

**R-03-15**

# **Partitioning and Transmutation**

## **Annual Report 2002**

S Andersson, C Ekberg, J-O Liljenzin, M Nilsson,  
N Rogues, G Skarnemark, J Östberg  
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Chalmers University of Technology

January 2003

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## Abstract

How to deal with the spent fuel from nuclear power plants is an issue that much research is attracted to in many countries around the world. Several different strategies exist for treating the waste ranging from direct disposal to reprocessing and recycling of plutonium and other long-lived nuclides. In either case the remains have to be stored for a long time to render it radio-toxically safe. One method to deal with this long-lived waste is to separate (separation) out the most long lived components and then transform them into shorter-lived ones (transmutation). Several methods exist for performing the separation for example via molten salts and through solvent extraction. The work presented here has been focused on solvent extraction. This technique is well known since many years and process scale plants have been operating for decades. The new demand is to separate chemically very similar elements from each other. Within this project this is done by new extracting agents developed for this purpose alone within the EU fifth framework programme, the PARTNEW project, particularly from the University of Reading. In this work we investigate different extraction systems for the separation of trivalent actinides from trivalent lanthanides using extraction agents following the so-called CHON (Carbon, Hydrogen, Oxygen and Nitrogen) principle. The main focus is to understand the basic chemistry involved but also some processing behaviour for use in future full scale plants.

# Sammanfattning

Hur man skall hantera det använda bränslet från kärnkraftverk är ett problem som mycket forskning har koncentrerats på över hela världen. Det finns flera olika strategier för hur man skall gå till väga, alltifrån att direktdeponera bränslet till att uppgradera och återanvända delar av det. Vilken metod man än väljer kommer det att finnas avfall som måste förvaras under lång tid för att det skall bli ofarligt i radiotoxisk bemärkelse. En metod för att hantera avfallet är att separera ut de mest långlivade nukliderna och transmutera dem till mer kortlivade nuklider. Det finns flera olika metoder för att uppnå denna separation, t ex via saltsmältor eller genom vätskeextraktion. Det arbete som presenteras här är fokuserat på vätskeextraktion. Denna teknik är välkänd sedan många år och stora processanläggningar har funnits i flera årtionden. Det nya som tillkommit är att separera kemiskt mycket lika ämnen från varandra. Inom detta projekt görs separationen med nya extraktionsreagens, speciellt utvecklade vid University of Reading för PARTNEW projektet inom EU:s femte ramprogram. Vi ägnar oss huvudsakligen åt separationen av trevärda aktinider från trevärda lantanider med extraktionsreagens som följer CHON-principen (endast innehållande kol, väte, syre och kväve). Målet är att förstå den grundläggande kemin men också att undersöka hur en eventuell fullskaleprocess skall kunna se ut och fungera.

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- II Nilsson M, Liljenzin J-O, Ekberg C, Wingefors S, 2002. *Modelling the Influence of Organic Phase Composition on the Extraction of Trivalent Actinides*, Proceedings of the International Solvent Extraction Conference ISEC 2002, p 1193–1198 28
- III Andersson S, Ekberg C, Foreman M R S, Hudson M J, Liljenzin J-O, Nilsson M, Skarnemark G, Spahiu K. *Extraction Behaviour of the Synergistic System 2,6-bis-(benzoxazolyl)-4-dodecyloxyipyridine and 2-bromodecanoic Acid Using Am and Eu as Radioactive Tracers*, submitted to Solvent Extraction and Ion Exchange 29
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# 1 Introduction

The Partitioning and Transmutation (P&T) project at the Department of Materials and Surface Chemistry<sup>1</sup>, Nuclear Chemistry – Actinides and Solvent Extraction, investigates the separation of different chemical elements in the spent nuclear fuel for purification and/or recovery in a future P&T process. Solvent extraction is chosen for this separation because it is a well know technique (already used in reprocessing around the world) and it makes it possible to fulfil the highly set separation demands on efficiencies and recoveries. Internationally other processes are investigated, such as molten salt electrolysis and different pyroprocesses.

PARTNEW is an international project funded by the European Union that concerns the design of a solvent extraction process for the treatment of spent nuclear fuel. The research can be divided into three different domains:

- Coextraction of actinides and lanthanides from acidic HARs (high active raffinate) or HACs (high active concentrate). DIAMEX process.
- Separation of actinides and lanthanides. SANEX process.
- Separation of Am and Cm.

The project is at present conducted as fundamental research investigating the extraction properties of new ligands that our partner laboratory at the University of Reading synthesizes. The influence of pH, ionic media and temperature is investigated as well as modelling extraction experiments using solubility parameters. Some applications have been introduced the past year as a French diploma worker started the set-up of an existing mixer-settler battery. It will hopefully be used in the future when some promising ligands are tested in a pilot scale process.

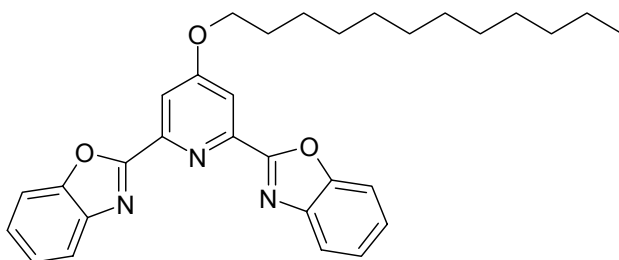
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<sup>1</sup> The Department of Nuclear Chemistry ceased to exist in a reorganisation at the School of Chemistry. The old department was divided into three different research groups, which now are parts of the Department of Materials and Surface Chemistry. The name of the group dealing with P&T is Nuclear Chemistry – Actinides and Solvent Extraction.

## 2 Solvent extraction and other research

During 2002 Sofie Andersson finished her licentiate thesis concerning two extracting agents and their properties in different systems. Mikael Nilsson has too been involved in this work, but has also continued with the modelling of extraction experiments using solubility parameters as well as making further improvements on the apparatus for continuous measurement of vapour pressure. A French diploma worker, Nicolas Rogues worked with a mixer-settler battery for a pilot scale investigation of separation of actinides and lanthanides. Sofie and Mikael have also been busy investigating several new ligands synthesized at the University of Reading in England. Some interesting results have been found and will be presented below.

### 2.1 Extraction properties of 2,6-bis-(benzoxazolyl)-4-dodecyloxy pyridine



*Figure 1.* 2,6-bis-(benzoxazolyl)-4-dodecyloxy pyridine.

The experiments done with this ligand are described in four different series:

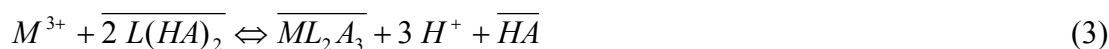
- Increasing  $[H^+]$ , constant ionic strength, I: 1 M (Na, H)ClO<sub>4</sub>
- Increasing  $[ClO_4^-]$ , constant  $[H^+]$ : 0.01 M
- Increasing  $[NO_3^-]$ , constant  $[H^+]$ : 0.01 M
- Constant I: 5 M, using different NaNO<sub>3</sub>/NaClO<sub>4</sub>-ratios, constant  $[H^+]$ : 0.01 M

The hydrogen ion concentration was chosen to give reasonable distribution ratios and the limits of the ionic strength were set by the concentration in salt stock solutions. The diluent chosen was TBB and a concentration of 1 M HA of the organic acid.

#### **Mechanism**

To be able to interpret the data from the extraction experiments the following mechanism of the extraction process was proposed, where it is assumed that BODO behaves similar to terpyridine [1]. 2-bromodecanoic acid (HA) forms a dimer in the organic phase (1) and an adduct is formed between BODO and HA (2). The adduct binds to the metal ion and extracts it into the organic phase, releasing three hydrogen ions in the process (3).



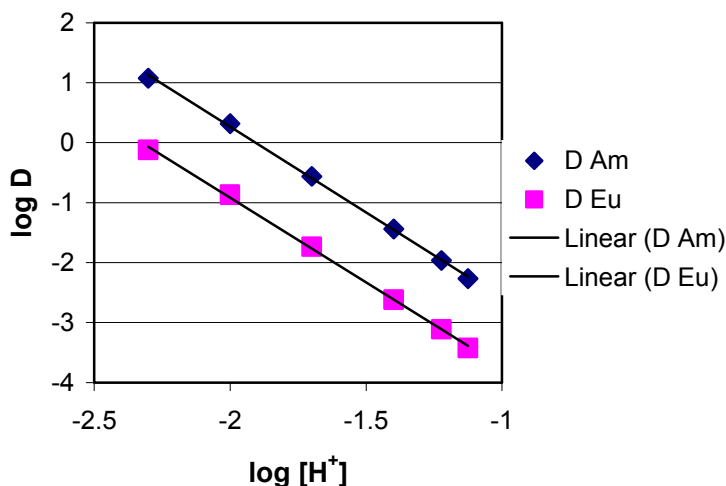


L is the BODO molecule and M is the metal ion (Am or Eu). The bars represent species in the organic phase. These reactions are believed to occur at the phase boundary because of the lipophilic nature of both BODO and HA. BODO is not soluble at its own in 0.01 M concentration in TBB. Adding HA will increase the polarity of the organic phase and the adduct formation will also increase the solubility of BODO.

### **Increasing hydrogen ion concentration**

In Figure 2 the results from the first test series are shown. The extraction decreases with increasing amount of  $H^+$  in the system, as indicated by the extraction mechanism. The slope of the lines in Figure 2 has been shown to be  $-3$ , which points out that three  $A^-$  are included in the extracted species.

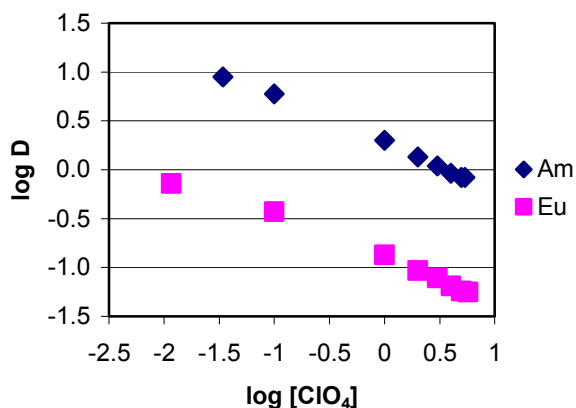
The linear relation also shows that the BODO molecule is not protonated since the decrease in distribution ratio is constant and not increasing with increasing  $[H^+]$ . Results presented in a PARTNEW half-yearly report [2] state that no BODO is transferred to the aqueous phase.



**Figure 2.** Results from experiments with increasing  $[H^+]$  (0.01 M BODO and 1 M HA in TBB; 1 M (H,Na,ClO<sub>4</sub>) in the aqueous phase; 298K).

### **Increasing perchlorate ion concentration**

In Figure 3 the results from experiments with increasing perchlorate ion concentration are shown. The  $[H^+]$  was held constant at 0.01 M.

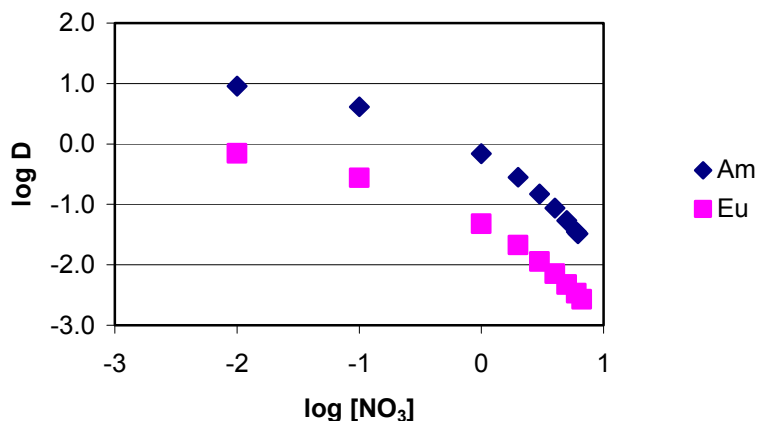


**Figure 3.** Results from experiments with increasing  $[ClO_4^-]$  (0.01 M BODO and 1 M HA in TBB; 0.01 M  $[H^+]$  in the aqueous phase; 298K).

The distribution ratios decrease linearly in this log-log plot. This behaviour can be explained by specific ion interaction theory [3] describing the change in activity coefficients. These calculations have not been included in this report. If the anions of the aqueous media would participate in the extraction mechanism an increase in extraction would be expected at higher ionic strengths.

#### **Increasing nitrate ion concentration**

Figure 4 shows the results from the series in which the nitrate concentration was increased gradually. Comparisons with results from the third semi-annual report show the same trend.

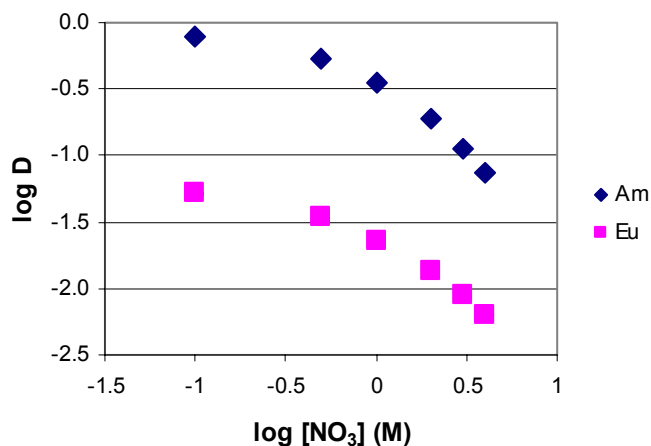


**Figure 4.** Results from experiment with increasing  $[NO_3^-]$  (0.01 M BODO and 1 M HA in TBB; 0.01 M  $[H^+]$  in the aqueous phase; 298K).

The linear decrease in distribution ratio is replaced by a curve with an increasing negative slope at successively higher nitrate ion concentrations. The reason for the decrease in D-values is the same as for the case above, but there may also be complex formation between nitrate ions and Am/Eu. Forming complexes with nitrate will prevent the metal ion from being extracted into the organic phase, hence the increasing slope in Figure 4. It has been shown that the formation of neutral complexes with Am/Eu and three nitrates in this concentration interval can be neglected [4].

### Constant ionic strength, but varying nitrate/perchlorate ion concentration ratio

In the last series the ionic strength was kept at 5 M, the  $[H^+]$  at 0.01 M and the ratio of nitrate and perchlorate ions was varied. The results can be found in Figure 5.

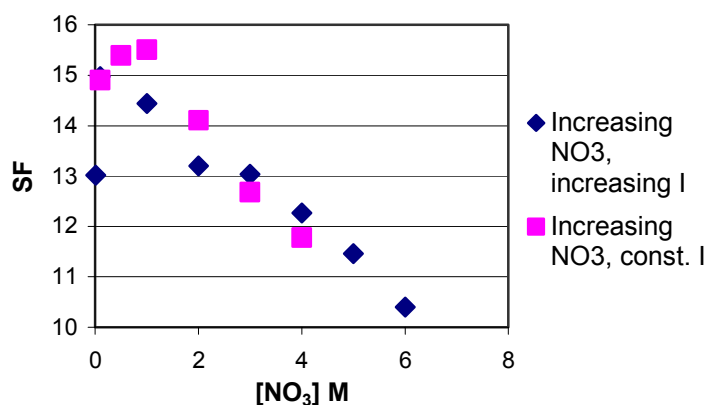


**Figure 5.** Results from experiments with constant ionic strength, but varied composition (0.01 M BODO and 1 M HA in TBB; 0.01 M  $[H^+]$  in 5 M ( $Na^+$ ,  $H^+$ ,  $ClO_4^-$ ,  $NO_3^-$ ) aqueous phase; 298K). Shown here is the logarithm of the nitrate concentration, but the perchlorate concentration is the difference between the total ionic strength and the actual nitrate ion concentration.

Results here only show the contribution to the decreased distribution ratios from the nitrate complex formation with Am and Eu, since the ionic strength is kept constant. The contributions from activity coefficients of the different species are here minimised.

### Separation factors

Throughout the experimental series the separation factor has been between 10 and 16, depending on the aqueous phase used. When plotting the separation factors as a function of nitrate ion concentration the curve shown in Figure 6 is obtained.



**Figure 6.** Separation factors as a function of nitrate concentration in the aqueous phase ((0.01 M BODO and 1 M HA in TBB; 0.01 M  $[H^+]$ , 298K).

The decrease in separation factor implicates that the nitrate complexes with Am are stronger than corresponding Eu complexes. This is common in comparisons of the strengths of complexes between the lanthanide and actinide series [5].

Doing the same thing for perchlorate shows no relation between separation factor and increasing concentration of perchlorate ions, which strengthens the earlier interpretation of extraction mechanisms in perchlorate/nitrate media.

## 2.2 Nitrate complexes with Am and Eu

It is rather difficult to determine the stability constants of the weak complexes formed between Am/Eu and nitrate. Generally these kinds of studies are done using potentiometric or spectroscopic techniques, but here the results presented in section 2.1 are used. Potentiometric titrations are best for the determination of the first stability constant whereas the problem with spectroscopy can be peak resolution and that high concentration must be used (which is problematic considering the small amounts of the ligands we receive). The well known method with solvent extraction is advantageous since it is possible to determine the constant of the highest complex directly from the slope of the curve of the logarithm of the distribution ratio versus the logarithm of the ligand concentration. It can, on the other hand, be difficult to differentiate between the constants if many of them exist. In this case this is no problem since only two complexes are considered.

The distribution of Am or Eu between an organic and an aqueous phase can be expressed as:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \quad (4)$$

The metal can form complexes either with the nitrate ions in the aqueous phase or with the BODO-HA adduct as described in section 2.1. The distribution ratio, considering those two possible complex formations, can be written as:

$$D_M = \frac{\lambda [MBODO_2A_3]}{[M] + [MNO_3] + [M(NO_3)_2] + [MBODO_2A_3]} \quad (5)$$

where  $\lambda$  is the distribution of the  $MBODO_2A_3$ -complex between the organic and aqueous phase. The concentration of the complex can be neglected in the denominator because of its lipophilic nature and in comparison with the other metal containing species in the aqueous phase.  $\lambda$  can also be considered as constant in the system used; no variations in pH and constant amount of BODO. The stability constants of the nitrate complexes can be expressed as:

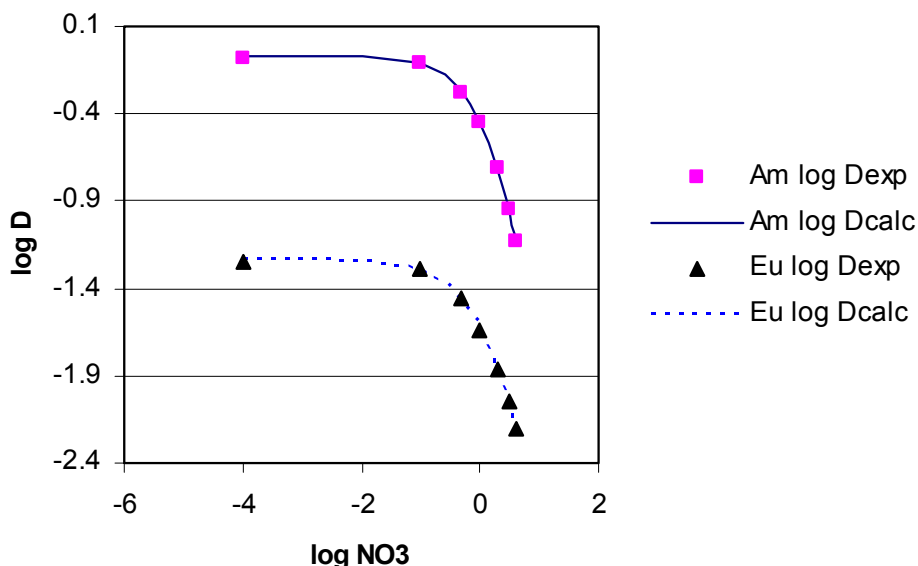
$$\beta_i = \frac{[M(NO_3)_i]^{3-i}}{[M][NO_3]^i} \quad (6)$$

Combination of (5) and (6) together with the assumptions mentioned above will give the following simple expression for the distribution ratio:

$$D_M = \frac{C}{1 + \sum_i \beta_i [NO_3^-]^i} \quad (7)$$

where  $C$  is a constant under the conditions stated earlier. A minimizing routine, comparing experimental distribution ratios to theoretical ones, can be used to calculate the stability constants,  $\beta_i$ .

Figure 7 shows the logarithms of the experimental and calculated distribution ratios for Am and Eu in the system described in section 2.1. The case with 5 M constant ionic strength has been used.



**Figure 7.** Calculated and experimental distribution ratios for Am(III) and Eu(III) as a function of nitrate ion concentration (298K, 5 M constant ionic strength (nitrate and perchlorate)) [6].

Specific ion interaction theory makes it possible to relate stability constants determined at different ionic strengths. (8) describes the relation between the stability constant  $\beta$  at  $I$  M ionic strength and the one at zero ionic strength,  $\beta_0$ .

$$\log \beta = \log \beta_0 + \Delta z^2 D_H(I) - \Delta \varepsilon I \quad (8)$$

where  $\Delta z^2$  is a factor describing the influence of the charges of the species involved (equals  $\Sigma(\text{charge product})^2 - \Sigma(\text{charge reactant})^2$ ),  $D_H(I)$  is the Debye-Hückel term and  $\Delta \varepsilon$  is the specific ion interaction coefficient.

The  $\log \beta_0$  was determined to be 1.45 and 1.38 for Am and Eu respectively and corresponding  $\Delta \varepsilon$  were 0.006 and  $-0.07$ . The values of  $\log \beta_0$  for Eu is in good agreement with earlier published results [7–11].

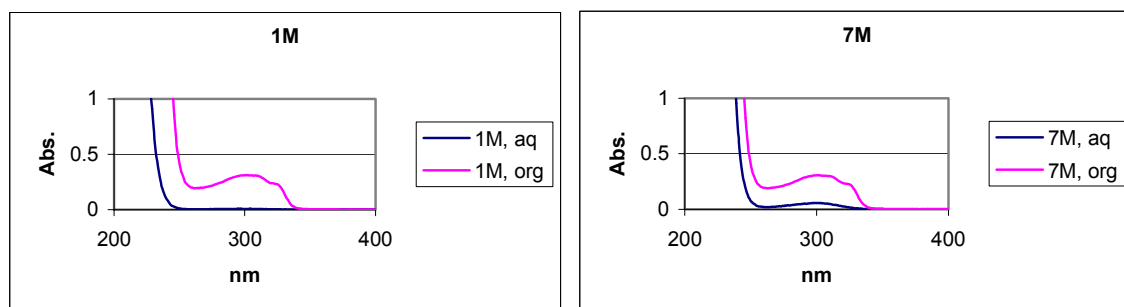
## 2.3 Protonisation of 2,6-bis-(benzoxazolyl)-4-dodecyloxy pyridine (BODO)

The determination of the protonation constants of terpyridine was readily performed [12] using a solvent extraction technique, some problems arose when applying the same method for BODO. It was not possible to dissolve the molecule in TBB in a desirable concentration (0.01M). In finding a better solvent different factors were taken into account:

- Ability to dissolve the molecule.
- Spectrophotometric behaviour.
- Solubility in water and vice versa.
- Different precipitations.
- Volatility and other chemical properties of the solvent itself.

A lot of different solvents were tested, but few were able to dissolve BODO at all. Nitrobenzene, dichlorobenzene and trichloroethylene (TRI) were all working as solvents but only TRI did not (or only partially) absorb at the same wavelengths as BODO (250–350 nm). Other solvents (e.g. diisopropyl benzene, dichloro benzene, cyclo hexanone, chloro benzene and bromo benzene) did not only fail to dissolve the BODO molecule but were also not suitable with respect to spectrophotometric concentration evaluation.

In contacting 0.01M BODO (dissolved in TRI) with the aqueous phases (1M H<sub>2</sub>NaNO<sub>3</sub> at different pH), no transfer of BODO into the aqueous phase was observed. Using an approximately 7M HNO<sub>3</sub> solution as aqueous phase resulted in change of colour of the organic phase and a change of spectrophotometric behaviour of the aqueous phase. What really happened will be further investigated, but theories involve ion pair extraction and/or oxidation of the molecule itself. In Figure 8 the change in the spectrum, using either 1M or ~7M hydrogen ion concentration in the aqueous phase, is illustrated. The absorbance in the organic phase does not change, implying no concentration decrease of BODO there – a fact that is contradicted by the concentration increase in the aqueous phase. The effect could perhaps be explained with the different ionic strengths of the aqueous phases or changes of the organic phase when contacting it with a strong nitric acid solution. Another possibility is that BODO is split into different organic compounds and that the increase in absorption around 300nm in the aqueous phase is caused by these new compounds.



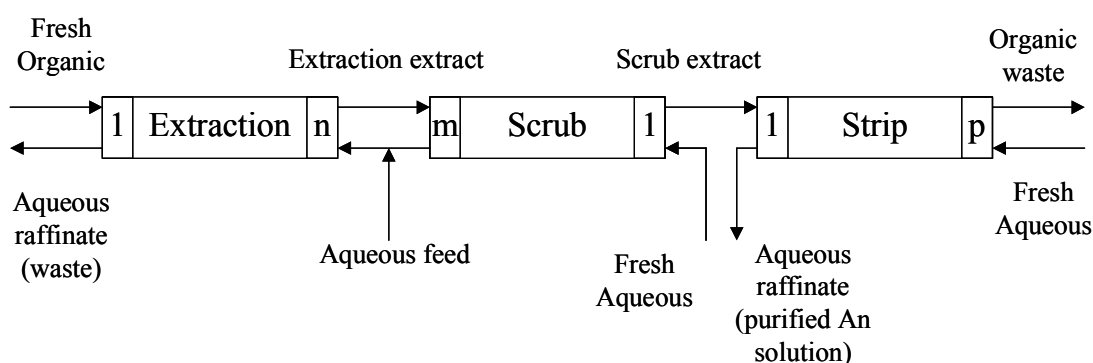
**Figure 8.** Difference in absorbance using different aqueous phases.

The fact that BODO does not seem to be protonated at moderate hydrogen ion concentration is an appreciated property. This means that the extraction and separation of selected elements might be performed at lower pH, since the extracting agent will remain in the organic phase.

## 2.4 Mixer-settler separation system

Through our contact with Ecole Nationale Supérieure de Chimie in France we made some progress with a mixer-settler battery for pilot scale tests of new promising ligands for separation of actinides and lanthanides. Nicolas Rogues finished his diploma work in this area and the abstract of his work can be found in Appendix VIII.

A schematic description of the system used can be seen in Figure 9.



**Figure 9.** Schematic description of the extraction, scrub and strip section of the mixer-settler battery.

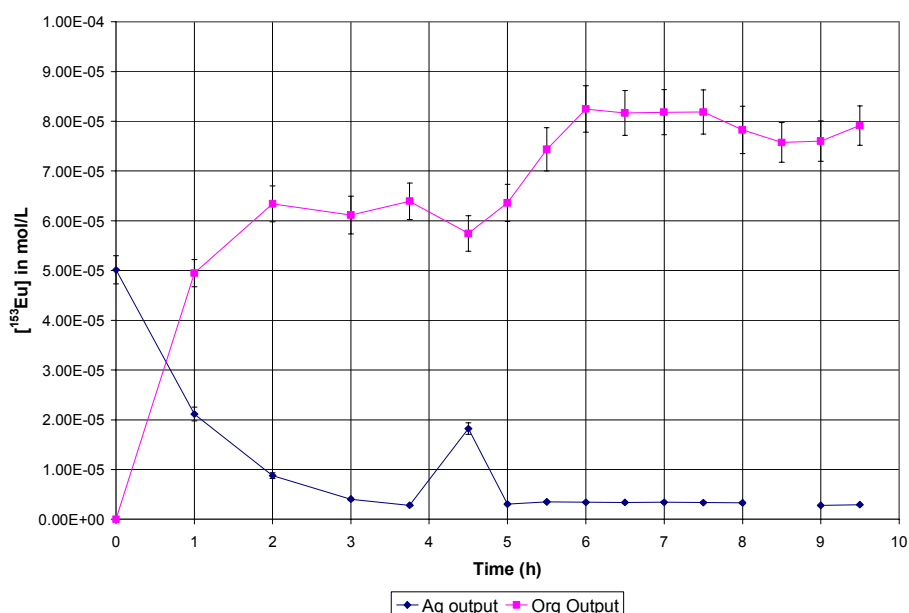
Nicolas constructed a simulation program for minimizing the number of stages in each section in a given system (in this case terpyridine, 2-bromodecanoic acid in Solvent 70) using Eu as radioactive tracer for the evaluation of distribution ratios.

To use reasonable values of the concentrations of terpyridine and 2-bromodecanoic acid the influence of their concentration ratio was investigated. The results showed that a concentration ratio of 55–60 (2-bromodecanoic acid/terpyridine) would be efficient in the separation process.

The mixer-settler equipment has been used earlier at the department. As soon as everything was connected the first test regarding the efficiency in one stage could begin. The influence of flow rates and mixing speed was investigated using HDEHP as reference (terpyridine is expensive and it was assumed that the results regarding the stage efficiency using HDEHP could be transferred to the terpyridine case). Also inactive Eu was used to avoid contamination of the equipment since it still needed adjustments. The analyses were made using ICP-MS.

Experiments were made to establish reasonable values of levels in the chambers of the mixer-settler, mixing speed and time needed for the system to reach steady state. It could not be shown that the flow or mixing speed did influence the efficiency within reasonable limits. The time necessary to reach steady state was determined to be 1 hour and 15 minutes after both pumps had been started.

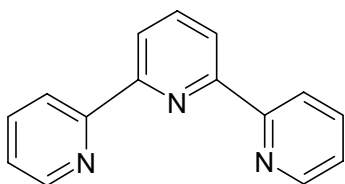
The experiments continued with 5 stages. In Figure 10 the results from one of those experiments is shown.



**Figure 10.** Start-up, transitory period and steady state for 5 extraction stages (1800 rpm, aqueous flow approximately 109 ml/h, theta approximately 0.664). This picture is taken from the diploma work of N Rogues.

This equipment will hopefully be used during 2003 to make test with one or more promising ligands to investigate their properties in a pilot scale process.

## 2.5 Investigation of new ligands



**Figure 11.** Terpyridine.

During the last year the extent of the cooperation with the University of Reading was increased. New molecules (approximately 20), synthesized within the PARTNEW project, was analysed regarding their the extraction properties. The BODO molecule (see Figure 1) came from Reading as well as some other very promising ones. Most of the ligands have the same basic structure as terpyridine (see Figure 11), but with various groups attached to the organic rings. Various carbon chain lengths between the nitrogen-containing rings were studied. Long side groups to increase or change the solubility of the ligand in the organic phase were also implemented. A synergistic system with 2-bromodecanoic acid was used (the acid is believed to form complexes with the ligand and to change the properties of the organic phase and to neutralize the charge of the metal ion).



The first thing that has to be established when receiving a new ligand is what solvent to use. During the first months of experiments a lot of different solvents were tested. Later an agreement to test the solubility properties during synthesizing in England was made to make the testing procedure more efficient. The solvent used in most experiments was *tert*-butylbenzene. As soon as a good solvent had been established the extractive ability of the ligand is investigated. The aqueous phase used consisted of 0.01M [H<sup>+</sup>] and trace amounts of Am, Eu and Cm. The ionic strength in the aqueous phase was 1 M and the contact time with the organic phase was always 5 minutes. Most of the ligands tested were bad extractants with distributions ratios close to the lower detection limit (at first the measurements were done on a HPGe-detector but then no Cm could be detected and the measuring time was very long. Later NaI(Tl) scintillation detector was used instead for Am and Eu and a liquid scintillation detector for Cm). Some tests gave reasonable distribution ratios, but with precipitation making the ligand non-usable considering process applications.

Another system consisting of BTPs and a malondiamide has been tested preliminary. The contact time used was one hour instead of five minutes and very high distribution ratios were found. These tests will continue next year. Most of the ligands tested are at the moment classified information and it is not possible to show pictures of them here.

The reason why we do these tests is to find a ligand that has all the correct properties – i.e. good solubility, extraction properties, separation efficiency and radiation resistance. The demands that are important can be used to build a system with goodness number, i.e. a method for marking ligands relative to each other.

## 2.6 Improvements of model for predicting extraction of trivalent metals

Earlier work (see P&T annual report 2001) resulted in a model, based on Hansen solubility parameters, which could be used to predict the outcome of a liquid-liquid extraction experiment. In the beginning of 2002 it was brought to our attention that the early model was based on invalid assumptions at distribution ratios above ~0.1. The theory was remade with much help from Dr Stig Wingefors<sup>2</sup> and the new model was reapplied and refitted to the same set of experimental data as used in the first case, over one year earlier. That dataset consisted of synergistic extraction of Am-241, Cm-244 and Pm-147 using terpyridine and 2-bromodecanoic acid in different organic diluents.

The first model only described the distribution of the uncharged metal-terpyridine-acid complex and did not take the full extraction mechanism into account. The revised model still uses Hansen solubility parameters in order to describe the properties of the organic phase. The dominating extraction reaction is assumed to be




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<sup>2</sup> Swedish Nuclear Power Inspectorate, SKI.

Where B is terpyridine and HA is the dimerised form of 2-bromodecanoic acid. The extracted complex,  $\overline{MA_3B_2}$ , is subsequently written as  $\overline{M}$ . The equations fitted to experimental data are

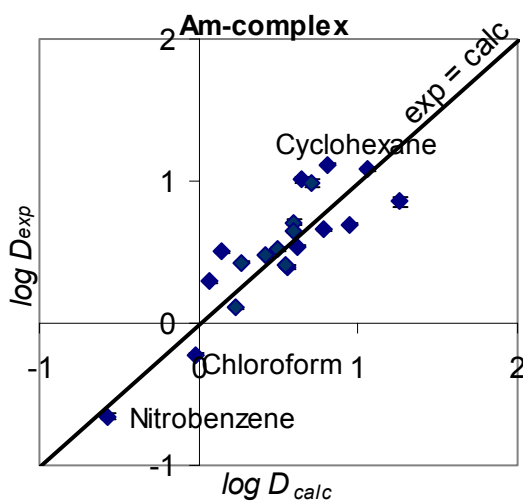
$$D \cdot \frac{\left(\frac{\overline{x}_M}{\overline{C}_M}\right)}{\left(\frac{\overline{x}_{HA}}{\overline{C}_{HA}}\right)^3 \left(\frac{\overline{x}_B}{\overline{C}_B}\right)^2} \frac{C_H^3}{\overline{C}_{HA}^3 \cdot \overline{C}_B^2} = K'_D \frac{\gamma_{HA}^{-3} \cdot \gamma_B^{-2}}{\gamma_M} \quad (10)$$

and

$$RT \ln \gamma_i = v_i \left[ (\delta_{d,i} - \delta_{d,tot})^2 + (\delta_{p,i} - \delta_{p,tot})^2 + (\delta_{h,i} - \delta_{h,tot})^2 \right] \quad (11)$$

where x is molar fraction and  $K'_D$  the thermodynamic equilibrium constant for the extraction reaction (9), referred to a standard state of infinite dilution of the organic solvent.  $\gamma$  is the activity coefficient,  $v$  is the molar volume and  $\delta$  the Hansen solubility parameters; dispersion (d), polar (p) and hydrogen bonding (h). The molar volume of the extracted metal complex can be well approximated as the sum of the ligand volumes. Furthermore,  $\delta_d$  for the extracted complex can also be calculated independently, which leaves only three parameters to fit.

Another improvement of this model is the fact that there are only three unknown parameters used in the fitting process, the original model used five unknown parameters. Although the fit is not as good as earlier it is still quite good and probably more valid according to current theories in physical chemistry.

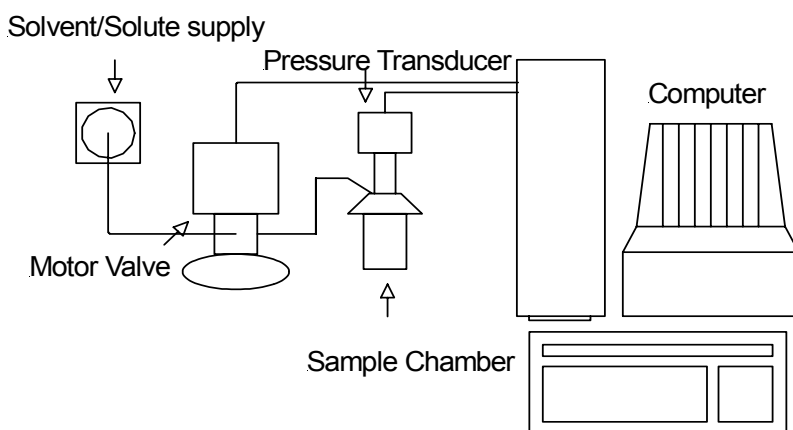


**Figure 12.** Comparison between experimental and calculated values of the distribution ratio.

## 2.7 Apparatus for continuous measurements of vapour pressure

A diploma worker, Johan Östberg, has been working with equipment to determine vapour pressures over different liquid solutions. This was done in an attempt to find activity coefficients of substances in an organic phase. See Appendix IX for abstract.

The construction layout is based on a diploma thesis made by Erik Strömqvist at the department [13]. The system is made up of four main components: an absolute pressure transducer, a seven port motor valve with a 20  $\mu\text{l}$  loop, a computer and a measuring instrument. The absolute pressure transducer is mounted on top of a stainless steel sample chamber-evacuation valve assembly, which is submerged in a temperature bath. The chamber is connected to a 7-port motorized valve with stainless steel capillary. The turning of the valve is controlled from the computer, which also registers the signal from the absolute pressure transducer and temperature in the bath via the measuring instrument.



**Figure 13.** System layout.

Some improvements on this setup have been made during the year. Most of these improvements are thought to minimize the risk of leakage and to facilitate all manual handling of the equipment. In working condition, this fully automated equipment will provide P-T-x datasets for binary systems of organic or inorganic substances.

A computer program is being made to handle and reduce these P-T-x datasets. To find the activity coefficients one has to calculate a theoretical value of P for a given T and x via a bubble-point pressure. This requires an expression and a set of parameters to calculate the excess Gibbs energy. The program will minimize the difference between the calculated and measured value of the vapour pressure using different expressions of excess Gibbs energy. When the best fit has been found the activity coefficients are found also. Besides the activity coefficients there will be a large amount of data as by-products from these calculations. For instance: molar ratios in the gas phase, second coefficients for the virial equation of state and the fugacity correction terms. A more thorough description of the theories behind the handling of the P-T-x datasets is found in Appendix X.

The activity coefficients obtained can be used directly through the Scatchard-Hildebrand theory to calculate solubility parameters, to be used in the model described earlier.

### 3 Collaborations

The following laboratories are involved in PARTNEW (more information can be found at <http://www.nc.chalmers.se/PARTNEW.HTM>).

- Commissariat á l'Énergie Atomique (F)
- The University of Reading (UK)
- Chalmers University of Technology (S)
- European Commission, DG-JRC, Institute for Transuranium Elements (EU)
- Ente per le Nuove Technologie, l'Energia e l'Ambiente (I)
- Politecnico di Milano (I)
- Forschungszentrum Karlsruhe, GmbH (D)
- Forchungszentrum Jülich, GmbH (D)
- Centro de Investigaciones Energeticas, Medioambientales y Technologicas(ESP)
- Universidad Autonoma de Madrid (ESP)

We have also had some contact with Ecole Nationale Supérieure de Chimie in France.

## 4 Meetings and lectures

**EU Cluster Meeting on Partitioning and Transmutation**, Karlsruhe, March 11–14. Jan-Olov Liljenzin, Sofie Andersson and Mikael Nilsson attended.

**International Solvent Extraction Conference**, Cape Town, March 17–21. Gunnar Skarnemark, Christian Ekberg, Sofie Andersson and Mikael Nilsson attended. Skarnemark made a poster presentation and Ekberg chaired one of the conference sessions. Andersson and Nilsson gave oral presentations of their work on protonation constants of terpyridine and the modelling of solubility parameters respectively.

**Visit to the University of Reading in England**, May 27–29. Jan-Olov Liljenzin, Gunnar Skarnemark, Christian Ekberg, Sofie Andersson and Mikael Nilsson attended a meeting with one of the participating laboratories in the PARTNEW project. New ligands were discussed and plans for the future made.

**EU Cluster Meeting on Partitioning and Transmutation**, Florence, October 21–24 2002. Jan-Olov Liljenzin, Christian Ekberg, Sofie Andersson and Mikael Nilsson attended.

**Visit to Forsmark Nuclear Power Plant and SFR**, September 17–18. Gunnar Skarnemark, Sofie Andersson and Mikael Nilsson attended.

**Educational meeting with Kastriot Spahiu**, SKB Stockholm, October 1. Christian Ekberg and Sofie Andersson attended. Spahiu gave some valuable information on activity coefficients and specific ion interaction theory.

**Ecole Nationale Supérieure de Chimie**, N Rogues and his fellow students presented their diploma works. Christian Ekberg attended the scientific committee.

## 5 Articles and publications

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

The abstracts of the two articles presented at the International Solvents Extraction Conference in Cape Town, South Africa, can be found in Appendices I and II, respectively. A short description of the conference is given in Appendix VI.

The articles which abstracts are given in Appendices 3 and 4 have not yet been published. They are included in Sofie Andersson's licentiate thesis (for which the abstract can be found in Appendix V).

Finally, the abstract of an article on the use of pH electrodes in the field of nuclear chemistry is given in Appendix VII. Christian Ekberg and Sofie Andersson were involved in this work.

Copies of the articles in Appendices I, II and VII as well the licentiate thesis (Abstract in Appendix V) of Sofie Andersson can be achieved from the Department of Materials and Surface Chemistry (Nuclear Chemistry), Chalmers.

## 6 Future work

We will continue our participation in PARTNEW to find appropriate new ligands for a future separation process. This goal can be achieved by investigation of several important areas summarized below.

**Extraction experiments.** Investigate the influence on pH, ionic strength, ionic medium and temperature on the distribution of Am, Eu and Cm in a two phase system. This part is given priority since it is part of the PARTNEW project and other laboratories depend on our results. These tests also includes the study of BTPs and malondiamide.

**Separation factors.** The separation of actinides and lanthanides is complicated because of their similar chemical properties. Other lanthanides than Eu should be tested to be able to foresee problems in a future separation process.

**Mixer-settler.** Nicolas Rogues diploma work included the start-up of an already existing (and functioning) mixer-settler battery. The knowledge from his work should be used to test new promising ligands in a pilot scale experiment. Other kinds of separation systems, e.g. including centrifugal extractors are also possible to introduce.

**Equipment for automatic vapour pressure measurements.** Some improvements have been made in 2002 and hopefully the experiments can start soon. The results from these tests are intended to be used as parameters in the modelling described in the next paragraph.

**Solubility parameters.** Using the results from extraction experiments it is possible to foresee the extractive properties of a ligand without performing the actual test. This could save a lot of time and more ligands could be scanned in shorter times.

**Goodness number.** This part of the project has only just begun, but hopefully there will be a system to mark ligands relative to each other.

Also Mikael Nilsson will prepare and present his licentiate thesis in the spring of 2003.

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Andersson S, Ekberg C, Liljenzin J-O, Skarnemark G, 2002. *Determination of Protonation Constants of 2,2':6',2''-Terpyridine from Liquid-liquid Distribution Data*, Proceedings of the international Conference on Solvent Extraction ISEC 2002, p 549–554

### Abstract

Spent nuclear fuel is a problem that has to be dealt with in the future. Transmutation of the most dangerous long-lived radionuclides into other less harmful ones can be considered a complement to direct disposal in a repository. Separation of the interesting nuclides is an important issue and liquid-liquid extraction is a suitable technique to achieve the necessary separation yields.

One group of extractants that can be used is oligopyridines and in this work basic research to determine the protonation constants of 2,2':6',2''-terpyridine has been performed. Results show that complexes with up to three hydrogen atoms, bound to the terpyridine molecule, exist. Terpyridine forms a strong complex with Cu(II)-ions, which facilitate spectrophotometric determination of the distribution of terpyridine between the two phases. This distribution, measured at different pH-values in the aqueous phase, makes it possible to determine the protonation constants.

Nilsson M, Liljenzin J-O, Ekberg C, Wingefors S, 2002. *Modelling the Influence of Organic Phase Composition on the Extraction of Trivalent Actinides*, Proceedings of the international Conference on Solvent Extraction ISEC 2002, p 1193–1198

### Abstract

A model for description of solvent influence on extraction of Am, Cm and Pm is proposed. The model comprises an extension of the Scatchard-Hildebrand theory for regular solutions employing Hansen's 3-D solubility parameters to describe interactions in the organic phase. The model was tested by performing a number of extraction experiments with 2,2':6',2''-terpyridine and 2-bromodecanoic acid as complexing agents in different combinations of organic solvents. The results obtained were used for fitting the parameters in the model and another set of experiments was performed to validate the model. The model shows good agreement between experimental and calculated distribution ratios for most of the extraction cases tested. From this analysis it can be concluded that the choice of solvent has a negligible effect on the selectivity of the studied extraction system.

Andersson S, Ekberg C, Foreman M R S, Hudson M J, Liljenzin J-O, Nilsson M, Skarnemark G, Spahiu K. *Extraction Behaviour of the Synergistic System 2,6-bis-(benzoxazolyl)-4-dodecyloxyipyridine and 2-bromodecanoic Acid Using Am and Eu as Radioactive Tracers*, submitted to Solvent Extraction and Ion Exchange

### Abstract

In this study, the extraction properties of a synergistic system consisting of 2,6-bis-(benzoxazolyl)-4-dodecyloxyipyridine (BODO) and 2-bromodecanoic acid (HA) in *tert*-butyl benzene have been investigated as a function of ionic strength by varying the nitrate ion and perchlorate ion concentrations. The influence of the hydrogen ion concentration has also been investigated. Distribution ratios between 0.03–12 and 0.003–0.8 have been found for Am(III) and Eu(III) respectively, but there were no attempts to maximise these values. It has been shown that the distribution ratios decrease with increasing amounts of  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{H}^+$ . The mechanisms, however, by which the decrease occurs, are different. In the case of increasing perchlorate ion concentration, the decrease in extraction is linear in a log-log plot of the distribution ratio versus the ionic strength, while in the nitrate case the complexation between nitrate and Am or Eu increases at high nitrate ion concentrations and thereby decreases the distribution ratio in a non-linear way. The decrease in extraction could be caused by changes in activity coefficients that can be explained with specific ion interaction theory (SIT); shielding of the metal ions, and by nitrate complexation with Am and Eu as competing mechanism at high ionic strengths.

The separation factor between Am and Eu reaches a maximum at ~1 M nitrate ion concentration. Thereafter the values decrease with increasing nitrate ion concentrations. This could be explained by the fact that nitrate ions interacts with Am(III) more strongly than Eu(III), resulting in the decrease of the distribution ratio of Am more than the one of Eu.

*Keywords: solvent extraction, partitioning of actinides and lanthanides, separation factors, Am(III), Eu(III)*

Andersson S, Ekberg C, Liljenzin J-O, Nilsson M, Skarnemark G. *Stability Constants of Nitrate Complexes with Am and Eu*, to be submitted

### Abstract

The stability constants of the nitrate complex formation with Am and Eu has been determined using a solvent extraction technique. The extraction of Am and Eu from an aqueous phase into an organic, using the synergistic system of 2,6-bis-(benzoxazolyl)-4-dodecyloxy pyridine (BODO), 1 M 2-bromodecanoic acid in *tert*-butyl benzene (TBB) has been studied. As the nitrate ion concentration was increased in the aqueous phase, a decrease in extraction was seen owing to complex formation between Am/Eu and nitrate ions. The found constants are in good agreement with earlier published results.

Andersson S, 2002. *Studies of the Extracting Agents 2,2':6',2''-terpyridine and 2,6-bis-(benzoxazolyl)-4-dodecyloxyipyridine. Protonation Constants and Extraction of Am and Eu as Function of pH and Ionic Medium*, Licentiate Thesis, Department of Materials and Surface Chemistry, Chalmers University of Technology

### Abstract

Partitioning and transmutation of spent nuclear fuel will reduce the amount of waste and its radiotoxicity in a long term perspective. It also makes it possible to use the inherent energy of the waste more effectively. To be able to transmute the most long-lived elements, they must be separated from the rest of the waste. Solvent extraction is a suitable technique to meet the strict demands on purity and separation efficiency.

Some basic properties of the 2,2':6',2''-terpyridine and 2,6-bis-(benzoxazolyl)-4-dodecyloxyipyridine ligands were studied. It is important to have good knowledge of e.g. protonation constants and extraction behaviour in different media to be able to find new ligands that will function even better in future complex extraction systems.

2,2':6',2''-terpyridine was investigated in an extraction system with a focus on its distribution between two phases: *tert*-butyl benzene and aqueous phases of varying hydrogen ion concentration. The terpyridine concentration, determined spectrophotometrically, as a function of hydrogen ion concentration in the aqueous phase offers a possibility to model the protonation constants.

The influence of hydrogen ion concentration, ionic strength and ionic medium on the synergistic extraction system of 2,6-bis-(benzoxazolyl)-4-dodecyloxyipyridine and 2-bromodecanoic acid were also investigated. The complex formation between nitrate ions and Am(III) and Eu(III) could be studied simultaneously and the stability constants for the complexes determined. The influence of increasing ionic strength without complex formation in the aqueous phase was studied using perchlorate ions. The task was then to explain the extraction behaviour with specific ion interaction theory.

The above mentioned experiments exemplify the importance of accurate pH measurements. The hydrogen ion concentration is one of the most important factors in extraction systems with ligands sensitive to protonation or with extraction mechanisms in which the hydrogen ions are involved.

*Keywords: solvent extraction, actinide/lanthanide separation, Am, Eu, separation factor, nitrate complex formation, partitioning and transmutation*

## Appendix VI

Short description of the journey to the International Solvent Extraction Conference 2002 in Cape Town, South Africa

### **International Solvent Extraction Conference Cape Town, South Africa 17–21 March 2002**

Gunnar Skarnemark, Christian Ekberg, Sofie Andersson and Mikael Nilsson visited and participated in the conference.

Solvent extraction constitutes important knowledge in hydrometallurgical and nuclear industries. Applications also extend to biotechnology, food technology, pharmaceuticals and petrochemicals. Many of these industries have had environmental problems that have been solved using solvent extraction. Other developments involve the use of other two-phase aqueous extraction systems, ionic liquids, magnetic fluid extraction and supercritical fluid extraction.

The conference was divided into five parallel sessions, where Andersson and Nilsson presented their work in Analytical Applications and Nuclear Applications respectively. Other sessions that also were interesting involved fundamental studies, extractants, biotechnology, membranes, environmental applications, hydrometallurgical applications, petrochemical applications, process engineering and design.

Skarnemark presented a poster during one of the poster sessions which were held in the evenings.

Ekberg C, Andersson S, Olsson M, 2002. *Uses of pH electrodes in Nuclear Chemistry*, Analytical and BioAnalytical Chemistry, **374**(5), p 824–830

### Abstract

Determination and definition of pH is a controversial subject in many areas in chemistry. For these reasons, the International Union of Pure and Applied Chemistry (IUPAC) has developed recommendations for pH measurements. These recommendations are currently (winter 2001) under revision; an increased focus is made on traceability of uncertainties in pH measurements. Here we present how glass electrodes designed for measuring pH are used within the field of nuclear chemistry. The use of pH electrodes is then related to the recommendations made by IUPAC. In applied chemistry, such as nuclear chemistry, a pH value is not sought as often as a hydrogen ion concentration or a simple equilibrium point during a titration. Moreover, ionic strengths are often above the range for which the IUPAC recommendations apply. Uncertainties must in these cases be individually assessed.

*Keywords: pH measurements, potentiometric titrations, surface charge, solvent extraction*



Rogues N, 2002. Setup of a mixer-settler battery for separation of actinides and lanthanides, Diploma Work, Department of Nuclear Chemistry

### Abstract

Research is being done to increase the reduction of the radiotoxicity of the spent nuclear fuel through advanced reprocessing. Minor actinides, which are potentially harmful for centuries in case of direct exposure, could be transformed by transmutation into less harmful or stable elements. However, they should first be separated from elements that have a too high neutron cross-section (*i.e.* they make the transmutation of minor actinides impossible).

Though Np may be recovered by a modified PUREX process, Am and Cm need a specifically designed process. Since lanthanides have chemical properties that are similar to those of trivalent actinides, a two steps way has been investigated: the DIAMEX process should recover the trivalent actinides and lanthanides from a modified PUREX raffinate, and after that the SANEX process should recover trivalent actinides from DIAMEX raffinate.

When used in synergy with 2-bromodecanoic acid, 2,2':6',2''-terpyridine is known to have a stronger affinity for Am than for Eu, used as representatives for the trivalent actinides and lanthanides respectively. Research is being done to find other ligands, but 2,2':6',2''-terpyridine has in this work been considered as a reference for process studies.

Mixer-settlers were designed for the so-called CTH Actinide Separation Process, and were recently used for studying iodine speciation in reactor water. The goal of this work was to design a SANEX process able to recover Am from a mixture of Am and Eu, using the mixer-settlers and the synergistic system made by 2-bromodecanoic acid and 2,2':6',2''-terpyridine. The mixture of aliphatic alkanes known as Solvent 70 was used as a diluent. Since the distribution ratios of Am and Eu depend on the diluent used, they were measured in Solvent 70 by gamma spectrometry. Distribution ratios that were suitable for process purposes were found.

A computer program was written to simulate the process and help with its design. The conceptual model developed in this work allows the mixer-settlers battery to be at steady state but not necessarily at equilibrium, using a parameter called *SE* for *stage efficiency*. The equipment was modified in order to show a more reproducible behaviour, which is suitable for modelling purposes. Experiments were carried out with inactive Eu and di-2-ethylhexyl-phosphoric acid (HDEHP) to investigate the dependency of *SE* on flows and mixing speed. It was found that for one modified mixer-settler, *SE* could be assumed non-flow dependant because of the uncertainties in measurements.

Studies with a battery of 5 modified mixer-settlers, inactive Eu and HDEHP showed that *SE* may vary within the battery, from stage to stage. It was found that the proportions of aqueous and organic phases in the mixer compartment may be involved in the variation of *SE*.

Östberg J, 2002. *Improved Apparatus for Automated Vapour Pressure Measurements*, Diploma Work, Department of Nuclear Chemistry

### Abstract

This project has involved the construction of an automated system, which is easy to operate for measuring vapour pressures above organic solutions. The system is constructed in such way that adding a known amount of solvent lowers the organic solutions concentration. The main parts of the system are a sample chamber with an absolute pressure transducer mounted on the top and a 7-port motorized valve with a 20  $\mu$ l sample loop. A computer program that is written in Borland C++ Builder 4 controls the system.

By adding known amounts of solvent,  $P$ - $T$ - $x$  data sets are obtained which can be used to calculate the activity coefficient. For a non-volatile solute the activity coefficient can be calculated by utilizing the Gibbs-Duhem equation for a two components solution.

The system has been tested on different inorganic and organic substances. Vapour pressure measurements were made on pure water, toluene, acetyl acetone and nitric acid and on solutions of LiCl/water and TBP/n-hexane. The results from tests were not especially accurate except for results from the pure water experiments.

The measured water vapour pressure results differed less than 0,4% compared to literature but for the other pure vapour pressure experiments the results differed with more than 10%. Two runs were made with LiCl and water and the mean activity coefficient was calculated. The last run gave for LiCl a mean activity coefficient of 34.7 at 16.7 m, which can be compared to literatures 42.2.

The vapour pressure above the mixture of TBP and n-hexane was higher than the upper limit of the pressure transducer and thus immeasurable and no results were obtained from these runs.

Though some of the results were inaccurate the system was proven to be comparatively easy to handle and operate and with some modifications the accuracy should increase.

## Appendix X

### Description of the theory for handling the data produced by the vapour pressure apparatus

The vapour pressure apparatus will, under working conditions, produce P,T,x-datasets.

T is the temperature of the vapour-liquid mixture in the sample chamber.

P is the pressure over the vapour-liquid mixture in the sample chamber.

x is the molar ratio of a substance in the liquid mixture in the sample chamber ( $x_1+x_2=1$ ) assuming the molar amount in the vapour is negligible compared to the molar amount in the liquid.

P and T are measured, while x is calculated from the volumes added to the sample chamber.

To calculate the activity coefficients,  $\gamma$ , the Barker method is used [1]. There the following function should be minimized:

$$f = \sum (P_{calc} - P_{exp})^2 \quad (1)$$

For a given T and x, P is calculated through a bubble point pressure calculation. This calls for an expression and a value of Gibbs free energy ( $G^E/RT$ ) [1]:

$$g \equiv \frac{G^E}{RTx_1x_2} = g(x_1) \quad (2)$$

The first thing to do is to choose an expression for g, e.g.

$$g=A$$

$$g=A_{21}x_1+A_{12}x_2$$

$$g=A_{21}x_1+A_{12}x_2+Bx_1x_2$$

$$g=A_{21}x_1+A_{12}x_2-\alpha_{12}\alpha_{21}*(\alpha_{21}x_1+\alpha_{12}x_2)^{-1}$$

A, B and  $\alpha$  are empirical constants obtained through the fitting of the pressure, but they must initially be given arbitrary values. The simplest working expression for g is chosen. It is possible to start with one parameter ( $g=A$ ). If the fitting of  $P_{calc}$  is good enough no further parameters are added. Otherwise a more complex expression for g with more parameters has to be used.

The equation used in a bubble point pressure calculation is the traditional vapour liquid equilibrium (VLE) equation [1]:

$$y_i \Phi_i P = x_i \gamma_i P_i^{sat} \quad (3)$$

y is the molar ratio for a substance in the vapour part of the vapour-liquid mixture.

$\Phi$  is the fugacity correction term, explained more in detail later.

$P^{sat}$  is the saturation pressure for a pure substance, obtainable from various tables.

The fugacity correction term is initially given the value of 1.

After calculating an initial value of  $g$ , the activity coefficients are calculated through equations:

$$\ln \gamma_1 = x_2^2 \left( g + x_1 \frac{dg}{dx_1} \right) \quad (4)$$

$$\ln \gamma_2 = x_1^2 \left( g - x_2 \frac{dg}{dx_1} \right) \quad (5)$$

$P_{calc}$  and all values of  $y$  are calculated:

$$P_{calc} = \sum_j \frac{x_j \gamma_j P_j^{sat}}{\Phi_j} \quad (6)$$

$$y_i = \frac{\frac{x_i \gamma_i P_i^{sat}}{\Phi_i}}{\sum_j \frac{x_j \gamma_j P_j^{sat}}{\Phi_j}} \quad (7)$$

$\Phi$  is calculated using the following equation:

$$\Phi_i = \exp \left\{ \frac{(B_{ii} - V_i^{liq})(P_{calc} - P_i^{sat})}{RT} + \left( \frac{P_{calc}}{RT} \right) \frac{1}{2} \sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \right\} \quad (8)$$

$B$  is the second coefficient in the virial equation of state.

$V^{liq}$  is the molar volume of the liquid.

$\delta$  is defined as:

$$\delta_{ij} \equiv 2B_{ij} - B_{ii} - B_{jj} \quad (9)$$

Now we need a way to express  $B$ .

The method used here is Tsonopolous correlation for  $B$  [2]. It is based on Pitzer-Curls correlations for  $B$  [3] for non-polar gases, where  $B$  is expressed as an empirical function of the reduced temperature  $T_R$ .

$$\frac{BP_c}{RT_c} = f_{PC}^{(0)}(T_R) + \omega f_{PC}^{(1)}(T_R) \quad (10)$$

$P_c$  and  $T_c$  are the critical pressure and temperature respectively, found in tables [4].

$\omega$  is the acentric factor, calculated according to [5].

$$\omega = -\log\left(\frac{P^{sat}}{P_C}\right)_{T_R=0.7} - 1.000 \quad (11)$$

The reduced temperature is calculated from [6]:

$$T_R = \frac{T}{T_C} \quad (12)$$

$f_{PC}$  are empirical functions developed by Pitzer and Curl. Tsonopoulos correlation for  $B$  is *similar* except for  $f^a(T_R)$ , which is not exactly identical [2].

$$f^{(0)}(T_R) = 0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^8} - \frac{0.000607}{T_R^8} \quad (13)$$

$$f^{(1)}(T_R) = 0.0637 + \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8} \quad (14)$$

For polar gases another term is added:

$$\frac{BP_c}{RT_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + f^{(2)}(T_R) \quad (15)$$

The polar term for non-hydrogen binding substances is:

$$f^{(2)}(T_R) = \frac{a}{T_R^6} \quad (16)$$

and for hydrogen binding *substances*:

$$f^{(2)}(T_R) = \frac{a}{T_R^6} - \frac{b}{T_R^8} \quad (17)$$

$a$  and  $b$  are calculated from the reduced dipole moment,  $\mu_R$ , defined as [2]:

$$\mu_R = \frac{10^5 \mu^2 P_C}{T_C^2} \quad (18)$$

To calculate the second virial *coefficient* for a mixture of two substances,  $B_{ij}$ , the same equations as for one substance are used. Although as *initial* parameters  $P_{Cij}$ ,  $T_{Cij}$ ,  $\omega_{ij}$ ,  $a_{ij}$  and  $b_{ij}$  are used. The following rules for the mixture are used [2]:

$$T_{Cij} = (T_{Ci} T_{Cj})^{1/2} (1 - k_{ij}) \quad (19)$$

$$P_{Cij} = \frac{4T_{Cij} \left( \frac{P_{Ci} v_{Ci}}{T_{Ci}} + \frac{P_{Cj} v_{Cj}}{T_{Cj}} \right)}{\left( v_{Ci}^{1/3} + v_{Cj}^{1/3} \right)} \quad (20)$$

$$\omega_{ij} = 0.5(\omega_i + \omega_j) \quad (21)$$

$v_C$  is the critical molar volume.

$k_{ij}$  is a characteristic constant for each binary mixture. There are some tables where it is found or simple methods to calculate it [2], [7].

Equations 19–21 are sufficient for binary mixtures where both substances are non-polar.

For binary mixtures between polar and non-polar substances,  $B_{ij}$  is assumed to have no polar term:

$$a_{ij} = 0 \quad (22)$$

$$b_{ij} = 0 \quad (23)$$

For binary mixtures between two polar substances the polar addition to  $B_{ij}$  is calculated from:

$$a_{ij} = 0.5(a_i + a_j) \quad (24)$$

$$b_{ij} = 0.5(b_i + b_j) \quad (25)$$

When the B values are calculated,  $\Phi$  can be calculated also. These new values for  $\Phi_i$  are recycled into the equations for  $P_{calc}$  and  $y_i$  to recalculate these values also. This initiates new calculations to find the new  $\Phi_i$  etc. In this way the values of  $\Phi_i$ ,  $P_{calc}$  and  $y_i$  are found through iteration.

The calculated values for  $P$  can now be compared to the experimental ones according to Barker's method. If the result is not good enough a new and more complicated expression for  $g$  is chosen and the entire operation is recalculated.

The values for  $B$  should not change when  $g$  is altered, which means the work of calculating these for every data point in the P,T,x dataset needs only be made once.

When all calculations are finished one will have a quite substantial amount of data:  $P$ ,  $T$ ,  $x$ ,  $y$  and  $\gamma$  together with, if one is interested, the fugacity correction terms,  $\Phi$ .

## References to Appendix X

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