	0.5138	7.7e-5	1.0738	0.5437	2.9e-4	1.0540
Pu^{239}	0.4616	2.9e-4	1.7511	0.4166	2.9e-4	1.9495
Pu^{240}	0.4685	2.3e-4	0.3534	0.6522	2.2e-4	0.3038
Pu^{241}	0.5213	1.8e-3	2.4262	0.4965	4.0e-4	2.9190
Pu^{242}	0.4256	5.7e-4	0.2394	0.6963	3.1e-4	0.2290

* to the ground state Np^{236g}

The isotope fractions calculated using this data are shown in fig. 1. The fractions have been normalised to the initial concentration of Th^{232} in the core.

Nuclide Radiotoxicity

The radiotoxicity of a nuclide is determined by its *effective dose coefficient e(T)* [5], which accounts for radiation and tissue weighting factors, metabolic and biokinetic information. The quantity T is the integration time in years following intake. For *adult workers*, the integration time is 50 years, such that the radiotoxicity (in Sv) resulting from intake of a particular nuclide is the product of the effective dose coefficient (units Sv/Bq) and the activity (in Bq) of that nuclide i.e.

Radiotoxicity = Activity x e(50)

For members of the public, these dose coefficients should be reduced further to reflect intake at an earlier age [6]. A useful quantity in connection with radiation exposure is the ALI value. The ALI value is the Annual Limit of Intake for a particular radio-

nuclide and can be obtained by dividing the annual average dose limit (0.02Sv for workers) by the dose coefficient i.e.

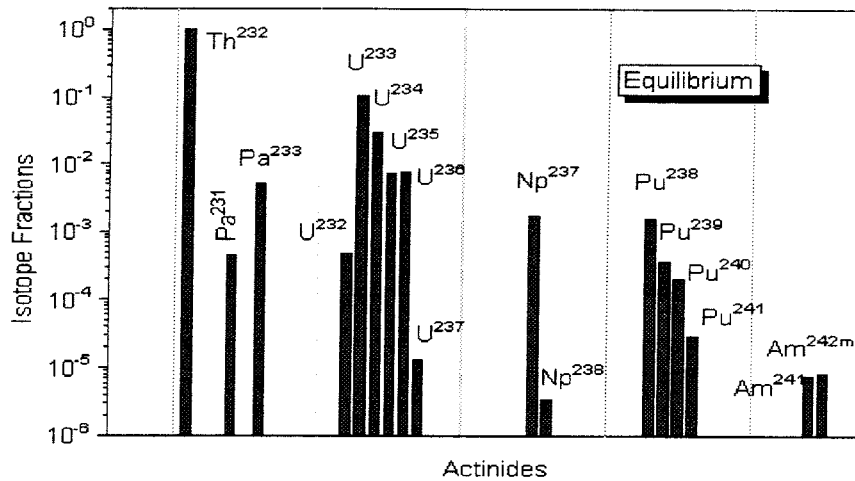$$ALI(Bq) = 0.02 \ Sv \ / \ e(50)$$

Fig. 1. Equilibrium fractions normalised to the initial amount of Th^{232} in the core.

Spent Fuel Reprocessing

A key aspect to the F-EA is that the spent fuel is reprocessed to separate the actinides from the fission products and thereby reduce the toxicity of the waste. In this step essentially all of the fission products become waste together with a percentage of the actinides. After reprocessing, the fission products plus actinides lost to the waste are sent for direct storage, while the recovered actinides together with some fresh thorium are returned to the reactor.

After a cooling time of one year the fuel is reprocessed to recover thorium and uranium. In this case an aqueous based separation process [7] is considered since a lot of experience is available in this area. The separation is carried out in counter-current mixer-settler batteries. Separation data necessary for the process calculation was taken from refs. [8, 9, 10]. The fuel is dissolved in concentrated nitric acid, diluted to 2 M acid and fed to the first extraction battery in the reprocessing plant, see fig. 2.
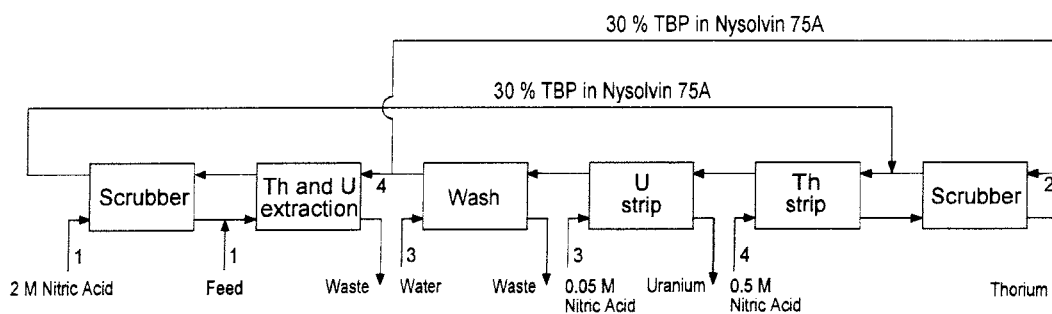
Fig. 2. Baseline flowsheet of the separation process used in the calculations. The numbers show the relative volume flow rates.

The thorium concentration in the feed is limited to 16 g/l in order to avoid third phase formation. The extractant used in the separation process is 30 % TBP (tri-n-butylphosphate) in an aliphatic kerosene, Nysolvin 75A. In the first extraction battery thorium and uranium are extracted to the organic phase in 10 stages with a volume phase ratio (organic to aqueous) of about 2. In the following 5 stage scrubber battery, with a phase volume ratio of about 4, the organic phase is contacted with 2 M nitric acid to remove unwanted elements from the organic phase. The outgoing organic phase contains except thorium and uranium also technetium, ruthenium, palladium, neptunium and plutonium. Thorium is then removed in the first stripper by contacting the organic phase in 8 stages with 0.5 M nitric acid at a phase volume ratio of 1.5. To decrease the uranium content in the thorium product a 5 stage scrubber is introduced after the thorium stripper. In the next step, uranium is removed from the organic phase in 10 stages by 0.05 M nitric acid. Finally the organic phase is washed with water to strip the remaining technetium and nitric acid. In this separation process the total losses of actinides to waste were calculated to be: thorium 0.6%, protactinium 100%, uranium 0.3%, neptunium 99.8%, plutonium 1%, americium 100% and curium 100%.

Multiple Recycling

In the following we have used ORIGEN2 to calculate the isotope concentrations resulting from the irradiation of Th^{232} in a fast neutron flux using the cross section data given in table 1. The calculational protocol is as follows: Fresh fuel ($Th^{232}+1\%U^{233}$) is irradiated at constant specific power of 55MW/tonne for 5 years to 100GWd/tonne. At the end of this time, the core material is decayed for one year. Thereafter, the spent fuel is reprocessed to separate the actinides from the fission products (loss values given above). Next the reprocessed material plus a little fresh Th^{232} (to make up the losses) is returned to the reactor again and irradiated for another 5 years followed by one year decay - this is our second cycle. We then repeat this process for ten cycles.
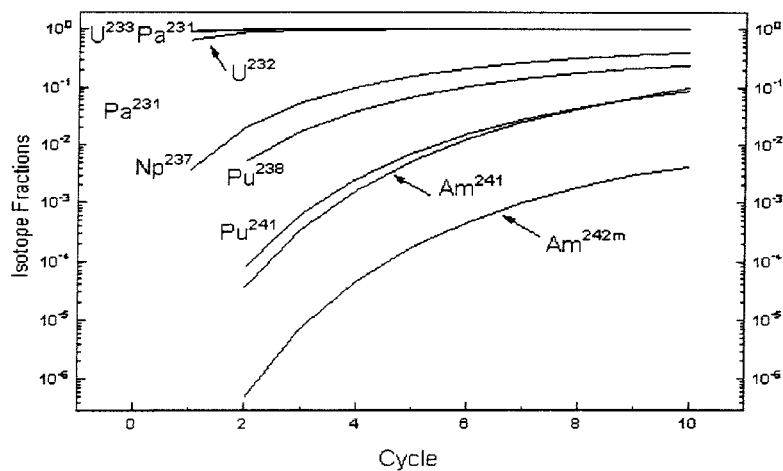

Fig. 3. Build-up of some nuclides vs. no. of recycles (normalised to equilibrium values).

From these calculations and the equilibrium results presented earlier, one can obtain the normalised nuclide evolution as a function of time. This is shown in fig. 3. Notice that the U^{233} reaches equilibrium already after the first cycle. This is not the case for nuclides with mass higher than 237. Even after 10 cycles, their concentrations are still increasing in time. The ingestion radiotoxicity of the waste is shown in fig. 4 for a period of 10^6 years after disposal. In this diagram, all isotopes of the same chemical element are grouped together. Hence, for example, the *curve denoted by 'Pu' represents the radiotoxicity resulting from all isotopes of Pu together with their daughter products*. The advantage of grouping the nuclides together in this manner is that one can see clearly what effects chemical reprocessing will have on the radiotoxicity of the waste.

It can be seen that the ingestion radiotoxicity of the waste is dominated by the Pa^{231} with half-life approximately 33,000y and its daughters. It appears therefore that the main effort in improving the chemical reprocessing should be directed at recovering Pa. Thereafter, the 'U' radiotoxicity starts to become important.
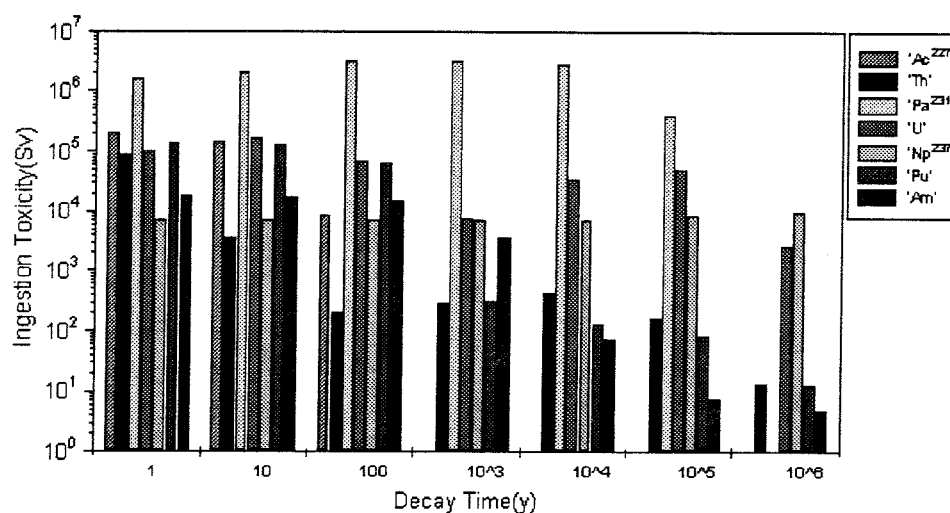
Fig. 4. Ingestion radiotoxicity of the waste from 1 tonne 10th cycle spent fuel.

Neutronics Calculations

The calculations presented in this paper have been performed using the cross sections reported in ref. [3] and listed in table 1. These cross section data were also independently evaluated in this present study. The method we used is based on the SCALE system [11]. This is a modular system of codes performing several tasks which can be automatically linked and executed. We used the standardised procedure CSAS1X which executes a sequence of three codes: BONAMI, NITAWL and XSDRNPM.

The starting point was a 123 group cross section library based on GAM-THERMOS data. These cross sections were first processed by performing a preliminary evaluation of the self-shielding for all the nuclides with the Bondarenko method. Then NITAWL was used for a more refined calculation of the self-shielding effect in the main resonant

nuclide Th^{232} with the Nordheim integral method. The 1-D discrete ordinate code XSDRNPM allows to solve the neutron transport equation in the reactor cell geometry and to obtain the space-energy flux distribution. This flux was finally used to condense the 123 group data to 1 group (spectrum averaged cross section) to perform fast burnup evaluations.

According to these calculations we obtained an infinite multiplication factor for the reactor cell of 1.09 for the fresh fuel in the first cycle and 1.04 for the equilibrium composition (fission products included). The resulting cross sections are listed in table 1. Table 2 compares the equilibrium fuel compositions using the two sets of cross section data. The cell geometry is described in [1]. With respect to the nuclides relevant to waste radiotoxicity the main differences in the equilibrium compositions show an increase of a factor two in Np^{237} and a decrease of about 40% in Pa^{231} and U^{232}. The other nuclides are affected by much smaller changes of the order of a few percent. Since Pa^{231} gives the highest contribution to the long term radiotoxicity, a significant reduction in the total waste toxicity may result. A detailed analysis is required to evaluate the Th^{232} (n,2n) cross section more precisely.

Table 2. Comparison of the relative equilibrium compositions (Th^{232} set to 1.)

Nuclide	Rubbia et al.	present work
Pa^{231}	4.40e-4	2.67e-4
U^{232}	5.07e-4	3.06e-4
U^{233}	1.05e-1	1.11e-1
U^{234}	3.10e-2	4.60e-2
U^{235}	7.49e-3	7.47e-3
U^{236}	7.61e-3	9.35e-3
Np^{237}	1.77e-3	3.89e-3
Pu^{238}	1.64e-3	1.53e-3
Pu^{239}	3.80e-4	3.52e-3
Pu^{240}	2.13e-4	1.53e-4
Pu^{241}	3.40e-5	2.90e-5
Pu^{242}	2.70e-5	1.60e-5

Conclusions

A characteristic feature of the Fast Energy Amplifier (F-EA) is that the spent fuel is reprocessed to separate actinides, which are returned to the reactor, from fission products thereby reducing the long term radiotoxicity of the waste. In this process, complete separation of the actinides and fission products is not possible and the waste stream must always contain a small amount of the actinides present in the core. These actinides losses dominate the long term toxicity of the waste.

In this paper we present equilibrium and time dependent models for the build-up of actinides in the core and waste streams in this multiple fuel irradiation and spent fuel reprocessing scenario. A comparison of the results shows that even after 10 cycles (a cycle involves a five year irradiation of the fuel in the reactor, one year decay, and a reprocessing step) covering a period of 60 years, the equilibrium concentrations of the higher actinides are not reached. In particular, after 10 cycles the concentrations of the nuclides Pu^{241} and Am^{241} have only reached 10% of their equilibrium values. The

concentration of Am^{242m} is less than 1% of its equilibrium value. Hence, these nuclides will never reach their equilibrium values since 10 cycles must be considered an upper limit to the reactor lifetime.

In the separation process described, actinide losses to the waste are calculated to be: thorium 0.6%, protactinium 100%, uranium 0.3%, neptunium 99.8% plutonium 1%, americium 100% and curium 100%. The resulting ingestion radiotoxicity of the waste (fig. 4) is dominated by the nuclide Pa^{231} for the first 10^5 years. After 1000 years, the radiotoxicity is a factor 300 higher than any other isotope. It can be concluded, therefore, that to reduce this radiotoxicity, one must improve the protactinium separation chemistry.

The protactinium separation can be considerably improved upon by using a technique such as pyro-processing [12]. However, it appears that a strong research effort over the next 20 years, including building and operation of a pilot plant, is required to demonstrate this technique. Nevertheless, because of the potential proliferation resistance (actinides stay mixed together) and low actinide toxicity of the waste the process merits careful investigation.

The results presented are based on the recent cross section data reported by Rubbia et al.[2]. We also performed independent calculations for the cross sections of selected nuclides and compared these to the above values. The main differences were a decrease in Pa^{231} and U^{232} by about 40%.

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Appendix
IV

EXTRACTION OF SOME METAL CATIONS AND NITRIC ACID BY N,N'-SUBSTITUTED MALONAMIDES

Lena Spjuth[1], Mats Skålberg[1], Jan-Olov Liljenzin[1], Michael J. Hudson[2], Gabriel Y.S. Chan[2], Michael G.B. Drew[2], Mark Feaviour[2], Charles Madic[3]

1)Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden.
2)Department of Chemistry, University of Reading, Box 224, Whiteknights, Berkshire RG6 2AD, UK.
3)CEA-Valrhô, Marcoule, BP 171, 30207 Bagnols-s-cèze, Cédex, France

ABSTRACT

Two newly synthesised malonamides; N,N'-dimethyl-N,N'-diphenyltetradecyl malonamide (DMDPHTD) and N,N'-dimethyl-N,N'-dicyclohexyl-tetradecyl malonamide (DMDCHTD) has been investigated concerning their extraction of Am(III), Tb(III), U(VI), Th(IV) and HNO_3 The dependence on nitric acid concentration and molecular structure of the extraction of metallic species from nitric acid solution has been considered. It is possible that for nitric acid solutions (0.1M to 1M), a coordinative mechanism dominates for the extraction of trivalent metal cations but at higher acid concentrations an ion-pair mechanism involving the mono- or diprotonated diamide and a metal nitrate anion appears to be more important. The diphenyl derivative, DMDPHTD, is able to extract metal species from solutions with very high nitric acid concentrations.

INTRODUCTION

In a Partitioning-Transmutation nuclear waste management strategy, long-lived radioactive waste may be converted to short-lived or stable nuclides in a transmutation process. To achieve an efficient process, the transmutable elements have to be separated from the short-lived and stable elements. Malonamides, which are completely incinerable extractants, have been suggested as possible molecules for the co-extraction of actinides and lanthanides in this process and thus have been previously investigated (Musikas et al., 1987). The chemical properties of the malonamides depend on the nature of the substituents on the nitrogen atoms and on the groups attached to the central carbon atom (Cuillerdier et al., 1991). In order to more deeply study the effect on metal extraction of substituents attached to the nitrogen atoms, two new malonamides were investigated
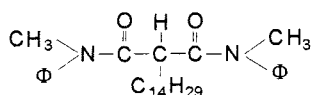
N,N'-dimethyl-N,N'-diphenyl tetradecyl malonamide (DMDPHTD)
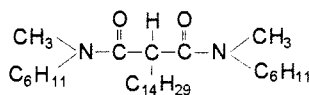
N,N'-dimethyl-N,N'-dicyclohexyl tetradecyl malonamide (DMDCHTD)

EXPERIMENTAL

Materials

The two new malonamides were synthesised and purified at the University of Reading, UK. The diluent used, *tert*-butylbenzene (tBB), was obtained from Aldrich and the purity was 99%. The purities of the new malonamides, as determined by high resolution electron impact-mass spectroscopy, 400 MHz ^{1}H-NMR and elemental analysis were over 99%.

Procedure and Apparatus

The malonamide, dissolved in tBB, was vigorously shaken with the pre-equilibrated aqueous phases for five minutes and after phase disengagement by centrifugation, aliquots of each phase were taken for radiometric analysis. The γ-energies at 59.6 keV, and 879 keV for ^{241}Am and ^{160}Tb respectively were measured using a HPGe detector. For the α- and β-emitters (^{233}U and ^{234}Th) a LKB Wallac 1219 Rackbeta liquid scintillation counter was used. The distribution of nitric acid between the aqueous and organic phases was determined by pH-metric titration using a Mettler DL20 Compact Titrator. The titrations were performed in ethanolic media to facilitate the titration of the organic solutions.

RESULTS AND DISCUSSION

Metal Extraction

In almost the whole range, of every nitric acid concentration investigated, the affinity order for both malonamides is as follows; U(VI)≥Th(IV)>>Me(III). The metal extraction by DMDPHTD increases constantly at high nitric acid concentration (above 7M HNO$_3$). This increase is not seen with DMDCHTD which shows a maximum in the metal extraction at *ca* 7M HNO$_3$ (Figure 1). There is evidence to indicate that below nitric acid concentrations of 1M the main species of the malonamide (E) is the unprotonated form and the dominant species in 5M nitric acid is the mono-protonated species, $EH^+NO_3^-$. Thus, for trivalent metal ions from 1M to 5M nitric acid concentration, the dominating extracted species could be $EH^+Me(NO_3)_4^-$. Above 7M nitric acid the diprotonated form $EH_2^{2+}(NO_3)_2^{2-}$ predominates, (Byers *et al.*, 1995), and the anion extracted could be two $Me(NO_3)_4^-$ anions or one $Me(NO_3)_5^{2-}$ dianion. These observations are supported by the data for the extraction of nitric acid, Figure 2.

A. DMDPHTD   B. DMDCHTD
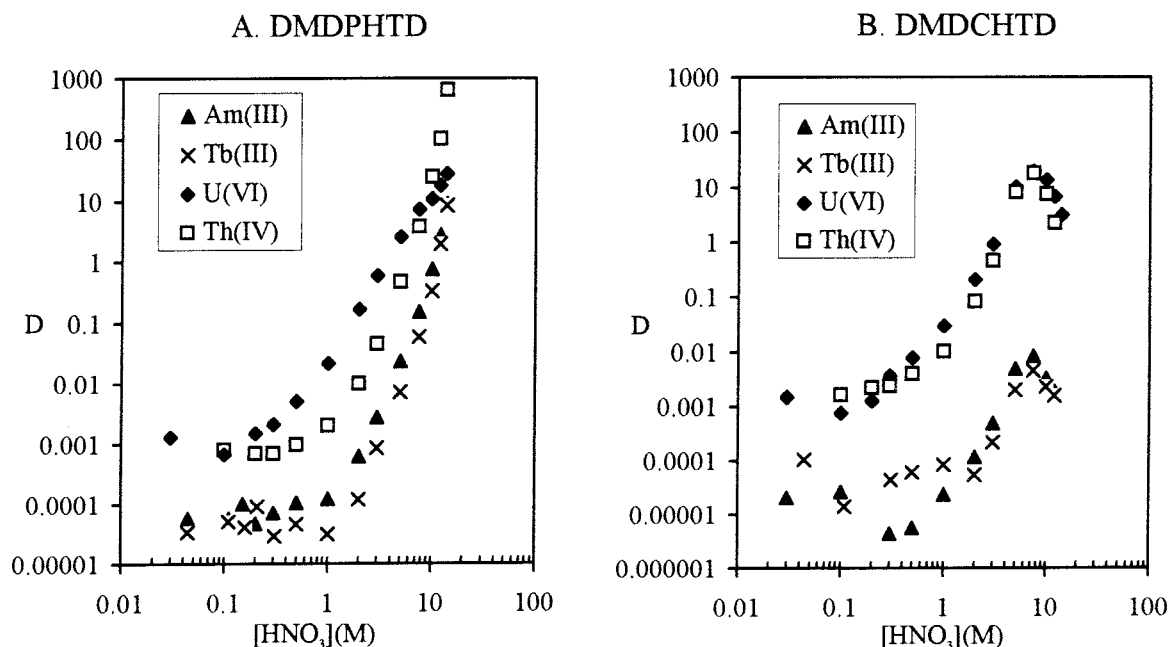
Figure 1. Extraction of some elements by 0.1M malonamide in *tert*-butylbenzene (room temperature).

Clearly, in order to extract these anions, the protonated carbonyl groups must be available and they appear to be more available for the diprotonated form of the diphenyl derivative than for the other diamide. The extraction of hexavalent uranium appears to proceed by

another mechanism. UV-vis spectra show the typical peaks for uranium extracted by a solvation mechanism, (Siddall *et al.* 1968), i.e. $UO_2(NO_3)_2E_n$ formation, with n probably equal to 1.

Nitric Acid Extraction

The extent of nitric acid extraction slightly differ between the two extractants, DMDPHTD and DMDCHTD (Figure 2), the former being a little less basic than the latter. This is quite understandable due to the electron withdrawing properties of the phenyl groups, leading to a decrease in the electron density on the carbonyl oxygens. The number of HNO_3 molecules extracted per diamide molecule increases uniformly with nitric acid concentration. At 5M HNO_3 the ratio between HNO_3 and diamide molecules is close to one for both malonamides, whilst in 7M HNO_3 the ratio is between one and two. These observations are consistent with an ion-pair mechanism for the extraction of Me(III) metal species.

A.   B.
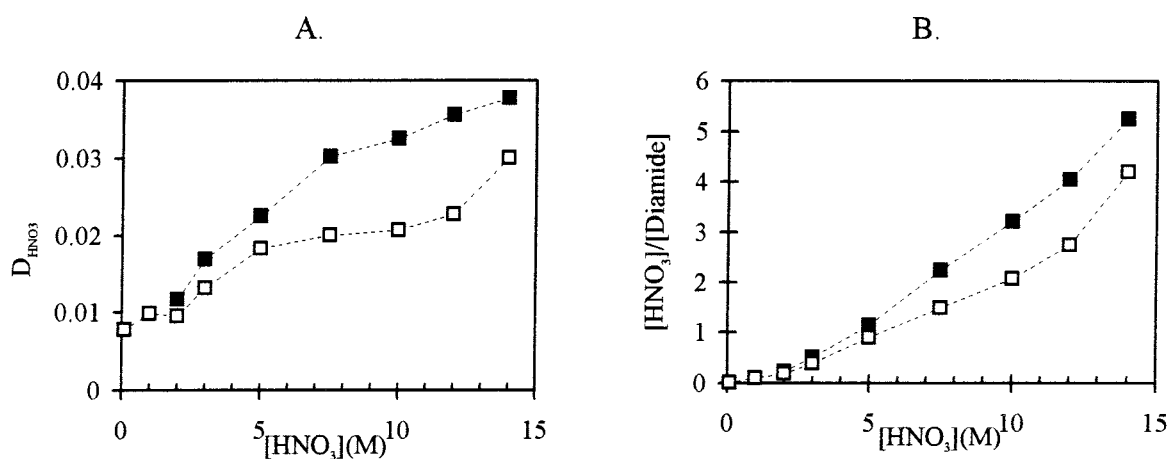
Figure 2. A) Extraction of nitric acid by 0.1M malonamide in *tert*-butylbenzene (room temperature).
B) The average number of HNO_3 molecules extracted per malonamide molecule.
Filled symbols; DMDCHTD. Unfilled symbols DMDPHTD.

Molecular Modelling

We have studied the conformations of above malonamides by molecular mechanics using the Dreiding force field within the CERIUS2 package (Molecular Simulations Inc., Cambridge, UK, 1995). Crystal data for malonamides are sparse as only six structures have been determined. The conformation can be characterised best by the O=C...C=O torsion angle and values obtained in these structures are either in the range 66° to 93° or 116° to 126°. We have carried out conformational searches on both DMDCHTD and DMDPHTD and the most stable structures obtained by molecular mechanics are shown in Figure 3.

Interestingly enough, the torsion angle obtained in DMDCHTD is 66°, a value comparable with those found experimentally, while that for DMDPHTD is only 19°, a value close to that obtained when the ligand is coordinated in a bidentate fashion to a metal or when there is intramolecular protonation. This could confirm that in DMDPHTD the carbonyl amide groups are more available than in other malonamides to coordinate or to form ion pairs with a metal-containing anion. In the case of DMDCHTD and other alkane-

substituted malonamides, the torsion angle of *ca* 60° does not facilitate the approach of the carbonyl amide group at the interfacial surface.
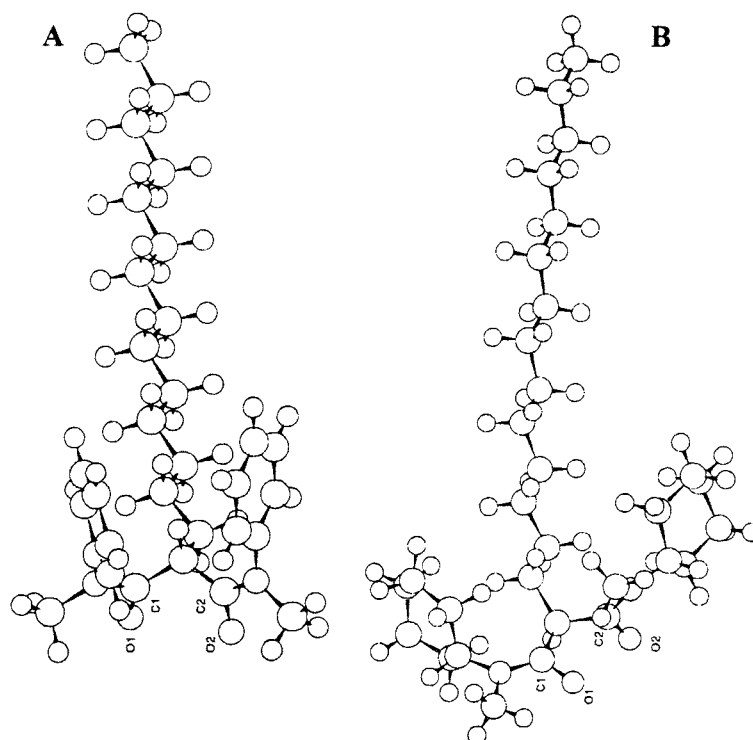

Figure 3. A. Model structure of DMDPHTD showing the O(1)=C(1)...C(2)=O(2) torsion angle is only 19° with an O(1)=O(2) distance of 2.87Å
B. Comparable model of DMDCHTD. The O(1)=C(1)...C(2)=O(2) torsion angle is 66° and the O(1)=O(2) distance of 3.06Å.

CONCLUSIONS

The points of inflection observed for the distribution ratios of trivalent metals seen as a function of nitric acid concentrations, have been related to changes in the mechanisms of extraction. At low acidities a coordination mechanism dominates but at higher values the ion-pair mechanism(s) are important. The diphenyl derivative DMDPHTD is able to extract metal species even at the highest acid concentrations used, probably because steric hindrances are minimised.

ACKNOWLEDGEMENTS

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Appendix
V

Extraction studies with
N,N'-substituted malonamides

Lars G S Ekengren
1996

EXAMENSARBETE 20P

DEPARTMENT OF NUCLEAR CHEMISTRY
CHALMERS UNIVERSITY OF TECHNOLOGY
GÖTEBORG
SWEDEN
960308

Examiner: Prof. Jan-Olov Liljenzin
Supervisors: Prof. Jan-Olov Liljenzin, Dr Mats Skålberg, M.Sc Lena Spjuth and
M.Sc Anders Landgren

ABSTRACT

Separation of actinides and lanthanides from spent nuclear fuel is a part of the process of recycling spent nuclear fuel. Recycling of spent nuclear fuel has three main purposes: reduced radiotoxicity in the waste, minimise the time required for safe disposal of the waste and reuse the fertile and fissile material.

Using malonamides for separation of actinides and lanthanides has a great advantage they do not produce any secondary, non-combustible waste since they only contain nitrogen, oxygen, carbon and hydrogen.

Extraction data for two malonamides N,N'-dimethyl-dibutyloctadecyl malonamide (DMDBOD) and N,N'-dimethyl-dicyclohexyl tetradecyl malonamide (DMDCHTD) dissolved in *tert*-butylbenzene was investigated. Seven different radionuclides was used: ^{234}Th, ^{147}Nd, ^{152}Eu, ^{147}Pm, ^{244}Cm, ^{160}Tb and ^{241}Am.

Extraction data such as distribution ratio versus nitric acid concentration and distribution ratio versus malonamide concentration was investigated. Slope analysis and non-linear simplex optimisation was performed in order determine the structure of the extracted complex and the extraction mechanisms.

TABLE OF CONTENTS

1. INTRODUCTION

Nuclear reactors generate nuclear waste that contains higher actinides and fission products. Underground disposal of spent nuclear fuel without reprocessing will require several hundred of thousands of years of safe storage. If the spent fuel is reprocessed and transmuted it will only require some hundreds of years of safe disposal. Except for reduced radiotoxicity of the waste there will be less amounts of uranium that has to be mined since a large part of the fissile and fertile material may be recycled in a transmutation process.

1.1 RECYCLING OF NUCLEAR WASTE

There is need for a non waste generating and efficient separation process that can work continuously with a transmutation reactor. Fission products has to be separated from actinides such as Np, Pu, Am and Cm. Fission products with long half-life such as Tc and I are also considered to be transmuted and thus has to be separated from short-lived fission products.

Transmutation has as a primary goal to transmute by neutron irradiation of radionuclides with long half-lives to short-lived or stable elements. A large part of the transmutable waste is fertile or fissile and generates a considerable amount of heat by fission when transmuted.

To be able to transmute different components in the spent fuel two main types of reactors can be used; conventional light water reactors and burner reactors.

Conventional light water reactors can use MOX (mixed oxide) and UOX (uranium oxide) fuel which are in commercial use today. The conventional reactor systems may take care of a major part of the fuel that is considered to be recycled.

There are two types of burner reactors that can be of interest; conventional fast reactors and accelerator-driven subcritical reactors. Fast breeder reactors are in use today and they are able to burn minor actinides in considerable amounts. Subcritical reactor systems has an advance in the ability to transmute long-lived fission products. To be able to reach 98% reduction of radiotoxicity there is a demand that 15% of the total installed nuclear power should be of burner type (TOM 95).

There is advancing research going on about accelerator-driven subcritical transmutation reactors at Los Alamos National Laboratory, USA. In order to visualise how an accelerator-driven reactor will show in size, it has been fitted into a drawing of a conventional PWR building, see fig (1.1). Such a reactor should be a net producer of electric energy to the grid. Experience from both the Canadian CANDU heavy water reactor and PWR light water reactors can be of use in construction of such a reactor. There are no insurmountable problems in design of such a reactor (BEA 95).
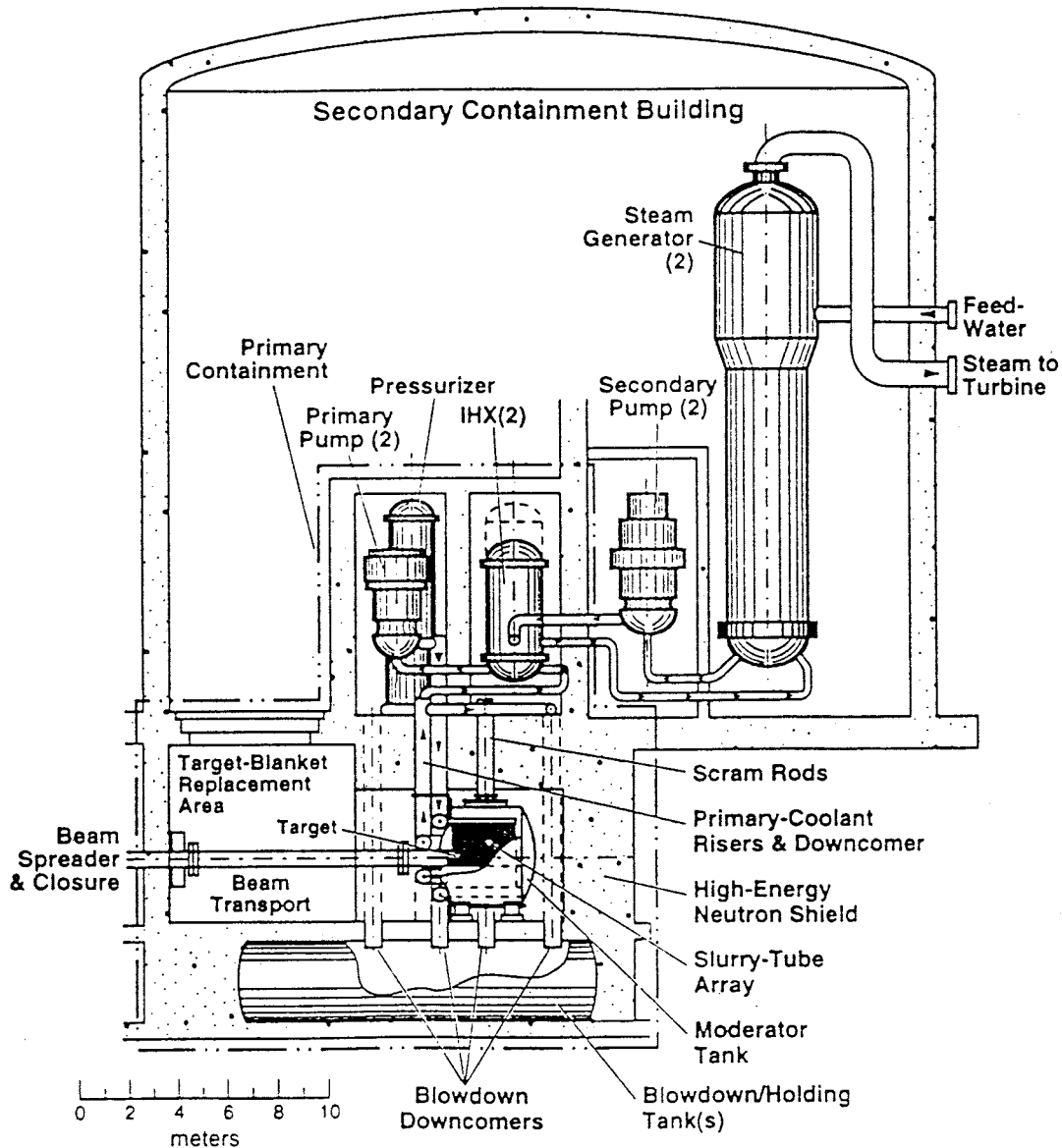
Fig1.1 Scaled layout of an aqueous ATW system to show relative sizes of system components

3

1.2 SOLVENT EXTRACTION

Solvent extraction is liquid-liquid distribution of a solute between two immiscible liquids. By varying the chemical properties of the two phases the distribution of the solute may be effected.

There are extraction reagents that may be used to separate actinides in a transmutation process but many of them have a serious disadvantage since they produce non-combustible waste.

Malonamides do not produce any secondary waste since they contain only hydrogen, carbon, nitrogen and oxygen and are therefore completely incinerable. Two malonamides were used in the extraction experiments; N,N'-dimethyl-dibutyl octadecyl malonamide (DMDBOD) and N,N'-dimethyl-dicyclohexyl tetradecyl malonamide (DMDCHTD).
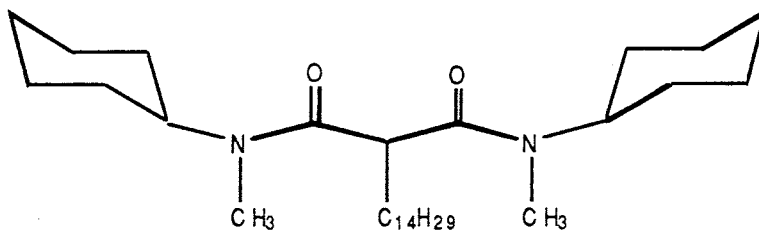
Figure 1.2.1 Model structure of DMDCHTD.
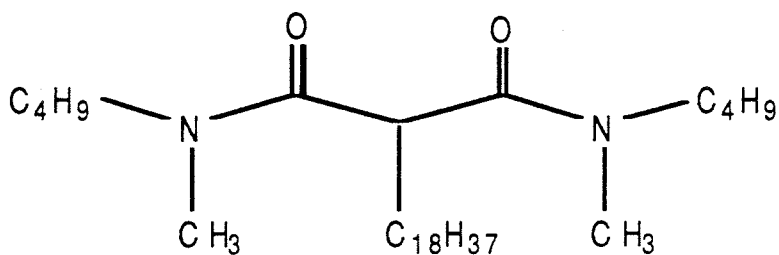
Figure 1.2.2 Model structure of DMDBOD

2. THEORY

2.1 DISTRIBUTION RATIO

The distribution ratio, D, is defined as the ratio between all the metal species (of the metal to be extracted) in the organic phase and all the metal species in the aqueous phase.

$$D_M = \frac{[M]_{tot,org}}{[M]_{tot,aq}} \qquad (2.1)$$

2.1.1 ERROR PROPAGATION

The measured number of counts is defined as N_{tot} and the standard deviation, σ_{tot}, is calculated as its own squareroot. Therefore $\sigma_{tot} = \sqrt{N_{tot}}$ and $\sigma_0 = \sqrt{N_0}$. Since $N_{Net} = N_{tot} - N_0$ the standard deviation of the net counts is calculated as:

$$\sigma_{net} = \sqrt{\sigma_{tot}^2 + \sigma_0^2} . \qquad (2.1.1)$$

Increased measuring time will decrease standard deviation as $\sigma_R = \frac{\sigma_N}{t}$ since the count rate $R = \frac{N}{t}$.

The standard deviation in the distribution ratio is calculated as:

$$\sigma_D = D \cdot \sqrt{\left(\frac{\sigma_{org}}{R_{org}}\right)^2 + \left(\frac{\sigma_{aq}}{R_{aq}}\right)^2} \qquad (2.1.2)$$

2.2 EXTRACTION MECHANISM

Extraction mechanisms are complex processes of equilibrium. In order to understand mechanisms of extraction these mechanisms are described as formation of charged or uncharged complexes that are to be extracted.

The nitric acid dissosation equilibrium can be described as:

$$H^+ + NO_3^- \overset{K_a}{\Longleftrightarrow} HNO_3 \qquad (2.2.1)$$

In order to calculate K_a, the degree of dissociation, α is used and K_a is expressed as a function of α and the total amount of added nitric acid X. K_a is a variable which depends on nitric acid concentration and includes activity constants.

$$K_a = \frac{(1-\alpha)}{X \cdot \alpha^2} \qquad (2.2.2)$$

In an aqueous phase with nitric acid, metal complexation can be described as:

$$M^{z+} + j(NO_3^-) \overset{\beta_j}{\Longleftrightarrow} M(NO_3)_j^{z-j} \qquad (2.2.3)$$

In the extraction mechanisms the overlined species are present in the organic phase and those who are not overlined are present in the aqueous phase.

Nitric acid extraction by diamide can be described as:

$$\overline{L} + HNO_3 \overset{P_1}{\Longleftrightarrow} \overline{LH^+NO_3^-} \qquad (2.2.4)$$

$$\overline{L} + 2HNO_3 \overset{P_2}{\Longleftrightarrow} \overline{LH_2^{2+}(NO_3)_2^{2-}} \qquad (2.2.5)$$
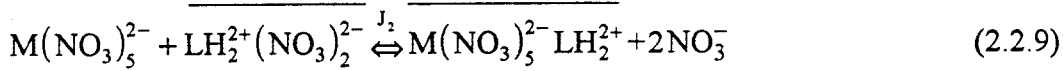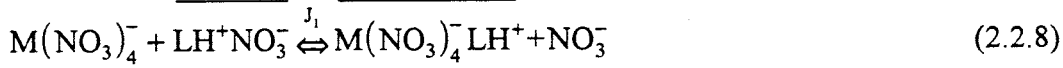
In non-acidic media or at low levels of acidity the extraction mechanisms can be described as extraction by uncharged nitrate complexes:
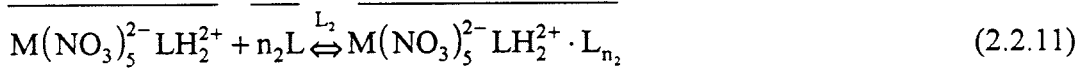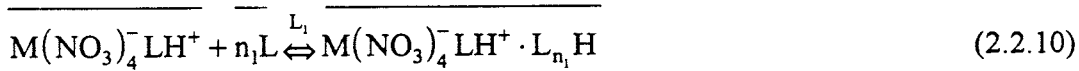
$$p\overline{L} + M^{z+} + zNO_3^- \overset{k_p}{\Longleftrightarrow} \overline{L_pM(NO_3)_z} \qquad (2.2.6)$$

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In acidic media the metal extraction can be described as ion-pair extraction with negatively charged nitrate complexes:

$$q\overline{L} + M^{z+} + tH^+ + (z+t)NO_3^- \overset{\overline{J_t}}{\Leftrightarrow} \overline{L_q M\left(NO_3\right)_{z+t} H_t} \tag{2.2.7}$$
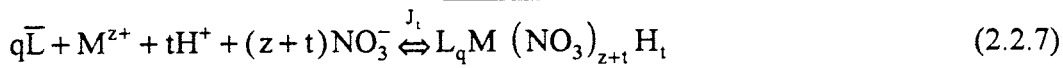
For trivalent metals, ion pair extraction can be described as:

$$M\left(NO_3\right)_4^- + \overline{LH^+ NO_3^-} \overset{\overline{J_1}}{\Leftrightarrow} \overline{M\left(NO_3\right)_4^- LH^+} + NO_3^- \tag{2.2.8}$$

$$M\left(NO_3\right)_5^{2-} + \overline{LH_2^{2+}\left(NO_3\right)_2^{2-}} \overset{\overline{J_2}}{\Leftrightarrow} \overline{M\left(NO_3\right)_5^{2-} LH_2^{2+}} + 2NO_3^- \tag{2.2.9}$$

Formation of larger organic complexes such as dimers or polymers are described as:

$$\overline{M\left(NO_3\right)_4^- LH^+} + n_1 \overline{L} \overset{\overline{L_1}}{\Leftrightarrow} \overline{M\left(NO_3\right)_4^- LH^+ \cdot L_{n_1} H} \tag{2.2.10}$$

$$\overline{M\left(NO_3\right)_5^{2-} LH_2^{2+}} + n_2 \overline{L} \overset{\overline{L_2}}{\Leftrightarrow} \overline{M\left(NO_3\right)_5^{2-} LH_2^{2+} \cdot L_{n_2}} \tag{2.2.11}$$

Distribution coefficient D_M in non or weak acidic media is described as a co-ordination mechanism.

$$D_M = \frac{\Sigma_p \overline{\left[L_p M(NO_3)_z\right]}}{\left[M^{z+}\right] + \Sigma_j \left[M(NO_3)_j^{z-j}\right]} \tag{2.2.12}$$

Distribution coefficient, D_M, in strong acidic media is described as an ion-pair mechanism.

$$D_M = \frac{\Sigma_q \overline{\left[L_q M(NO_3)_{(z+t)} H_t\right]}}{\left[M^{z+}\right] + \Sigma_j \left[M(NO_3)_j^{z-j}\right]} \tag{2.2.13}$$

The distribution coefficient of trivalent metals when both a co-ordination mechanism and an ion-pair mechanisms are considered can be expressed as:

$$D_M = \frac{\Sigma_p \overline{\left[L_p M(NO_3)_3\right]} + \overline{\left[M(NO_3)_4^- LH^+ \cdot L_{n_1}\right]} + \overline{\left[M(NO_3)_5^{2-} LH_2^{2+} \cdot L_{n_2}\right]}}{\left[M^{3+}\right] + \Sigma_i \left[M(NO_3)_i^{3-i}\right]} \tag{2.2.14}$$

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The total concentration of nitric acid is expressed as $[HNO_3]_{tot}$. In order to calculate $[NO_3^-]$ it is assumed that $[M] \langle\langle [HNO_3]_{tot}$ and $[H^+] \cong [NO_3^-]$.

$$[HNO_3] = K_a [NO_3^-]^2 \qquad (2.2.15)$$

$$[HNO_3]_{tot} = [HNO_3] + [NO_3^-] + \overline{[HNO_3]}_{tot} \qquad (2.2.16)$$

The distribution of nitric acid between the organic and aqueous-phases is described by λ.

$$[HNO_3] \overset{\lambda}{\Leftrightarrow} \overline{[HNO_3]} \qquad (2.2.17)$$

Concentration of nitric acid in organic phase $\overline{[HNO_3]}_{tot}$ is measured by potentiometric titrations. $\overline{[HNO_3]}_{tot}$ can also be expressed as a function of nitric acid in aqueous phase.

$$[HNO_3]_{tot} - \overline{[HNO_3]} = K_a [NO_3^-]^2 + [NO_3^-] \qquad (2.2.18)$$

$$[NO_3^-] = -\frac{1}{2*K_a} \pm \sqrt{\frac{1}{4*K_a^2} + \frac{[HNO_3]_{tot}}{K_a} - \frac{\overline{[HNO_3]}}{K_a}} \qquad (2.2.19)$$

Free diamide concentration $\overline{[L]}$ is a function of total diamide concentration $\overline{[L]}_{tot}$ and the nitric acid concentration in the organic phase.

$$\overline{[L]}_{tot} = \overline{[L]} + \overline{[LH^+NO_3^-]} + \overline{[LH_2^{2+}(NO_3)_2^{2-}]} \qquad (2.2.20)$$

The total concentration of diamide includes both free diamide and the protonated diamide species. Trace amounts of metal is used and metal-species can therefore be neglected.

$$[\overline{L}] = \frac{[\overline{L}]_{tot}}{1 + P_1 \cdot [\overline{HNO_3}] + P_2 \cdot [\overline{HNO_3}]^2} \qquad (2.2.21)$$

The distribution ratio of the metal species M, can therefore be expressed as

$$D_M = \frac{\dfrac{k_p \cdot \beta_3 \cdot [NO_3^-]^3 \cdot [\overline{L}]_{tot}^p}{\left(1 + P_1 \cdot [\overline{HNO_3}] + P_2 \cdot \lambda [\overline{HNO_3}]^2\right)^p} + \dfrac{J_1 \cdot P_1 \cdot L_1 \cdot \beta_4 \cdot [NO_3^-]^3 \cdot [\overline{HNO_3}] \cdot [\overline{L}]_{tot}^{n+1}}{\left(1 + P_1 \cdot [\overline{HNO_3}] + P_2 \cdot [\overline{HNO_3}]^2\right)^{n+1}} + \dfrac{J_2 \cdot L_2 \cdot P_2 \cdot \beta_5 \cdot [NO_3^-]^3 \cdot [\overline{HNO_3}]^2 \cdot [\overline{L}]_{tot}^{n+1}}{\left(1 + P_1 \cdot [\overline{HNO_3}] + P_2 \cdot [\overline{HNO_3}]^2\right)^{n+1}}}{1 + \sum_i \beta_i \cdot [NO_3^-]^i}$$

$$(2.2.22)$$

2.3 STOICHIOMETRIC COMPLEX DETERMINATION

Two useful ways of determining the number of amide molecules in an organometallic complex (q) are; organic phase saturation and slope analysis (NIG 94I). In acidic media q can be determined by slope analysis according to:

$$\log(D_M) = q \log([\overline{L}]) + \text{constant} \qquad (2.3)$$

By plotting the logarithm of distribution ratio D_M versus the logarithm of diamide concentration $[\overline{L}]$ the number of amide molecules q equals the slope.

Organic phase saturation method is performed with an aqueous phase that is concentrated with metal ions. All the extractant will then co-ordinate the metal and the concentration ratio C_{amide}/C_{metal} is equal to the number of diamide molecules in the complex.

2.4 COMPLEXATION OF METAL IONS

At high acidities metal complexation are significant and anions such as: $M(NO_3)_j^{z-j}$ $(j\rangle z)$ will form according to equation 2.2.3

M is the metal, L is the substituted ligand and β is the stability constant for each number of ligands.

The general formula is; $\beta_n = \dfrac{[ML_n][L]^n}{[M]}$ $\qquad (2.4.1)$

Empirical data on Am^{3+} complexation (β) with nitrate does not exist for higher order than three. N is the co-ordination number for the ion in question. In order to se how the different complexes of higher order than three behave at high concentrations of nitric acid, statistical calculations were made according to (RYD 92):

$$\beta_{n+1} = (\beta_1)^{n+1} \cdot \frac{(N-n)\cdot n}{(N-n+1)\cdot(n+1)} \qquad (2.4.2)$$

3. EXPERIMENTAL

Metal distribution as a function of nitric acid concentration for different actinides and lanthanides were determined with two different malonamides. Distribution coefficient as a function of diamide concentration for one lanthanide and one actinide at some nitric acid concentrations was also studied.

3.1 DETERMINATION OF EXTRACTION CURVES

Extraction studies were performed in 3.5 ml glass tubes. A small volume of stock solution of a specific radionuclide was added to the nitric acid in the test tube. It was set to equilibrate for one hour and then the organic phase was added and the test tube was shaken for five minutes. The test tube was let to stand for five minutes to allow phase separation. Finally it was centrifuged for ten minutes at 4500 rpm to achieve complete separation.

3.1.1 SAMPLING

Both the organic and the aqueous phase was sampled with a "Gilson" automatic pipette. Samples that should be analysed by a HPGe detector were diluted with nitric acid or organic solvent to achieve the same geometry. Samples that were analysed with the liquid scintillation detector were diluted to 0.8 ml and scintillation cocktail was added immediately.

3.1.2 DETECTION

Detection of radioactivity was performed using a HPGe detector and a liquid scintillation detector. The HPGe system consisted of an EG&G ORTEC coaxial detector that was connected to an ORTEC ADCAM multichannel analyser system. The gammaspectra were analysed using GAMMA VISION (EG&G ORTEC). Detection by liquid scintillation was performed with an LKB WALLAC 1219 RACKBETA liquid scintillation counter.

3.2 PREPARATION OF CHEMICALS

3.2.1 NITRIC ACID

Concentrated nitric acid Normapur (pour analyses) 69 wt% was used. Nitric acid was weighed to an amount that corresponds to the chosen concentration and then diluted to 100 ml. The solutions with lowest concentration were made by dissolving nitric acid of higher concentration e.g. 10M diluted 100 times equals 0.1M. The following nitric acid concentrations were prepared 0.03M, 0.1M, 0.15M, 0.3M, 0.5M, 1.0M, 2.0M, 3.0M, 4.0M, 5.0M, 6.0M, 7.5M, 9.0M, 10M and 12M.

3.2.2 DIAMIDE

Diamide solutions of DMDBOD and DMDCHTD were prepared by weighing a specific amount of solid diamide and dissolve it in different solvents. All solutions was set to equilibrate over night before use. Both diamides were made in 0.1, 0.2, 0.3, 0.6, and 1.0 M solutions. Dodecane 99% and tert-butylbenzene 99% were used as solvents.

3.3 RADIONUCLIDES

Stock solutions of ^{234}Th, ^{147}Nd, ^{152}Eu, ^{147}Pm, ^{244}Cm, ^{160}Tb, ^{241}Am, in tracer metal concentrations were used. If necessary the tracers were purified from their mother/daughter nuclides. All radionuclides were dissolved in 0.5 M nitric acid except for ^{147}Pm which was dissolved in 0.0123M HCl. ^{234}Th was separated from natural uranium. ^{244}Cm was purified from tracers of Pu by solvent extraction with Aliquat-336.

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4. RESULTS

Experiments were performed in two ways; determination of distribution ratio versus nitric acid concentration and determination of distribution ratio versus diamide concentration for the two diamides DMDBOD and DMDCHTD. The reversibility of the extraction process was examined for thorium with DMDBOD. Metal extraction data from the experiments was analysed in two different ways. Stoichiometric complex determination was performed in order to find out the structure of the extracting organometallic complexes. Simplex optimisation of extraction data was performed in order to analyse the theory of extraction in aspects such as size of organometallic complexes and equilibrium constants for the equations in chapter 2.2. The limit of solubility for both diamides in *tert*-butylbenzene is more than 1M at room temperature (25°C).

4.1 DISTRIBUTION RATIO AS A FUNCTION OF NITRIC ACID CONCENTRATION

Distribution ratio (D) as a function of nitric acid concentration is used to determine how useful a malonamide is for extraction of a specific metal ion. These results are also used to analyse the mechanisms of extraction.
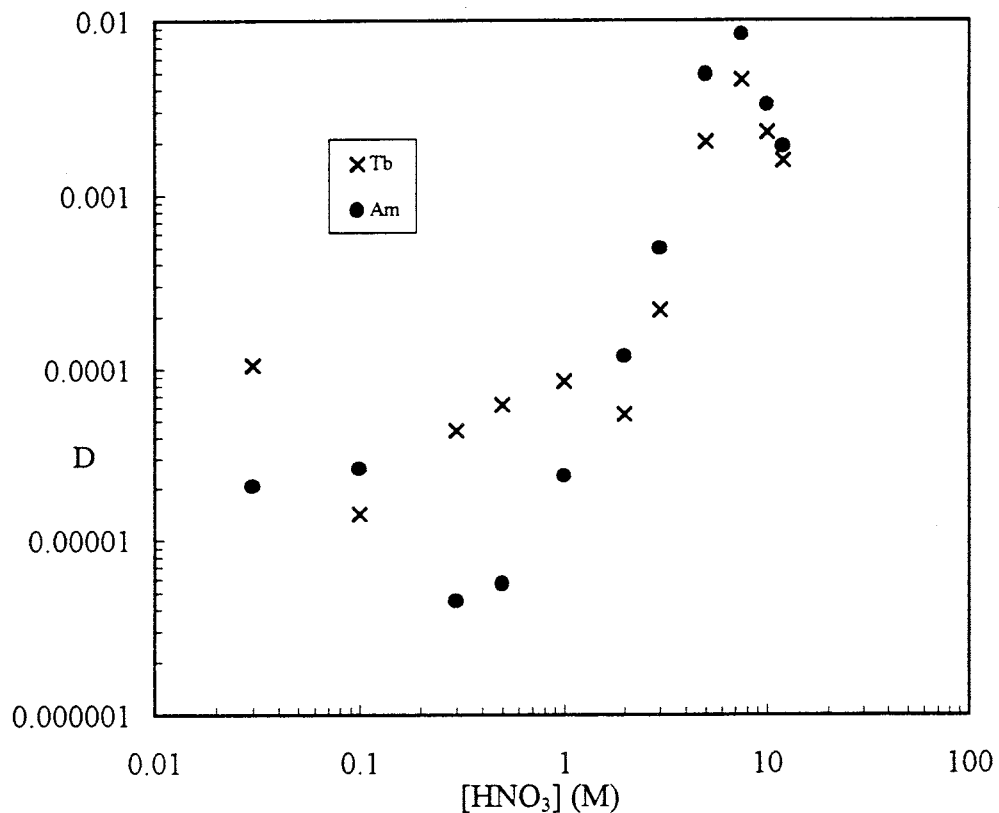
Figure 4.1.1 Distribution ratio for Am and Tb with 0.1 M DMDCHTD in *tert*-butylbenzene at different concentrations of nitric acid.
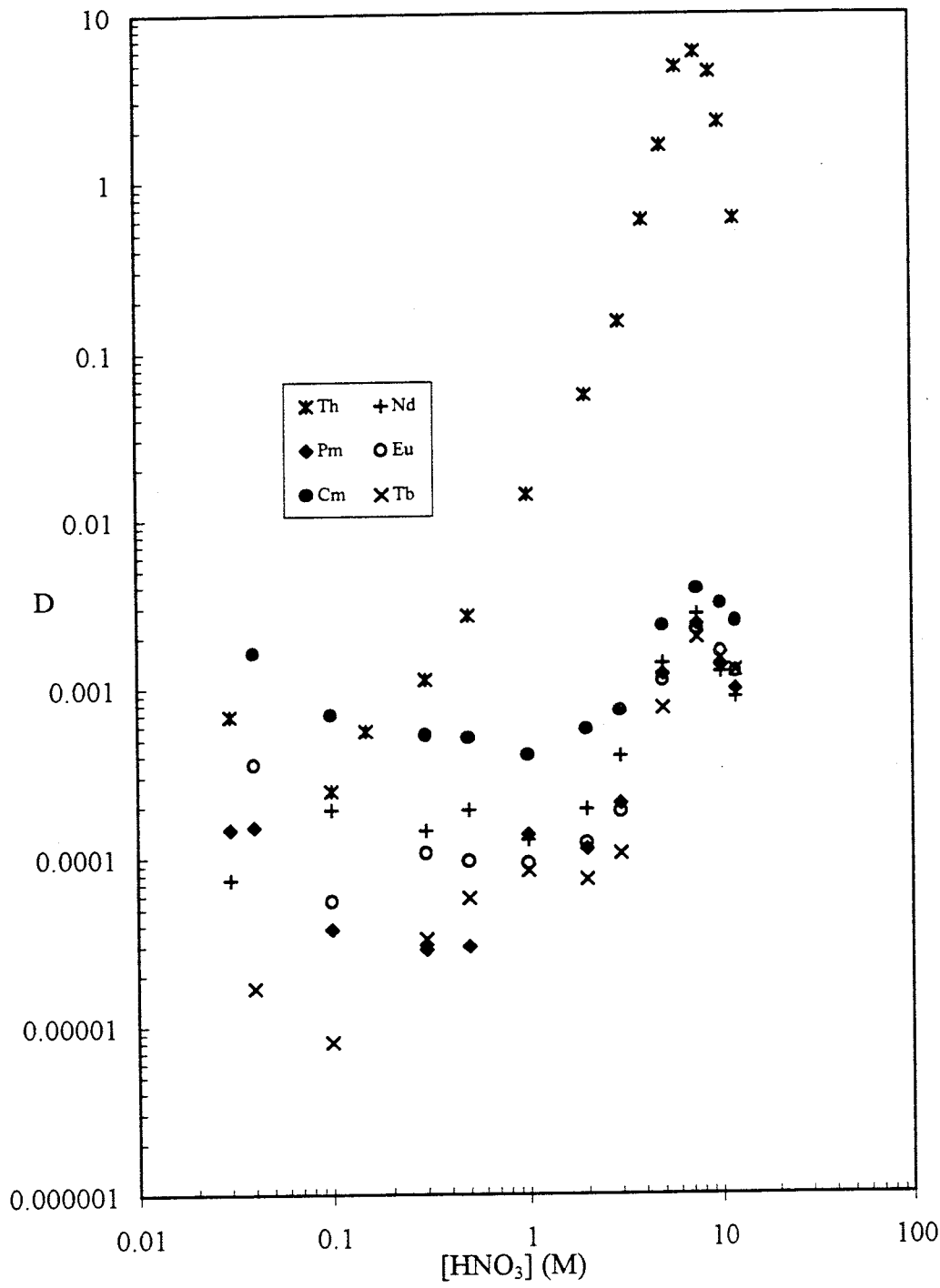
Figure 4.1.2 Distribution ratio for some metals with 0.1 M DMDBOD in *tert*-butylbenzene at different concentrations of nitric acid.

4.2 REVERSIBILITY OF THORIUM EXTRACTION

In order to examine the reversibility of the extraction process, then thorium was extracted from 9.0 M nitric acid with 0.1 M DMDBOD. Thorium was then stripped from the organic phase with 0.1 M nitric acid. A distribution coefficient of 4.4 was reached at 9.0 M nitric acid and back extraction with 0.1 M nitric acid gave a distribution ratio of 0.0045.

4.3 STOICHIOMETRIC COMPLEX DETERMINATION

In order to determine the number of diamide molecules in the extracted organometallic complex a linearisation of D_M as a function of amide concentration was performed for different nitric acid concentrations. Results from table 4.2.1 and 4.2.2 imply that the number of diamide molecules in the organometallic complex vary with nitric acid concentration. For both diamides the structure of the organometallic complex seems to change with increasing nitric acid concentration.

4.3.1 STOICHIOMETRIC COMPLEX DETERMINATION FOR DMDCHTD.

TABLE 4.2.1

Results of slope analysis for DMDCHTD at 0.2-1.0M malonamide.

Ion	$[HNO_3](M)$	Slope	R^2
Am^{3+}	0,3	2,98	0,976
Am^{3+}	1,0	3,89	0,996
Am^{3+}	7,5	2,15	0,998
Tb^{3+}	1,0	3,83	0,995
Tb^{3+}	3,0	3,18	0,999
Tb^{3+}	7,5	2,12	0,998

4.3.2 STOICHIOMETRIC COMPLEX DETERMINATION FOR DMDBOD.

TABLE 4.2.2

Results of slope analysis for DMDBOD at 0.2-1.0M malonamide.

Ion	$[HNO_3](M)$	Slope	R^2
Am^{3+}	0,3	2,48	0,994
Am^{3+}	3,0	2,28	0,994
Tb^{3+}	1,0	2,93	0,998
Tb^{3+}	5,0	2,40	0,999

4.4 SIMPLEX OPTIMISATION OF EXTRACTION DATA

Simplex optimisation was used on equation 4.3.1 which is a condensed version of equation 2.2.22. Extraction data for Am^{3+} and Tb^{3+} with DMDBOD was used. Non-linear simplex optimisation of empirical data was performed in order to determine the structure of the organic complex and to verify the mechanisms of extraction that are discussed in chapter two.

Results from distribution ratio versus diamide concentration and distribution ratio versus nitric acid concentration was used simultaneously in the simplex optimisation. Nelder and Mead algorithm for constrained simplex optimisation was used in a FORTRAN program. No negative constants were allowed to appear. Data of nitric acid extraction with DMDBOD was used from (SPJ 96).

$$D_M = \frac{\dfrac{a_1 \cdot [NO_3^-]^3 \cdot [\overline{L}]_{tot}^P}{\left(1 + a_2 \cdot [\overline{HNO_3}] + a_3 \cdot [\overline{HNO_3}]^2\right)^P} + \dfrac{a_4 \cdot [NO_3^-]^3 \cdot [\overline{HNO_3}] \cdot [\overline{L}]_{tot}^{n_1+1}}{\left(1 + a_2 \cdot [\overline{HNO_3}] + a_3 \cdot [\overline{HNO_3}]^2\right)^{n_1+1}} + \dfrac{a_5 \cdot [NO_3^-]^3 \cdot [\overline{HNO_3}]^2 \cdot [\overline{L}]_{tot}^{n_2+1}}{\left(1 + a_2 \cdot [\overline{HNO_3}] + a_3 \cdot [\overline{HNO_3}]^2\right)^{n_2+1}}}{1 + \sum_6^{10} a_i \cdot [NO_3^-]^i}$$

$$(4.3.1)$$

Results from simplex optimisation of Am^{3+} and Tb^{3+} is shown in appendix 3. The best fit is achieved with exponents p=3, n_1=2 and n_2=2.

Exponent p refers to equation 2.2.6 with p=3, the equation will be:

$$3\overline{L} + M^{z+} + zNO_3^- \overset{k_3}{\overline{\Longleftrightarrow}} \overline{L_3 M(NO_3)_z} \qquad (4.3.2)$$

Exponents n_1 and n_2 refers to equations 2.2.10 and 2.2.11 with n_1=2 and n_2=2 the equations will be:

$$\overline{M(NO_3)_4^- LH^+} + 2L \overset{\overline{L_1}}{\overline{\Longleftrightarrow}} \overline{M(NO_3)_4^- LH^+ \cdot L_2 H} \qquad (4.3.3)$$

$$\overline{M(NO_3)_5^{2-} LH_2^{2+}} + 2L \overset{\overline{L_2}}{\overline{\Longleftrightarrow}} \overline{M(NO_3)_5^{2-} LH_2^{2+} \cdot L_2} \qquad (4.3.4)$$
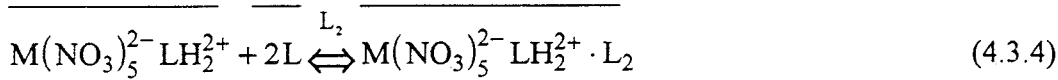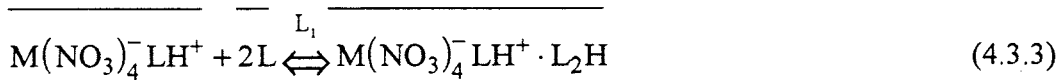
5.   CONCLUSIONS

Results from simplex optimisation and slope analysis shows that the organic complex contains several diamide molecules per extracted metal ion. How the complexes are arranged is difficult to predict. There is evidence from both simplex and slope analysis that there is three diamide molecules per metal in the complex. Results in order to determine constants a_i in formula 4.3.1 was difficult to achieve. Result from the extraction tests shows that these malonamides are effective extracting reagents for actinides and lanthanides. Back extraction of thorium shows that the reversibility of the extraction is good.

6. DISCUSSION

In order to describe mechanism and equilibrium constants of extraction with malonamides there is a need for further investigations. More extraction data and an improved mechanism of extraction for simplex optimisation are required. The problems with differences in extraction data from experimental and calculated results at low acidity must be further investigated.

An extended test program in order to get results that will improve statistical errors. Simplex optimisations of results from other diamides and metals can be very useful for comparison in order to find matching and/or mismatching results. In order to improve understanding of the mechanisms involved in extraction with malonamides some important points have to be considered:

* Improved model for simplex optimisation.

* Larger amounts of indata for simplex calculations in order to achieve better statistics.

* Examine extraction behaviour at low concentrations of nitric acid.

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Experimental distribution ratios for terbium

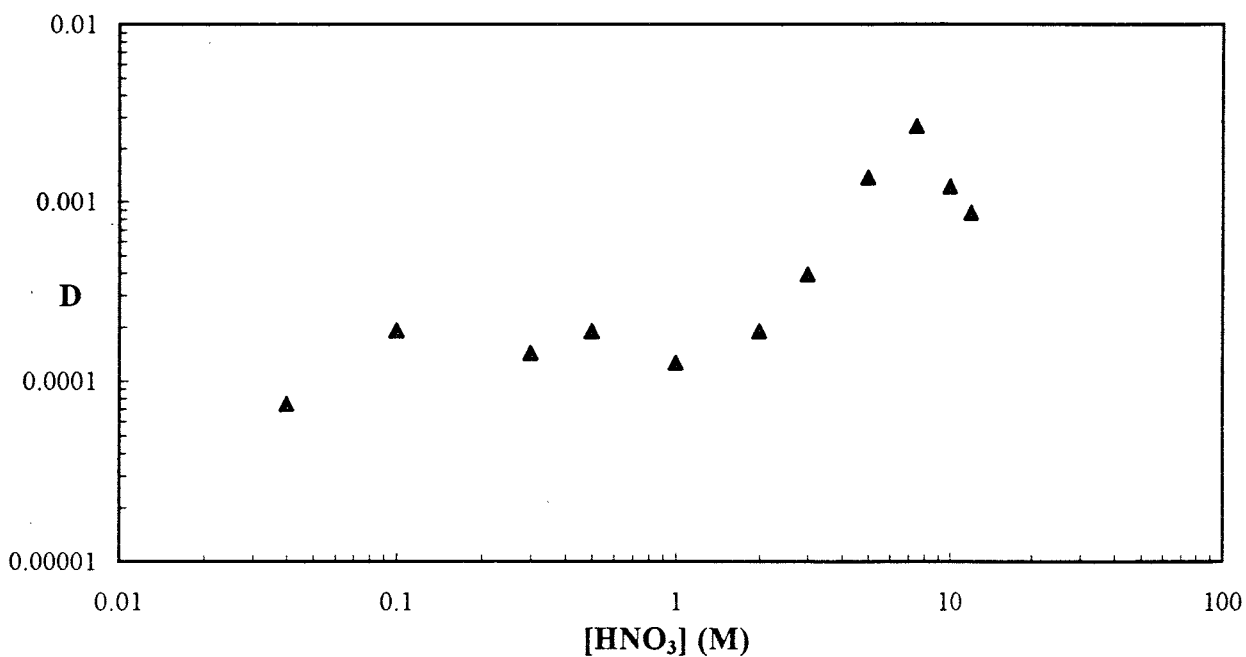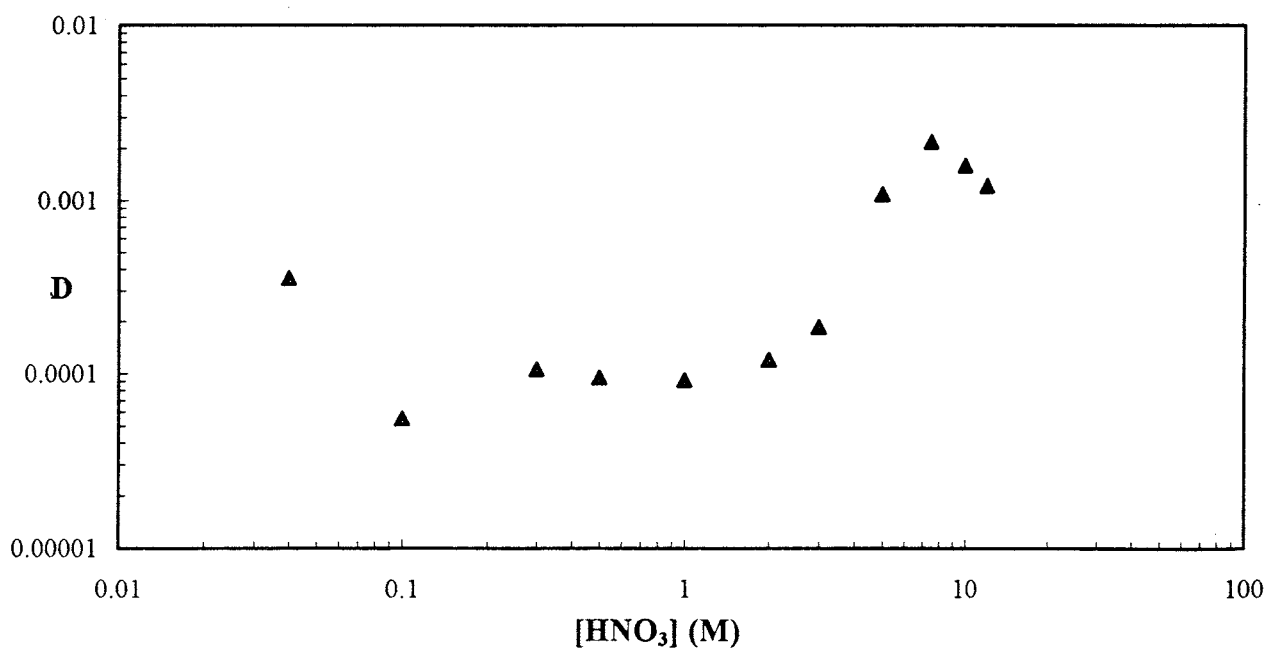Table 1:1 Experimental distribution ratios for extraction of terbium from various concentrations of nitric acid by 0.1 M DMDBOD in *tert*-butylbenzene.

| $[HNO_3]$ (M)	D	error in D (%)
0.04	1.7E-05	3.9
0.1	8.1E-06	3.1
0.3	3.3E-05	2.2
0.5	5.8E-05	1.0
1	8.4E-05	1.2
2	7.5E-05	2.0
3	0.00011	1.9
5	0.00075	1.4
7.5	0.0019	1.0
10	0.0015	1.4
12	0.0012	1.5
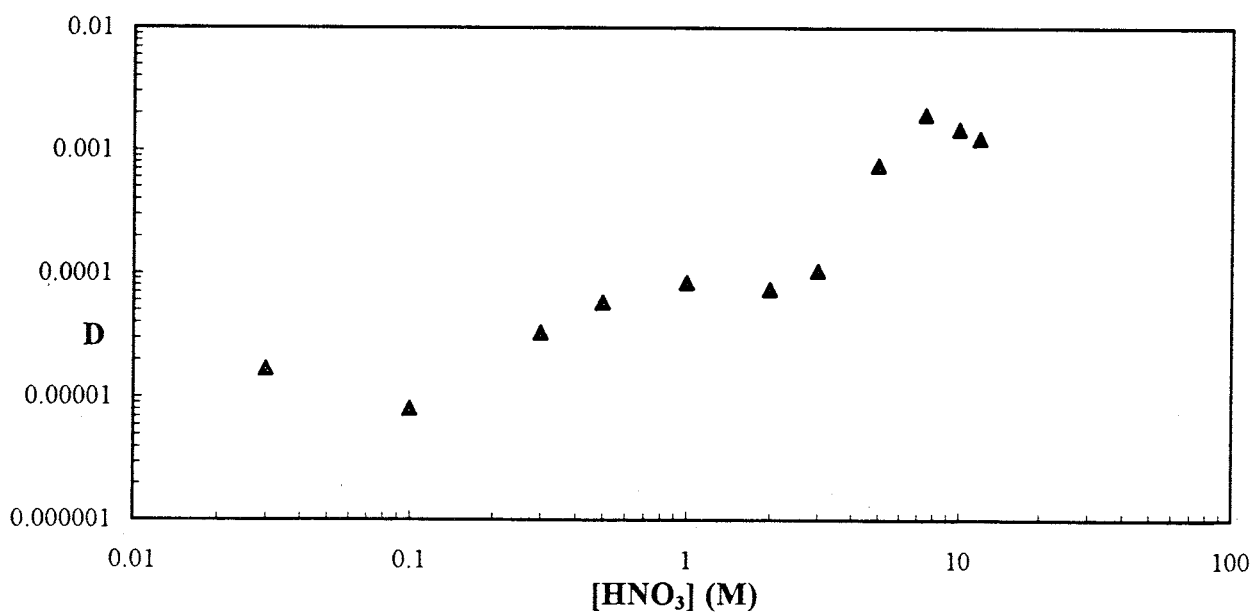
Figure 1:1 Experimental distribution ratios for extraction of terbium from various concentrations of nitric acid with 0.1 M DMDBOD in *tert*-butylbenzene.

Experimental distribution ratios for neodymium

Table 1:2 Experimental distribution ratios for extraction of neodymium from various concentrations of nitric acid by 0.1M DMDBOD in *tert*-butylbenzene.

| $[HNO_3]$ (M)	D	error in D (%)
0.04	7.5E-05	3.1
0.1	0.00019	4.4
0.3	0.00014	2.7
0.5	0.00019	2.3
1	0.00013	2.2
2	0.00019	2.0
3	0.00039	2.2
5	0.0014	1.5
7.5	0.0027	1.1
10	0.0012	1.5
12	0.00087	1.5

Figure 1:2 Experimental distribution ratios for extraction of neodymium from various concentrations of nitric acid with 0.1M DMDBOD in *tert*-butylbenzene.

Experimental distribution ratios for europium

Table 1:3 Experimental distribution ratios for extraction of europium from various concentrations of nitric acid by 0.1M DMDBOD in *tert*-butylbenzene.

| $[HNO_3]$ (M)	D	error in D (%)
0.04	0.00036	1.4
0.1	5.5E-05	1.3
0.3	0.00011	2.1
0.5	9.5E-05	1.2
1	9.2E-05	1.2
2	0.00012	1.5
3	0.00019	1.9
5	0.0011	1.5
7.5	0.0022	1.2
10	0.0016	1.3
12	0.0012	1.6

Figure 1:2 Experimental distribution ratios for extraction of europium from various concentrations of nitric acid with 0.1M DMDBOD in *tert*-butylbenzene.

Experimental distribution ratios for promethium

Table 1:4 Experimental distribution ratios for extraction of promethium from various concentrations of nitric acid by 0.1M DMDBOD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	error in D (%)
0.04	0.00015	2.3
0.1	3.8E-05	6.5
0.3	2.9E-05	8.4
0.5	3.0E-05	16
1	0.00014	2.4
2	0.00011	4.9
3	0.00021	3.0
5	0.0012	0.99
7.5	0.0023	0.69
10	0.0013	0.94
12	0.00097	1.1
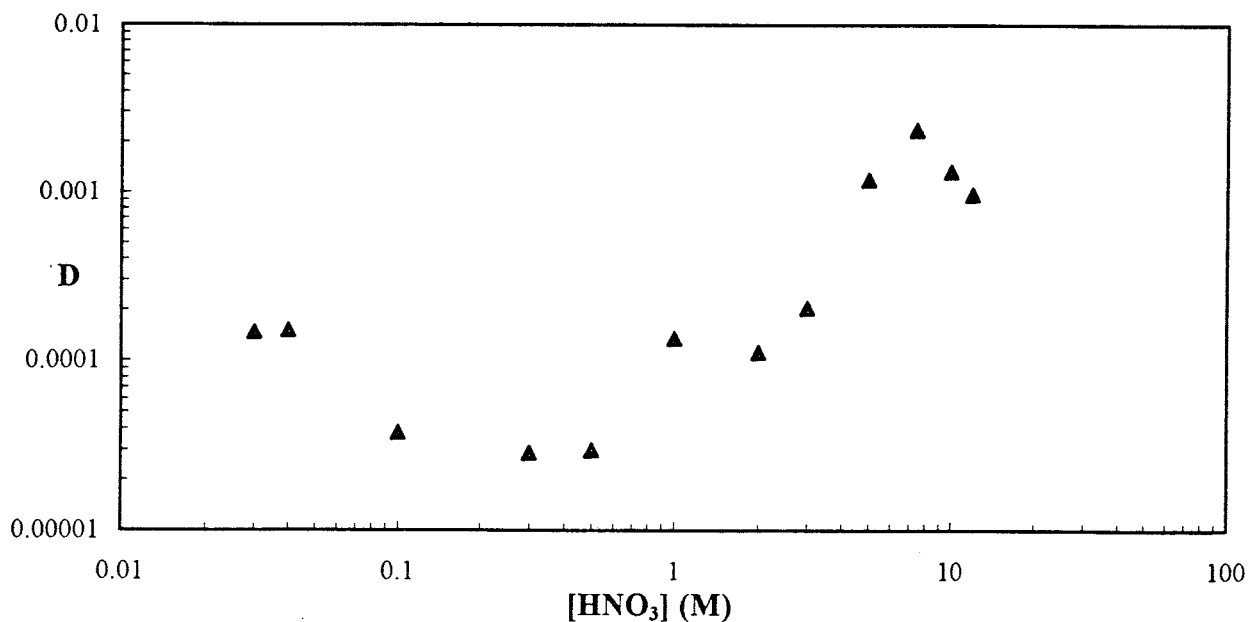
Figure 1:4 Experimental distribution ratios for extraction of promethium from various concentrations of nitric acid with 0.1M DMDBOD in *tert*-butylbenzene.

Experimental distribution ratios for curium

Table 1:5 Experimental distribution ratios for extraction of curium from various concentrations of nitric acid by 0.1M DMDBOD in *tert*-butylbenzene.

| $[HNO_3]$ (M)	D	error in D (%)
0.04	0.0016	1.3
0.1	0.00072	2.1
0.3	0.00051	2.5
0.5	0.00051	2.5
1	0.00042	2.8
2	0.00056	2.4
3	0.00073	2.0
5	0.0023	1.1
7.5	0.0038	0.85
10	0.0030	0.96
12	0.0023	1.1
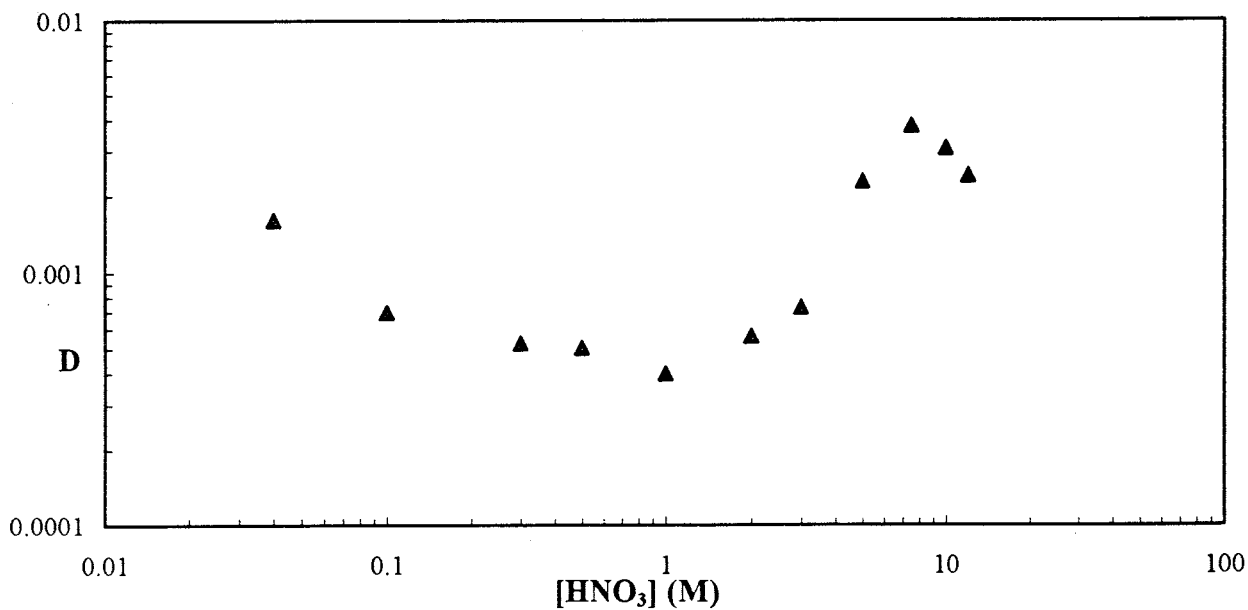
Figure 1:5 Experimental distribution ratios for extraction of curium from various concentrations of nitric acid with 0.1M DMDBOD in *tert*-butylbenzene.

Metal Extraction

Experimental distribution ratios for thorium

Table 1:6 Experimental distribution ratios for extraction of thorium from various concentrations of nitric acid by 0.1M DMDBOD in *tert*-butylbenzene.

| $[HNO_3]$ (M)	D	error in D (%)
0.04	0.00053	11
0.1	0.00017	27
0.15	0.00056	20
0.3	0.0011	6.7
0.5	0.0027	4.4
1	0.0140	1.7
2	0.0548	0.87
3	0.15	0.59
4	0.59	0.52
5	1.6	0.46
6	4.8	0.66
7.5	5.8	0.66
9	4.4	0.71
10	2.2	0.50
12	0.60	0.43
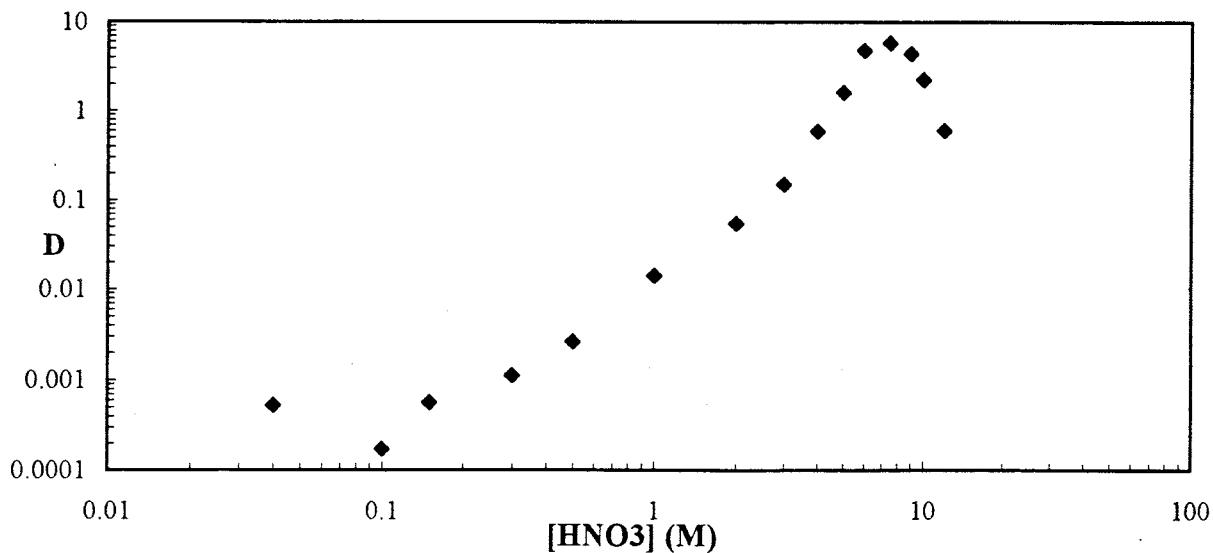
Figure 1:6 Experimental distribution ratios for extraction of thorium from various concentrations of nitric acid with 0.1M DMDBOD in *tert*-butylbenzene.

Experimental distribution ratios for americium

Table 1:7 Experimental distribution ratios for extraction of americium from various concentrations of nitric acid by 0.1M DMDCHTD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	error in D (%)
0.04	2.1E-05	8.2
0.1	2.6E-5	6.8
0.3	4.5E-5	29
0.5	5.6E-5	23
1	2.4E-5	7.0
2	0.00012	2.5
3	0.00049	1.1
5	0.0049	0.36
7.5	0.0083	0.28
10	0.0033	0.43
12	0.0019	0.56
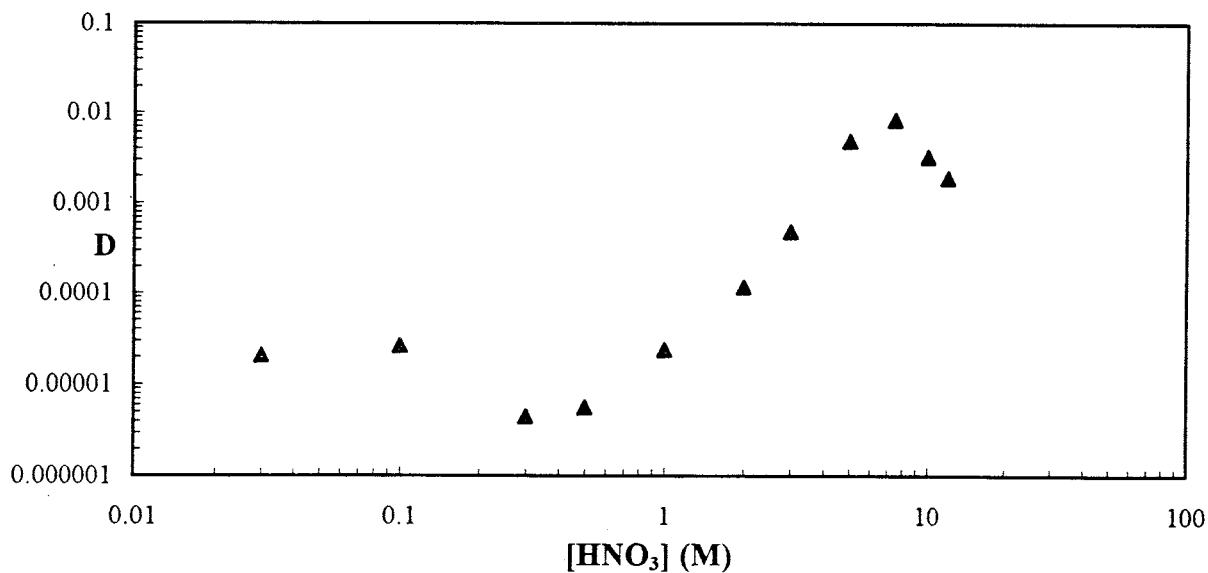
Figure 1:7 Experimental distribution ratios for extraction of americium from various concentrations of nitric acid with 0.1M DMDCHTD in *tert*-butylbenzene.

Experimental distribution ratios for terbium

Table 1:8 Experimental distribution ratios for extraction of terbium from various concentrations of nitric acid by 0.1M DMDCHTD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	error in D (%)
0.04	0.00011	1.7
0.1	1.4E-5	1.3
0.3	4.4E-5	1.6
0.5	6.2E-5	0.99
1	8.5E-5	1.2
2	5.5E-5	2.5
3	0.00022	2.5
5	0.0020	1.5
7.5	0.0045	1.1
10	0.0023	1.6
12	0.0016	1.3
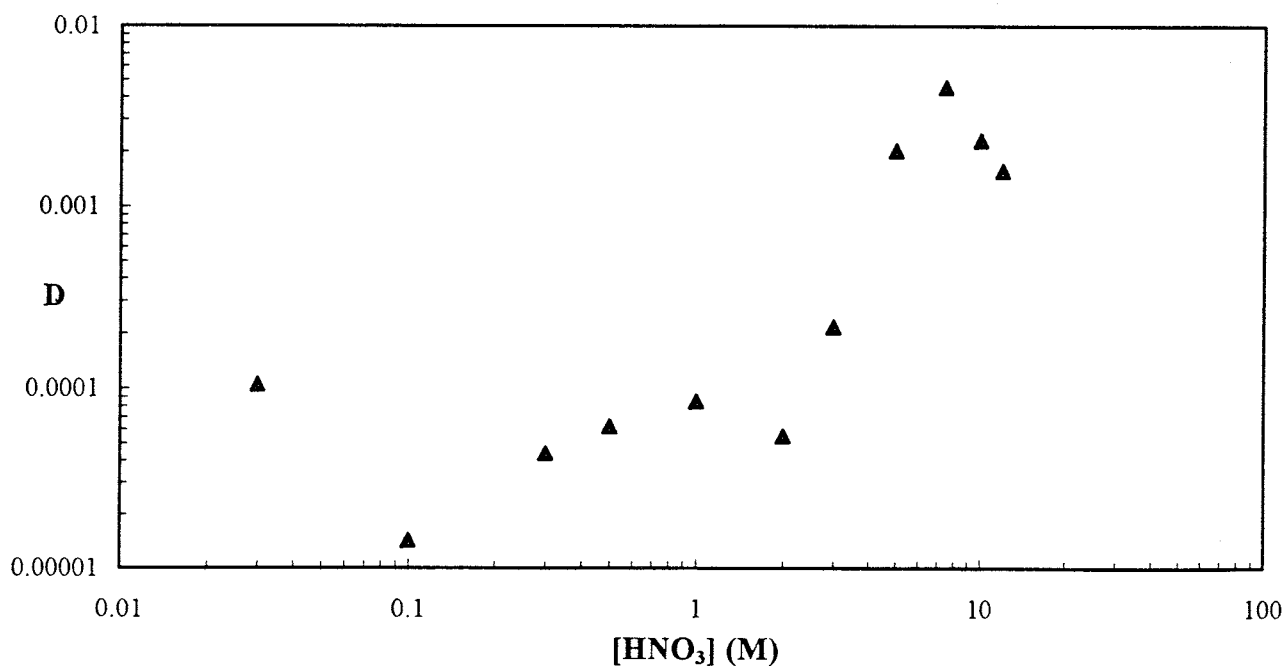
Figure 1:8 Experimental distribution ratios for extraction of terbium from various concentrations of nitric acid with 0.1M DMDCHTD in *tert*-butylbenzene.

Stoichiometric complex determination.
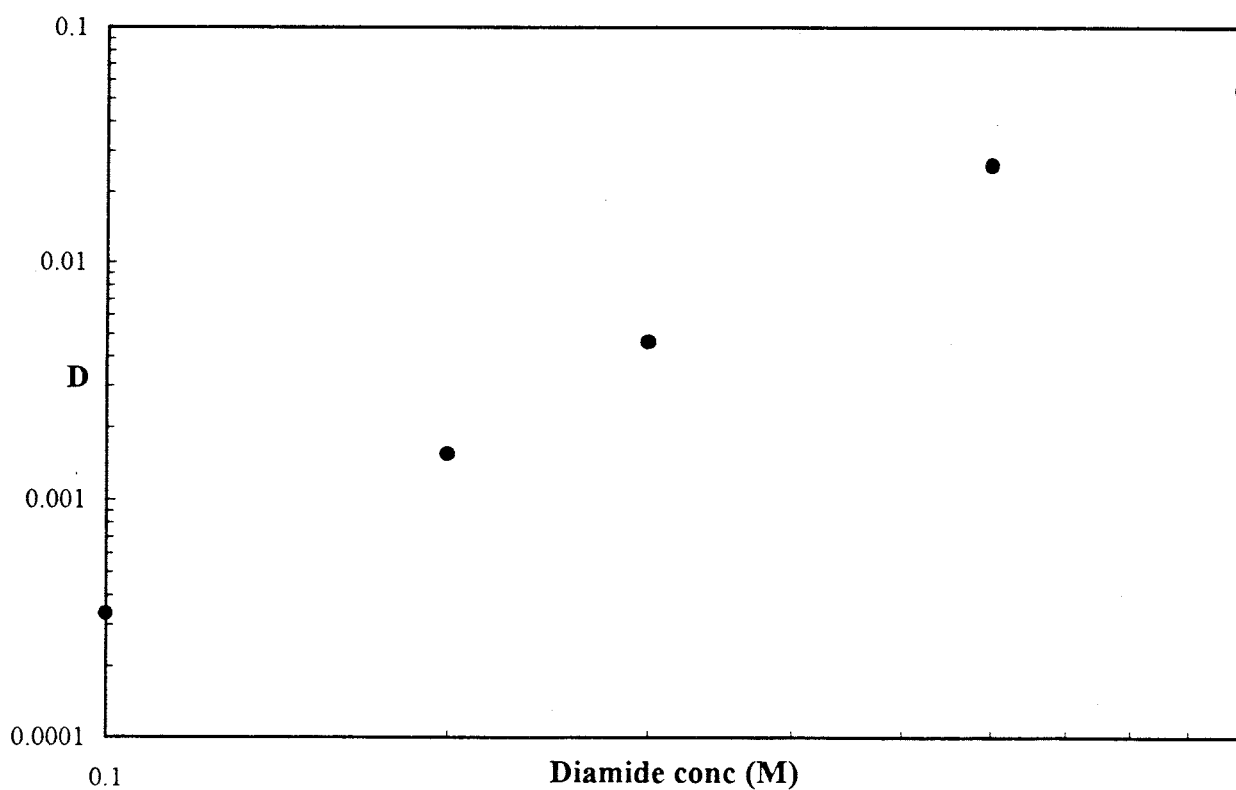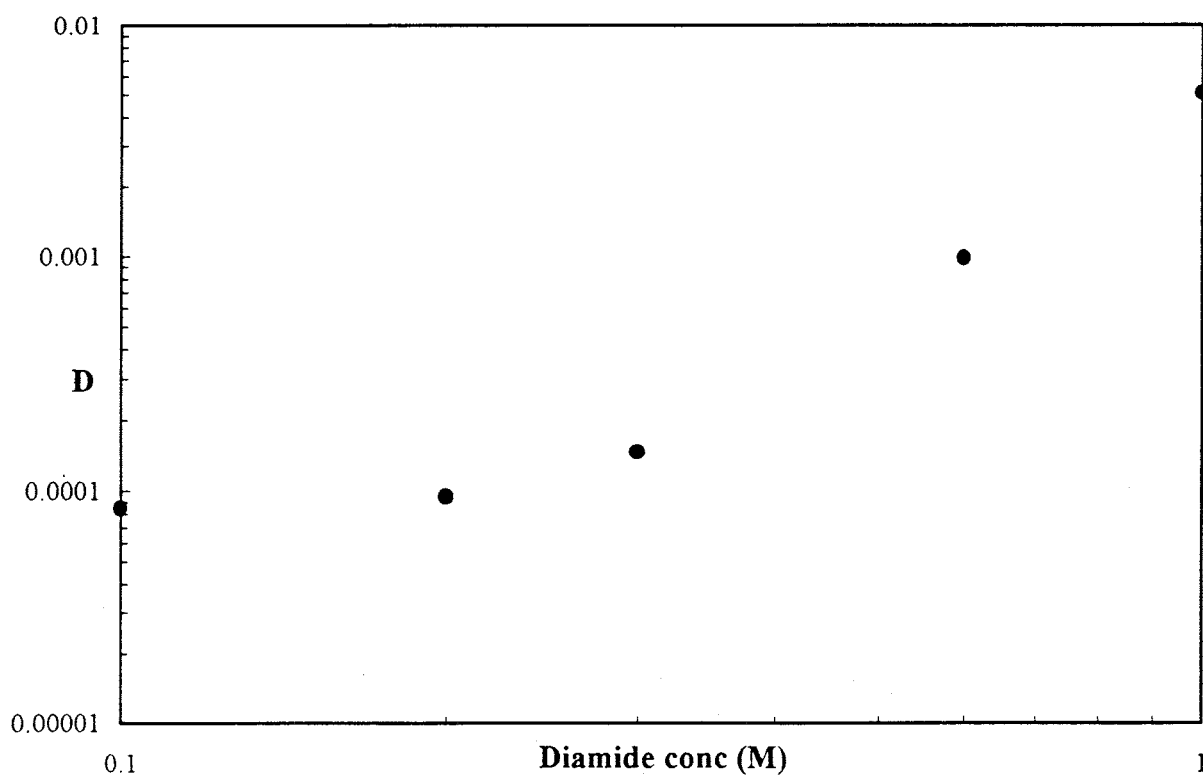
Stoichiometric complex determination for DMDBOD

Table 2:1 Experimental distribution ratios for extraction of americium from 0.3 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	1.08E-05	0.1
0.3	1.97E-05	0.2
0.3	3.87E-05	0.3
0.3	0.000262	0.6
0.3	0.000967	1.0
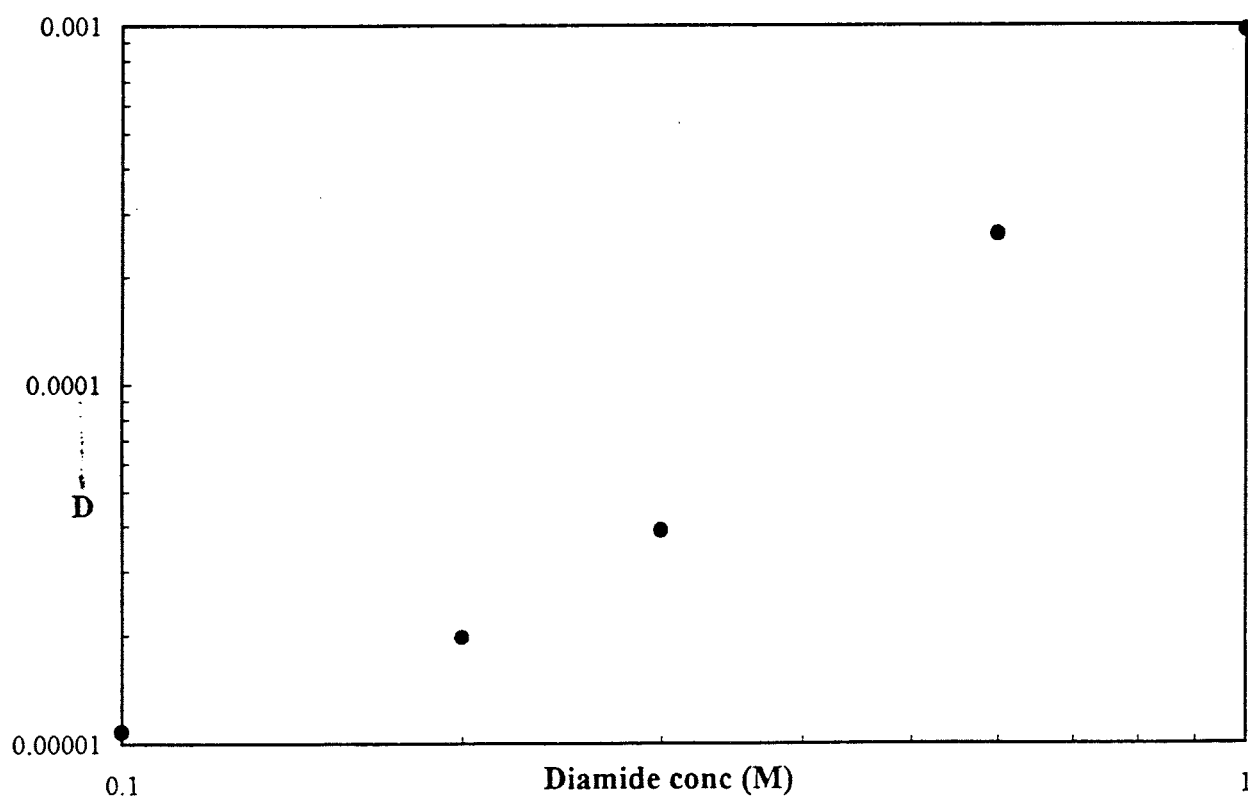
Figure 2:1 Experimental distribution ratios for extraction of americium from 0.3 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

Stoichiometric complex determination.

Stoichiometric complex determination for DMDBOD

Table 2:2 Experimental distribution ratios for extraction of americium from 3.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	0.000334	0.1
0.3	0.001542	0.2
0.3	0.004614	0.3
0.3	0.025962	0.6
0.3	0.05436	1.0

Figure 2:2 Experimental distribution ratios for extraction of americium from 3.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.
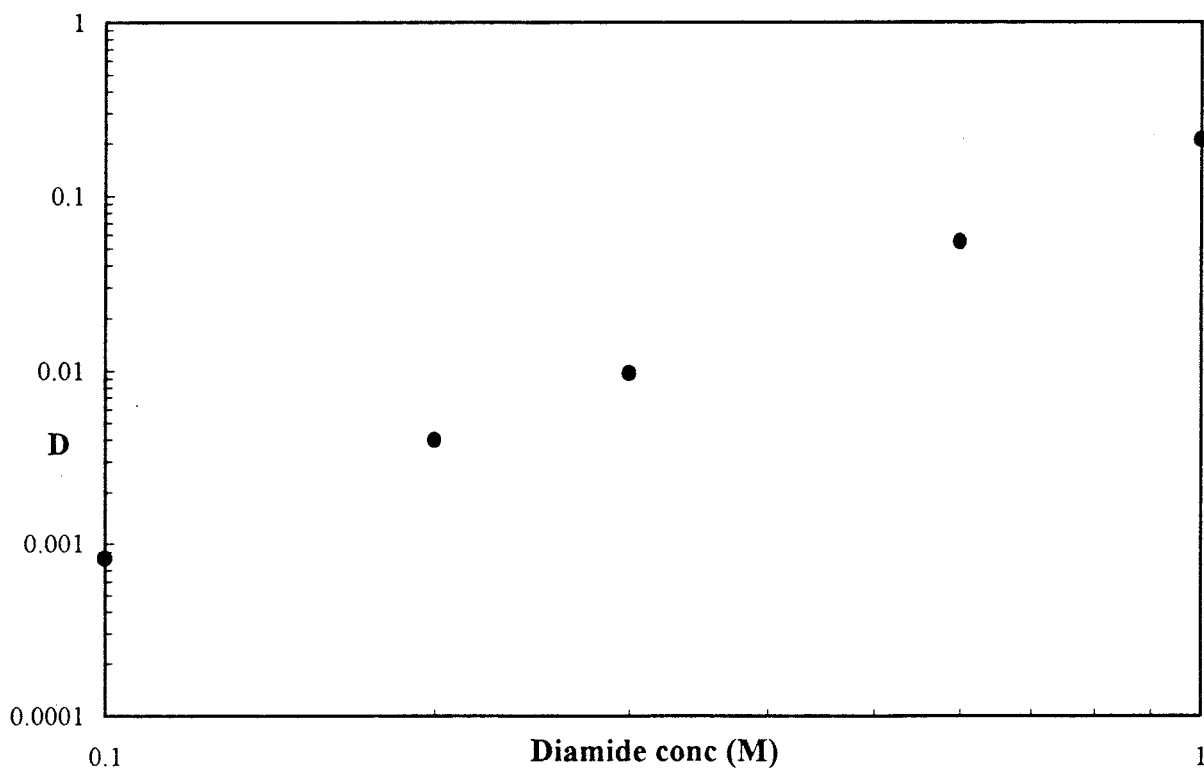
Stoichiometric complex determination for DMDBOD

Table 2:3 Experimental distribution ratios for extraction of terbium from 1.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	8.45E-05	0.1
0.3	9.47E-05	0.2
0.3	0.000147	0.3
0.3	0.000986	0.6
0.3	0.005087	1.0

Figure 2:3 Experimental distribution ratios for extraction of terbium from 1.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

Stoichiometric complex determination for DMDBOD

Table 2:4 Experimental distribution ratios for extraction of terbium from 5.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

| $[HNO_3]$ (M)	D	$[\bar{L}]_{tot}$ (M)
0.3	0.000815	0.1
0.3	0.003991	0.2
0.3	0.009627	0.3
0.3	0.054485	0.6
0.3	0.209165	1.0

Figure 2:4 Experimental distribution ratios for extraction of terbium from 5.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

Stoichiometric complex determination for DMDCHTD

Table 2:5 Experimental distribution ratios for extraction of americium from 0.3 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	1.9E-05	0.1
0.3	2.36E-05	0.2
0.3	5.49E-05	0.3
0.3	0.000329	0.6
0.3	0.003096	1.0
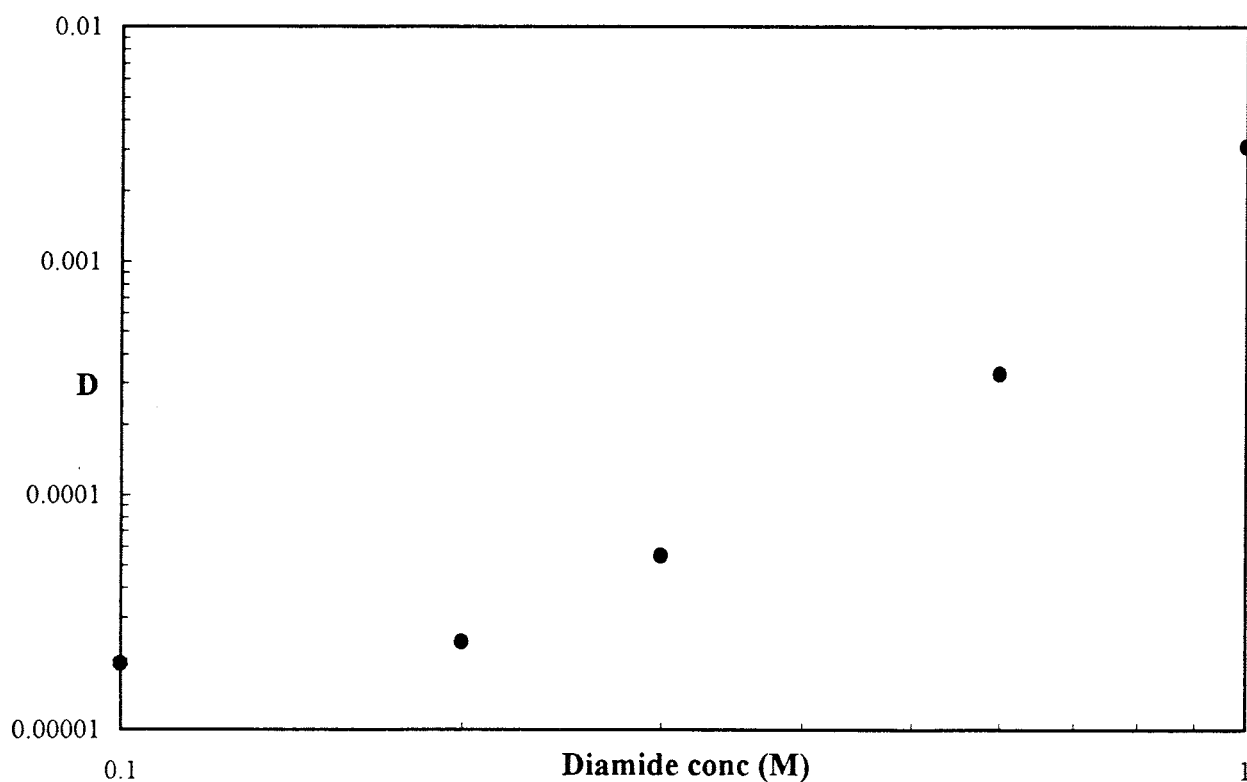
Figure 2:5 Experimental distribution ratios for extraction of americium from 0.3 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

Stoichiometric complex determination.
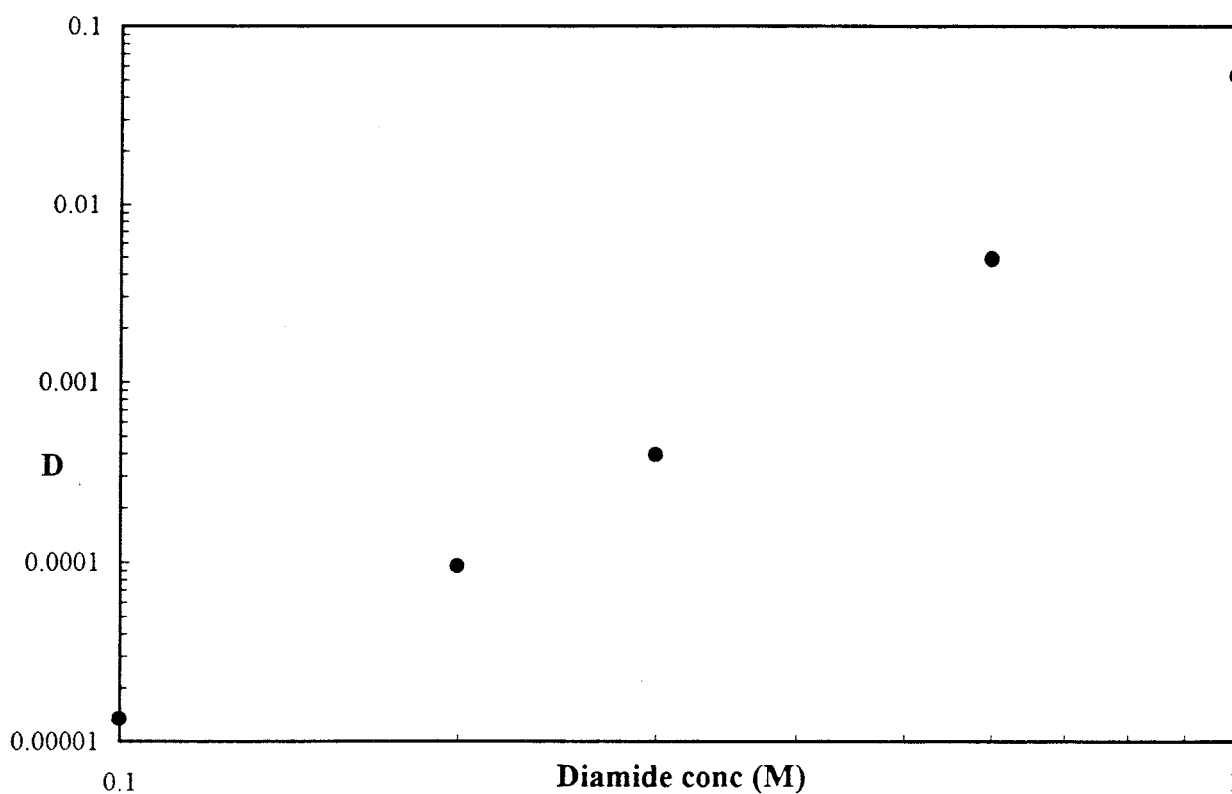
Stoichiometric complex determination for DMDCHTD

Table 2:6 Experimental distribution ratios for extraction of americium from 1.0 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	1.33E-05	0.1
0.3	9.49E-05	0.2
0.3	0.000395	0.3
0.3	0.004869	0.6
0.3	0.05274	1.0

Figure 2:6 Experimental distribution ratios for extraction of americium from 1.0 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.
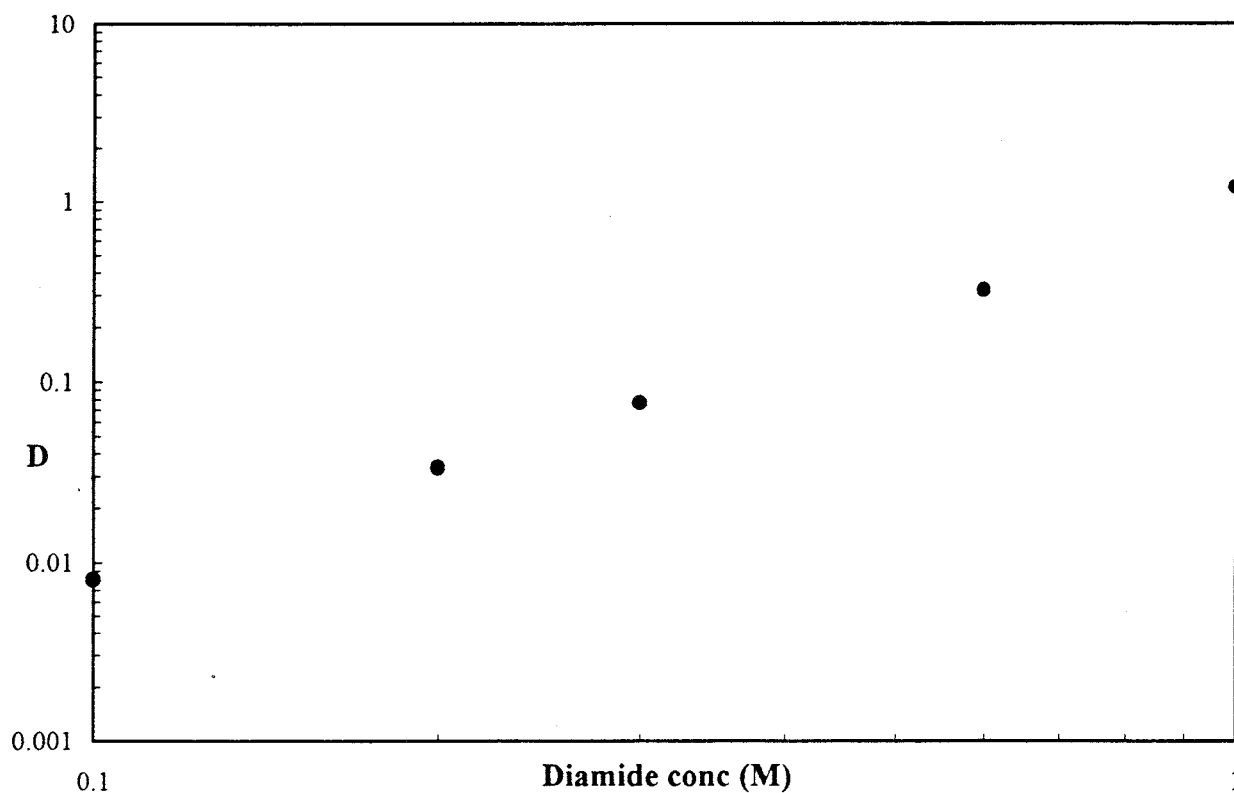
Stoichiometric complex determination for DMDCHTD

Table 2:7 Experimental distribution ratios for extraction of americium from 7.5 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

$[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	0.007993	0.1
0.3	0.033518	0.2
0.3	0.076753	0.3
0.3	0.320647	0.6
0.3	1.210579	1.0

Figure 2:7 Experimental distribution ratios for extraction of americium from 7.5 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

Stoichiometric complex determination.

Stoichiometric complex determination for DMDCHTD

Table 2:8 Experimental distribution ratios for extraction of terbium from 1.0 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

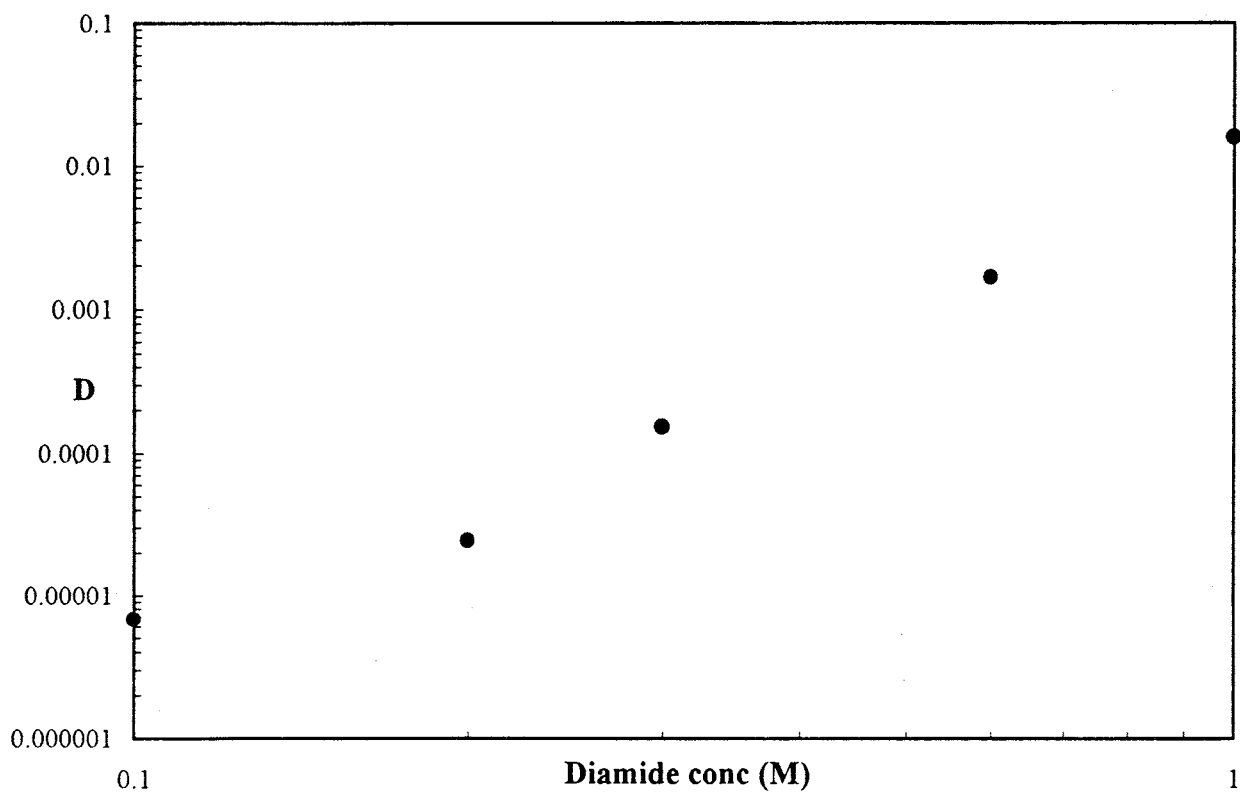| $[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	6.77E-06	0.1
0.3	2.44E-05	0.2
0.3	0.000153	0.3
0.3	0.001665	0.6
0.3	0.015966	1.0

Figure 2:8 Experimental distribution ratios for extraction of terbium from 1.0 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

Stoichiometric complex determination for DMDCHTD

Table 2:9 Experimental distribution ratios for extraction of terbium from 3.0 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

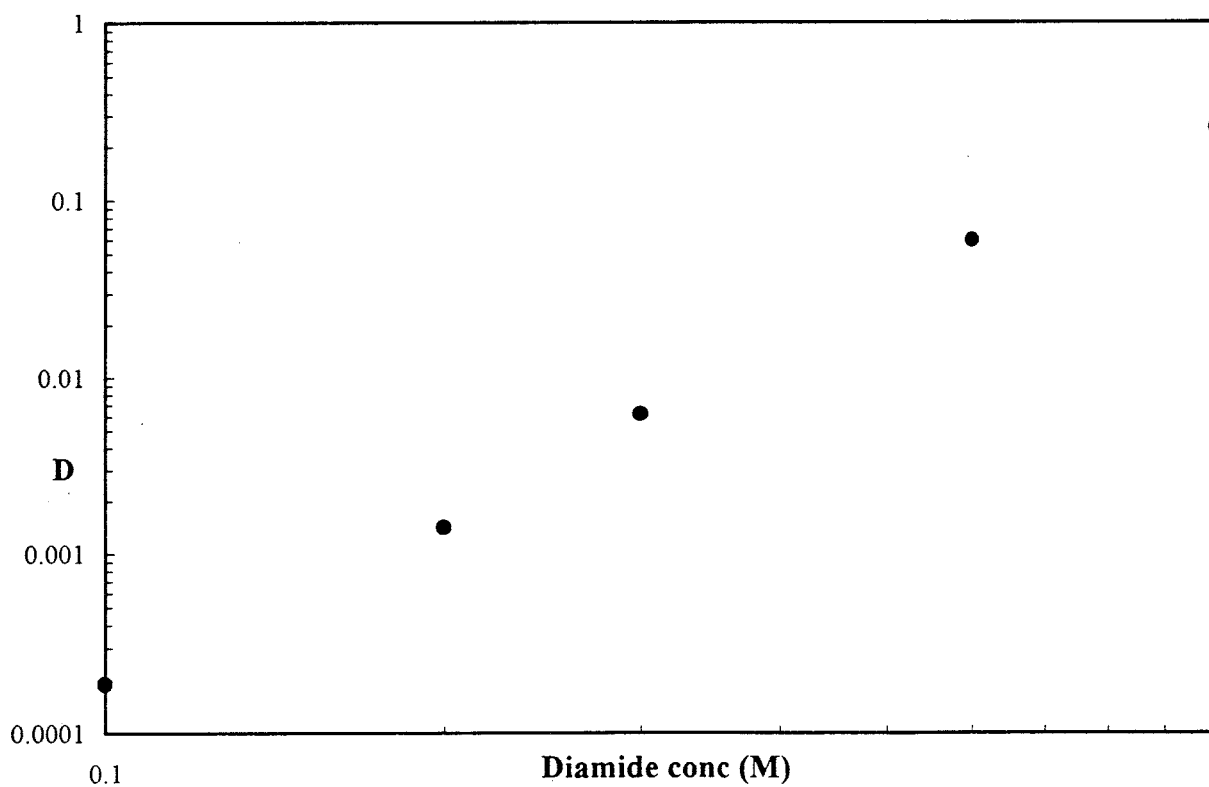| $[HNO_3]$ (M)	D	$[\bar{L}]_{tot}$ (M)
0.3	0.000188	0.1
0.3	0.001403	0.2
0.3	0.006226	0.3
0.3	0.059564	0.6
0.3	0.256452	1.0

Figure 2:9 Experimental distribution ratios for extraction of terbium from 3.0 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

Stoichiometric complex determination for DMDCHTD

Table 2:10 Experimental distribution ratios for extraction of terbium from 7.5 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

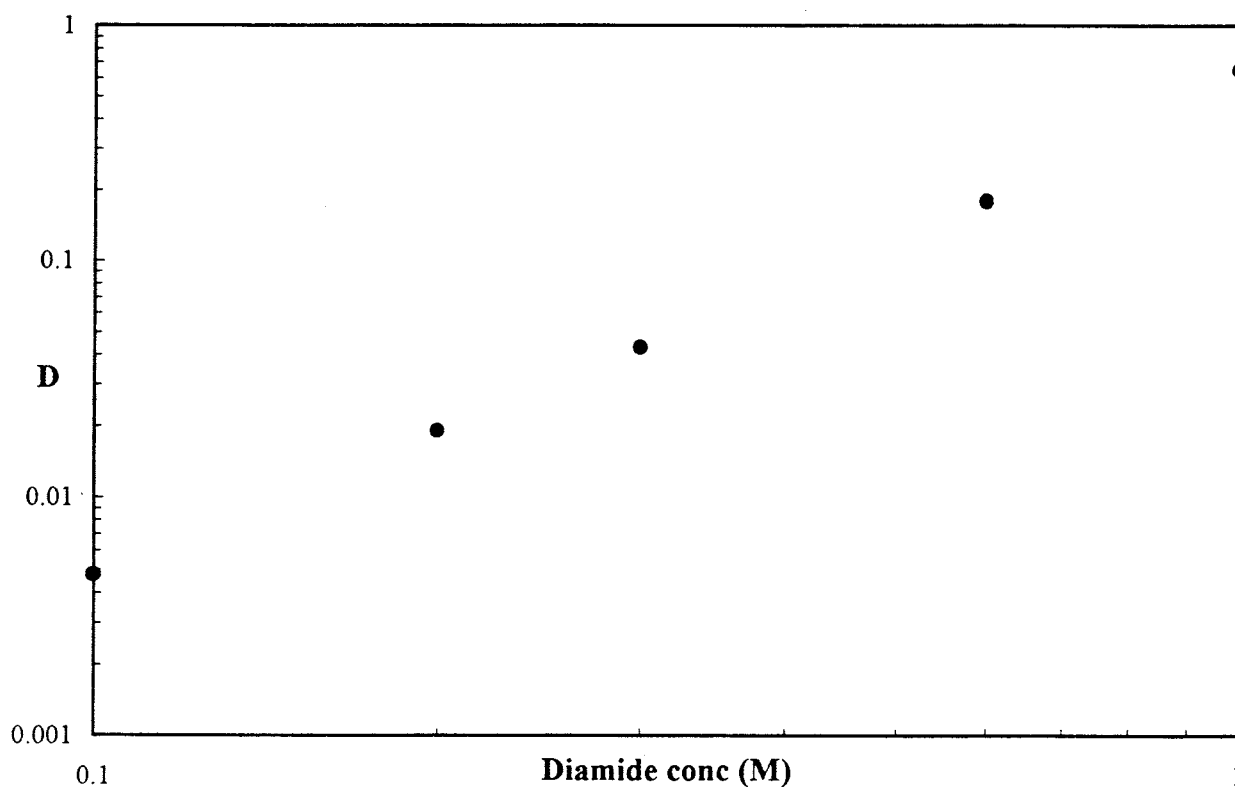| $[HNO_3]$ (M)	D	$[\overline{L}]_{tot}$ (M)
0.3	0.004715	0.1
0.3	0.019119	0.2
0.3	0.042914	0.3
0.3	0.178826	0.6
0.3	0.647854	1.0

Figure 2:10 Experimental distribution ratios for extraction of terbium from 7.5 M nitric acid with various concentrations of DMDCHTD in *tert*-butylbenzene.

Experimental and calculated distribution ratios for terbium

Table 3:1 Experimental and calculated distribution ratios for extraction of terbium from various concentrations of nitric acid and by various concentrations of DMDBOD in *tert*-butylbenzene. Superscript from eq 2.2.21 is set to p=3, n_1=2 and n_2=2.

| $[HNO_3]$ (M)	D Experimental	D Calculated	$[\overline{HNO_3}]$ (M)	$[\overline{L}]_{tot}$ (M)
0.1	8.1E-06	4.6E-08	1.3E-03	0.1
0.3	3.3E-05	4.1E-07	2.9E-03	0.1
0.5	5.8E-05	1.2E-06	3.0E-03	0.1
1	8.4E-05	5.2E-06	9.8E-03	0.1
2	7.5E-05	3.2E-05	2.4E-02	0.1
3	1.1E-04	1.1E-04	4.1E-02	0.1
5	7.5E-04	4.0E-04	7.5E-02	0.1
7.5	1.9E-03	8.3E-04	1.4E-01	0.1
10	1.5E-03	9.3E-04	2.3E-01	0.1
12	1.3E-03	6.7E-04	3.3E-01	0.1
5	8.2E-04	4.0E-04	7.5E-02	0.1
5	4.0E-03	4.0E-03	1.9E-01	0.2
5	9.6E-03	1.3E-02	2.7E-01	0.3
5	5.5E-02	6.4E-02	5.4E-01	0.6
5	2.1E-01	1.6E-01	8.6E-01	1.0
1	8.5E-05	5.2E-06	9.8E-03	0.1
1	9.5E-05	4.2E-05	1.1E-02	0.2
1	1.5E-04	1.6E-04	1.9E-02	0.3
1	9.9E-04	1.5E-03	5.5E-02	0.6
1	5.1E-03	7.4E-03	1.1E-01	1.0
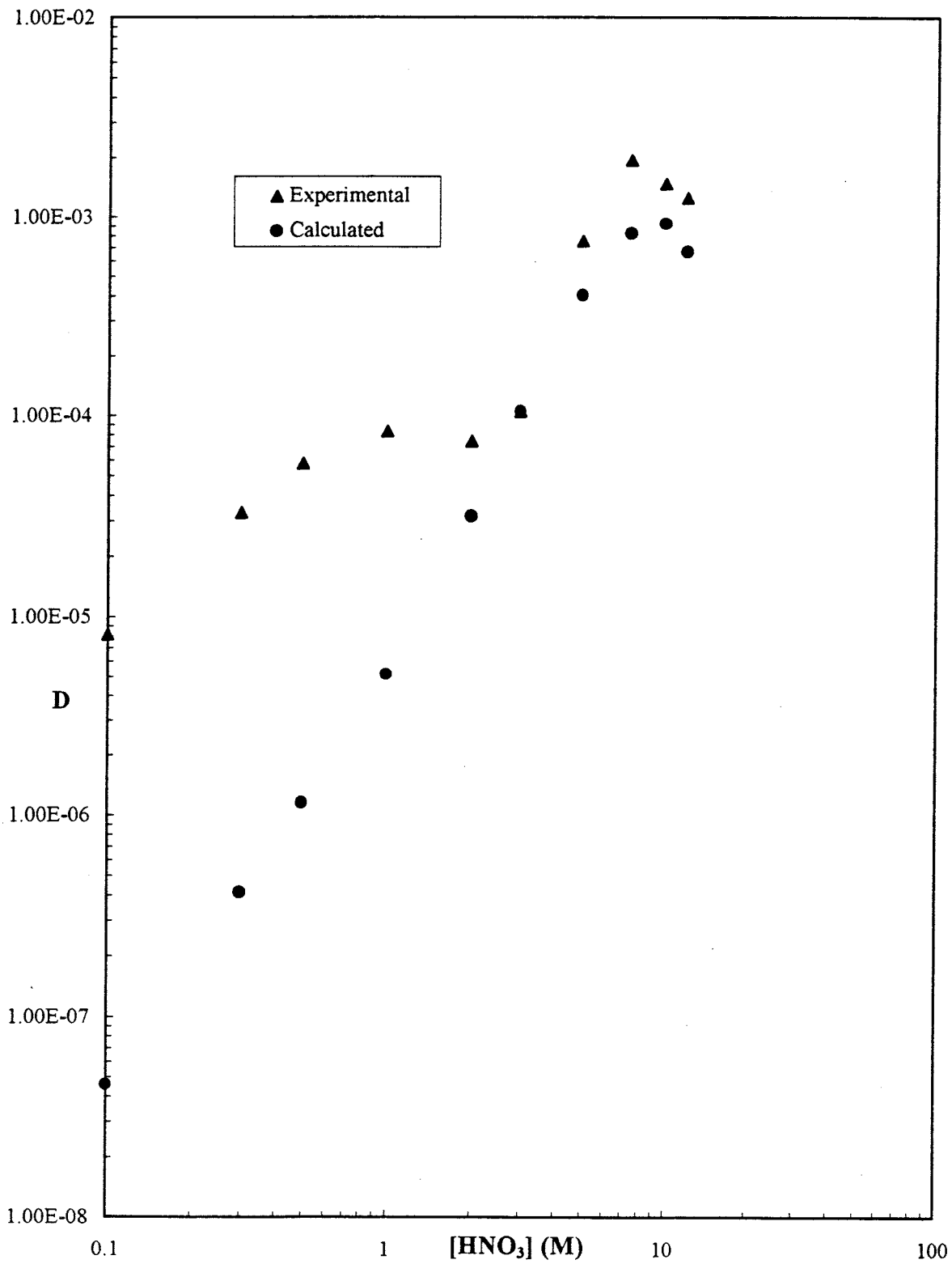
Figure 3:1.1 Experimental and calculated distribution ratios for extraction of terbium from various concentrations of nitric acid with 0.1 M DMDBOD in *tert*-butylbenzene.

Figure 3:1.2 Experimental and calculated distribution ratios for extraction of terbium from 5.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.
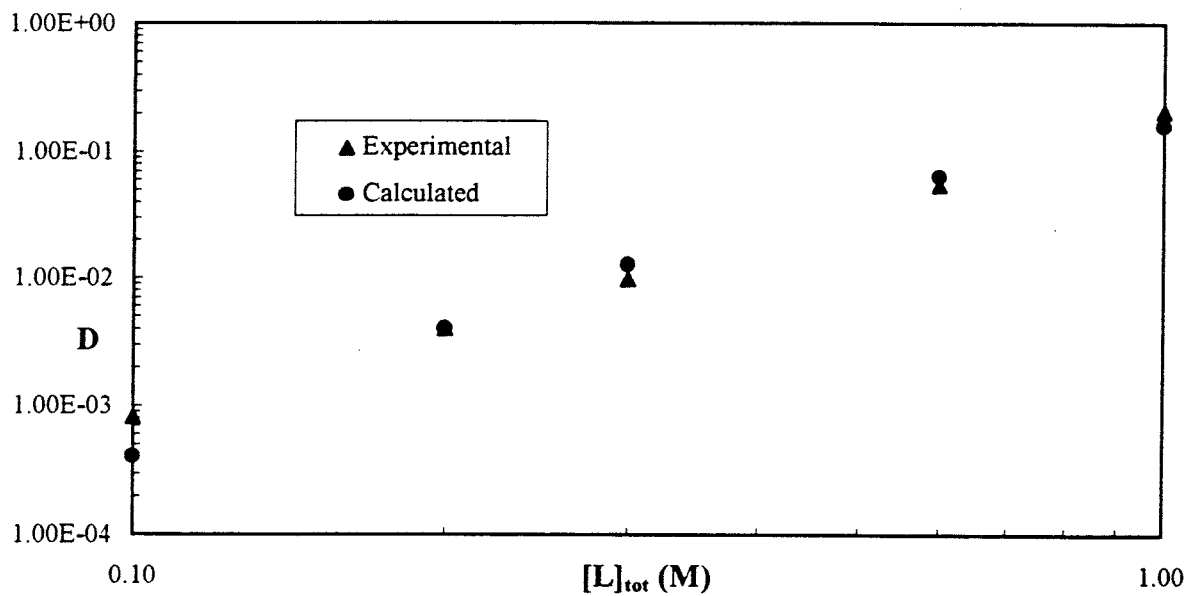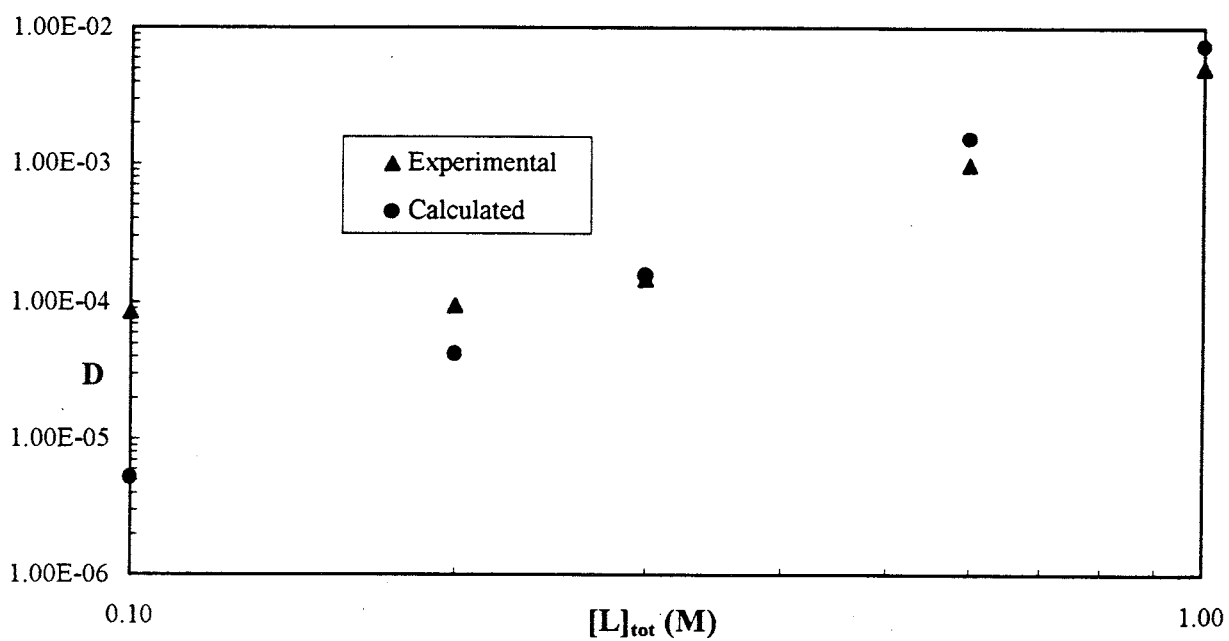

Figure 3:1.3 Experimental and calculated distribution ratios for extraction of terbium from 1.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

Optimisation of metal extraction data.

Experimental and calculated distribution ratios for americium

Table 3:2 Experimental and calculated distribution ratios for extraction of americium from various concentrations of nitric acid and by various concentrations of DMDBOD in *tert*-butylbenzene. Superscript from eq 2.2.21 is set to p=3, n_1=2 and n_2=2.

$[HNO_3]$ (M)	D Experimental	D Calculated	$[\overline{HNO_3}]$ (M)	$[\overline{L}]_{tot}$ (M)
0.1	3.0E-05	5.6E-08	1.3E-03	0.1
0.3	4.4E-05	1.4E-06	2.9E-03	0.1
0.5	4.8E-05	2.4E-06	3.0E-03	0.1
1	1.1E-04	1.1E-05	9.8E-03	0.1
2	1.3E-04	8.70-05	2.4E-02	0.1
3	3.7E-04	2.5E-04	4.1E-02	0.1
5	1.6E-03	5.9E-04	7.5E-02	0.1
7.5	3.3E-03	7.2E-04	1.4E-01	0.1
10	1.4E-03	5.2E-04	2.3E-01	0.1
12	1.1E-03	2.8E-04	3.3E-01	0.1
3	3.3E-04	2.5E-04	4.1E-02	0.1
3	1.5E-03	2.2E-03	7.2E-02	0.2
3	4.6E-03	6.6E-03	1.1E-01	0.3
3	2.6E-02	2.7E-02	2.6E-01	0.6
3	5.4E-02	5.8E-02	4.2E-01	1.0
0.3	1.1E-05	1.4E-06	4.1E-03	0.1
0.3	2.0E-05	1.1E-05	1.6E-03	0.2
0.3	3.9E-05	3.8E-05	2.9E-03	0.3
0.3	2.6E-04	3.1E-04	8.9E-03	0.6
0.3	9.7E-04	1.4E-03	1.7E-02	1.0

Figure 3:2.2 Experimental and calculated distribution ratios for extraction of americium from 3.0 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.
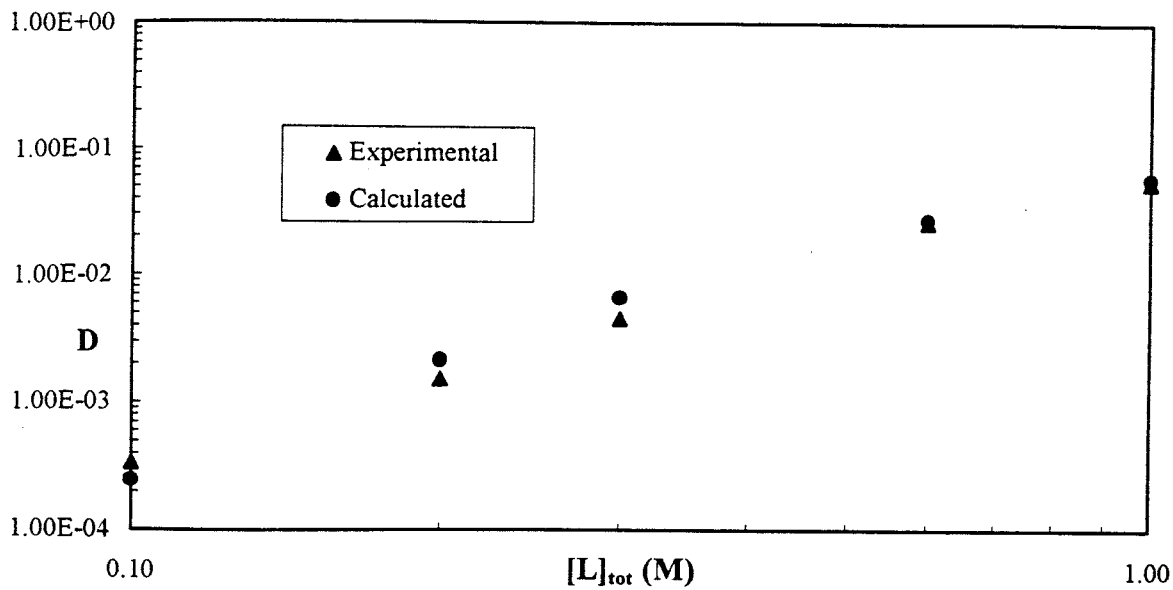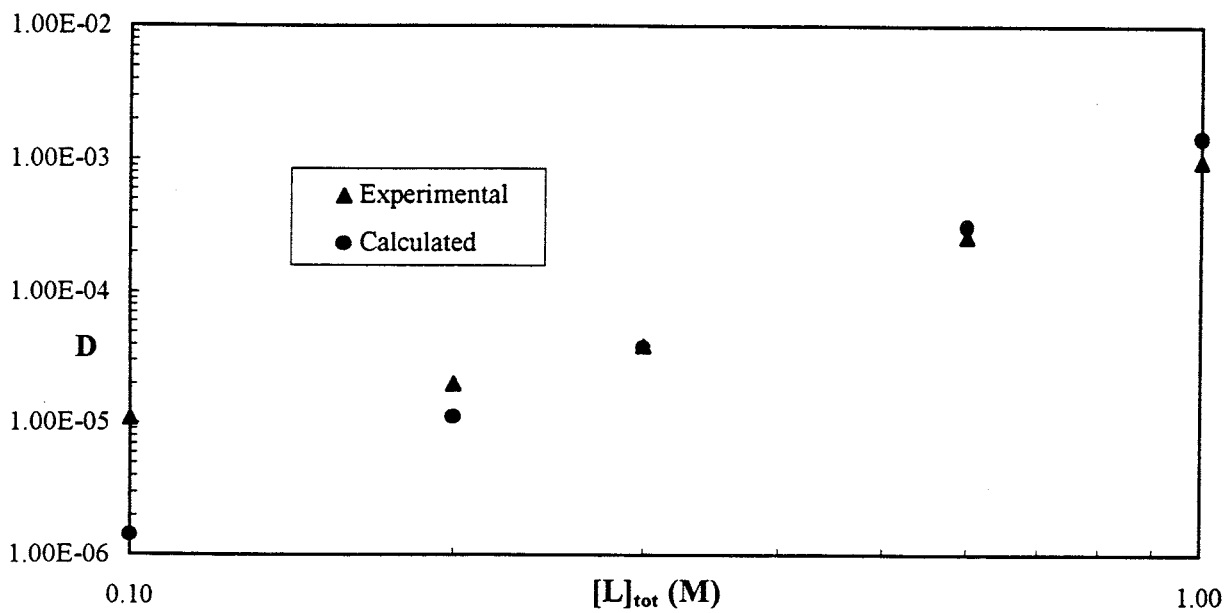

Figure 3:2.3 Experimental and calculated distribution ratios for extraction of americium from 0.3 M nitric acid with various concentrations of DMDBOD in *tert*-butylbenzene.

Appendix
VI

International Solvent Extraction Conference (ISEC)
March 19-23, 1996
Melbourne, Australia

In the end of March 1996 three delegates from the P&T project from the Department of Nuclear Chemistry, Chalmers, left Sweden to participate in the International Solvent Extraction Conference (ISEC) in Melbourne, Australia. The theme of this years conference was "Value Adding Through Solvent Extraction" and the conference was attended by more than 300 delegates from 34 different countries. The different oral and poster sessions covered both fundamentals, metal extraction, extraction equipment and design, extractants and diluents, simulation and modelling, plant experience, organic and inorganic product application, nuclear fuel applications, supercritical extraction, liquid membranes, analytical applications, hydrometallurgy, petrochemical applications and biotechnology applications.

The main part of the sessions covered industrial metal extraction applications like separation of nickel, iron, cobolt,copper and zinc. There were also new and interesting areas like the design of new extractants e.g. organophosphorus extractants with two functional groups for the extraction of rare earth metals. The steric hindrance in these extractants is very important for the selectivity and thus for the design of the molecule.

Two posters from the swedish P&T project were presented at the conference; "A separation process based on Aliquat-336, TBP and HDEHP" and "Extraction of some metal cations from nitric acid solution by N,N′-substituted malonamides"

During the post-conference technical tour we visited Queensland Nickel Joint Venture (QN) and Copper Refineries Limited (CRL) in Townsville which both are using solvent extraction in their processes.

QN treats 3 Mt/y of nickel laterite ore by ammonia/ammoium carbonate leaching instead of the more common acid leaching. The nickel is recovered by solvent extraction (SX) whereafter nickel is precipitated as nickel carbonate which is calcinated and reduced to rondelles. Cobalt is obtained as a by-product in the process and QN has become the largest producer of cobalt in Australia. About 24000 t nickel and 1500 t cobalt are anually produced.

CRL process blister copper from Mount Isa Mines at a tankhouse capacity of about 40000 t/y. Arsenic is removed from the tankhouse electrolyte by SX to produce a final bi-cupric arsenate by-product.

Appendix
VII

Accelerator-Driven Transmutation Technologies and Applications
June 3-7, 1996
Kalmar, Sweden

The second International Conference on Accelerator-Driven Transmutation Technologies and Applications was held in Kalmar, 3-7 June, 1996. About 220 participants from 24 different countries attended the conference.

The different objectives considered on the ADTT conference were; waste management (ATW), burning of weapon plutonium (ABC) and efficient energy production (ADEP). A lot of political and non-proliferation issues were discussed. Many different accelerator-driven concepts were proposed during the conference, concerning liquid- or solid fuel, fast- or thermal reactors, cyclotron or linear accelerators. Many of the participants would like to see a joint proposal to be able to concentrate on the development of one specific system.

At the separation and chemistry session the paper "Inherent Limitations In Toxicity Reduction Associated with Fast Energy Amplifiers" was presented. This contribution is a collaboration between the Department of Nuclear Chemistry, Chalmers and the Transuranium Institute in Karlsruhe.

Mark A. Williamson (LANL) presented a separation process based on molten salt. Molten salt is taken out from the blanket and treated in three different parts. The transition metals e.g. Zr, Nb, Mo, Ru, Rh and Ag are removed by electrowinning while the volatile fission products are separated with fractional destillation. Finally the trivalent actinides are separated from the lanthanides in centrifugal contactors where the fluoride melt is in contact with liquid bismuth.

During the separation break-out group the areas where separations are needed were first identified. The target, where spallation products will be formed, and the blanket were both considered. The optimal separation method will depend on what accelarator-driven system is chosen. The discussions were concentrated on molten salt separation techniques. It seems to be an interesting separation method with high separation factors but it will probably be difficult to use it in an industrial process (high temperature, corrosion problems etc.). It was concluded that there is lack of people with an overview of the whole P&T area i.e. with knowledge in both chemistry and physics and the group proposed a formation of a reference group.

On the studytour to Oskarshamn, the O3 nuclear power reactor, CLAB and the Äspö laboratory were visited.

Appendix
VIII

Fourth International Conference on Nuclear and Radiochemistry
(NRC4)
September 8-13, 1996
St Malo, France

The fourth International conference on Nuclear and Radiochemistry was held in St Malo, France, 8-13 September, 1996. About 300 participants from 33 different countries attended the conference. Some of the different sessions are shortly presented below. An excursion to the reprocessing plant in La Hague was arranged during the conference.

During the conference a meeting was also held with our collaborators in the European Union Nuclear Fission Safety Programme Task 2 (Contract F12W-CT91-0112). Future investigations were discussed.

Nuclear chemistry and transactinide chemistry
There were several interesting sessions about new discoveries in nuclear chemistry. Element 112 was discovered in February this year by irradiating a target of ^{208}Pb with projectiles of ^{70}Zn. The element was detected by its radioactive α-decay chain.

The emission of nuclides with Z=6 to 14 (C to Si) from heavier elements is called cluster radioactivity and was discovered 12 years ago. It has now been proven that both Ra, Th, Pa, U, Np and Pu are able to emit these clusters and by this decay they become more stable nuclides, closer to lead.

Chemistry of the transactinide element 106, recently named seaborgium (Sg), was presented and some of the experiments concluded that the chemistry of Sg is similar to the chemistry of W and Mo. This result was somewhat expected since they are all members of the same group in the periodic table (group 6).

Fission is most often a binary process where a heavy nuclide is fissioned into two new nuclides. About 0.2% of the fissions produce three particles rather than two. This is called ternary fission. Experiments with ^{249}Cf showed a spectra of 35 different ternary particles, the heaviest particle being Mg.

Actinides are known not to form stable divalent oxidation states. E.g. Am(III) is the most stable oxidation state of americium in aqueous solution. By using strontium tetraborate it was shown that Am(II) and Cf(II) can be stabilised in a crystal structure. It was also shown that oxidised americium (Am(IV) and Am(VI)) can be stabilised by a heteropolyanionic ligand.

Non nuclear methods in nuclear and radiochemistry
A lot of non nuclear methods is used in nuclear- and radiochemistry today. ICP/MS is a masspectrometry method, that can determine concentrations as low as pg/ml. This method is especially useful for long-lived radionuclides. Synchrotron based X-ray absorption spectrometry (XANES and EXAFS) can give information about oxidation

states and structural information like bondlength and coordination chemistry. LASER techniques are considered to be important for tracer amount analysis in the future.

Radioanalysis and use of tracers in the environment and geochemistry,
Radioanalysis is an efficient method used for environmental samples and in geochemistry. E.g. NAA (neutron activation analysis) of volcanic gases can give information about the composition of the gas and from that it is possible to predict whether the vulcano is active or not.

The discharge of ^{129}I from the reprocessing plants in La Hague and Sellafield can be used as an oceanographic tracer. By an efficient masspectrometer technique, called AMS, it is possible to detect ^{129}I in one drop of water from the English channel or from the Irish sea and in one liter of water from the rest of the Atlantic. The measurements are used to determine the water flow in the Atlantic sea.

If the isotopic ratio between ^{131}I and ^{129}I is measured and compared with archived samples, it is possible to estimate the doses received from the Chernobyl accident.

Catalytic converters in cars consist of platinum. The converters reduce the emission of toxic gases but instead the platinum may be exhausted. Platinum in oxidation state zero has no toxicity but in the oxidised form it causes allergies and it is therefore important to be able to measure the concentration of exhausted platinum. One method for determination of platinum in soil samples using NAA was presented.

Chemistry of the nuclear fuel cycle
Improvements in the reprocessing of spent nuclear fuel was presented at the conference. In the reprocessing 97% of the spent nuclear fuel can be recycled. By separation of the highly active fission products and recycling of uranium and plutonium, the disposed waste volume may be reduced to $0.5m^3$/tonne fuel compared with $2m^3$/tonne fuel when disposed in a geological repository without reprocessing.

Transmutation blankets with high amounts of minor actinides was shown to be difficult to dissolve in nitric acid, but dissolution in a mixture of $HNO_3/HCl/HF$ showed no significant amount of actinides in the undissolved residues.

It was shown that ultrasonic can be used to generate HNO_2 in a nitric acid solution. HNO_2 catalyses the oxidation of Np(V) to Np(VI) which is an important step in the separation of Np from spent nuclear fuel, since Np(VI) is more easily separated than Np(V).

Ruthenium is also an important element to separate from the nuclear waste because ruthenium is produced in large amounts in a nuclear reactor and contributes with 17% of the total radioactivity in the waste after 3 years. The problem with this element is that it can exist in numerous oxidation states and only 60-70% is soluble in nitric acid and it is also hard to dissolve in glass. The presented method consider oxidation of Ru with Ag(II) forming the volatile RuO_4 which can be trapped in an alkaline solution and thereafter incorporated in glass.

A delegate from China presented their proposal of nuclear waste disposal. By separating not only the long-lived transuranium elements but also cesium and strontium from the nuclear waste, the storage can be simplified and the cost can be reduced. The separation technique of cesium concerned the sorption of cesium by KTi-hexacyano ferrate.

Radionuclides in the life sciences.
Biological effects of high and low doses of radiation was discussed. There is a contradiction in what biological effect low radiation dose may cause. Some scientists claim that there is a threshold level at low radiation dose and below this limit the biological effect is negligible. Other scientists consider a linear extrapolation from high radiation dose down to zero. Investigations about biological effects on humans living in areas with high background radiation have started in France.

A Russian presentation concerned fast evacuation of radionuclides from the human body using specific enterosorbents (oxidised carbon). This method was used for workers who had been contaminated during the Chernobyl accident.

Nuclear methods in cosmochemistry
The interaction of cosmic-ray particles with extraterrestrial matter in space produces a large variety of nuclides. Measurements of these nuclides in meteorites can give information about the history of the meteorites and the flux of galactic cosmic-rays.