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## Annual Report 2001

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January 2002

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# Abstract

The project Partition and Transmutation (P&T) at the department of Nuclear Chemistry, Chalmers University of Technology, is aimed at investigating new solvent extraction reagents and new processes for the separation of different chemical elements needed in a possible future P&T process.

During the year 2001, the work has mainly been in five areas: 1) method development and testing of means to determine protonation constants of two model reagents (2,2':6',2''-terpyridine and 2,4,6-tri-(2-pyridyl)-1,3,5-triazine), 2) modelling the influence of organic phase composition on the extraction of trivalent metals (Pm, Am, Cm), 3) determination of the density and refractive index of 2,2':6',2''-terpyridine, 4) the extraction behaviour of four new nitrogen based reagents (2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine, 2,6-bis-(benzimidazol-2-yl)-4-dodecyloxylpyridine, 2,6-bis-(benzimidazolyl)-pyridine, 2,4-bis-(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine), and 5) a study of the effect of temperature on the synergistic extraction of Eu and Am with 2,2':6',2''-terpyridine or 2,4,6-tri-(2-pyridyl)-1,3,5-triazine in the presence of 2-bromodecanoic acid dissolved in a series of organic diluents. Åsa Enarsson has obtained her tekn.lic. degee.

# Sammanfattning

Projektet separation och transmutation (S&T) vid institutionen för kärnkemi vid Chalmers syftar till undersökning av nya reagens och utveckling av nya processer för de kemiska separationer som kan behövas i ett eventuellt framtida S&T system.

Under år 2001 har arbetet i huvudsak behandlat fem områden: 1) metodutveckling och utprovning av sätt att mäta protoniseringskonstanter med användning av två modellsubstanser (2,2’:6’,2’’-terpyridin och 2,4,6-tri-(2-pyridyl)-1,3,5-triazin), 2) modellering av inverkan av organfasens sammansättning på extraktion av trevärda metalljoner (Pm, Am, Cm), 3) mätning av densitet och brytningsindex för 2,2’:6’,2’’-terpyridin, 4) studier av extraktionsegenskaperna hos fyra nya kvävebaserade reagens(2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridin, 2,6-bis-(benzimidazol-2-yl)-4-dodecyloxylpyridin, 2,6-bis-(benzimidazolyl)-pyridin, 2,4-bis-(3,5-dimetylpyrazol-1-yl)-6-metoxy-1,3,5-triazin), och 5) studier av temperaturens inverkan på synergistisk extraktion av Eu och Am med 2,2’:6’,2’’-terpyridin eller 2,4,6-tri-(2-pyridyl)-1,3,5-triazin i närvaro av 2-bromdekansyra i ett antal olika organiska lösningsmedel. Åsa Enarsson har avlagt sin tekn lic examen.

# Content

# 1 Introduction

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

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

The project is at present conducted as fundamental research, which is the basis for the work of three PhD students. During this year one new PhD student, Mikael Nilsson, started his PhD work and there has also been a postdoc scientist, Claire Mesmin, working with the P&T project.

# 2 Solvent extraction research

During 2001 Åsa Enarsson finished her licentiate thesis on synergistic extraction with nitrogen coordinating ligands and 2-bromodecanoic acid. Claire Mesmin worked with a triazine, TPTZ, until September when her employment ended. Sofie Andersson has investigated protonation constants for terpyridine and sent an article to ISEC'2002 for publication [AND 02]. Mikael Nilsson has also sent an article to ISEC regarding development of a model for extraction behaviour based on solubility parameters [NIL 02]. Åsa, Sofie and Mikael have also investigated solvent extraction and physical and chemical properties of a number of new extraction reagents acquired from the University of Reading, England.

## 2.1 Determination of the protonation constants of some nitrogen containing extractants

To be able to understand the extraction behaviour of different extracting reagents, it is important to have knowledge of their basic thermodynamic properties. At Chalmers we have been studying the protonation constants of some nitrogen containing ligands (2,2':6',2''-terpyridine and 2,4,6-tri-(2-pyridyl)-1,3,5-triazine) and the methods developed during this work will be applied to the new molecules sent to us from the University of Reading.

### 2.1.1 Protonation of 2,2':6',2''-terpyridine (terpy)

The protonation of terpy can be written as:

$$Tp + H^{+} \Leftrightarrow TpH^{+} \tag{1}$$

$$Tp + 2H^{+} \Leftrightarrow TpH_2^{2+} \tag{2}$$

$$Tp + 3H^{+} \Leftrightarrow TpH_3^{3+} \tag{3}$$

The protonation constants, often expressed as *β*, can be expressed as:

$$\beta_1 = \frac{[TpH^{+}]}{[Tp][H^{+}]} \qquad \beta_2 = \frac{[TpH_2^{2+}]}{[Tp][H^{+}]^2} \qquad \beta_3 = \frac{[TpH_3^{3+}]}{[Tp][H^{+}]^3} \tag{4}$$

The definition of the protonation constants includes activities instead of concentrations. By using a constant ionic strength in the system, the activity coefficients can be assumed constant. They are often included in the protonation constants as discussed above and further in [EKB 99].

By varying the pH of the aqueous phase, the distribution of the extracting agent between the two phases can be determined as a function of the free hydrogen ion concentration and the protonation constants. The analysis of the extracting agent in the two phases can be made for example by spectrophotometry.

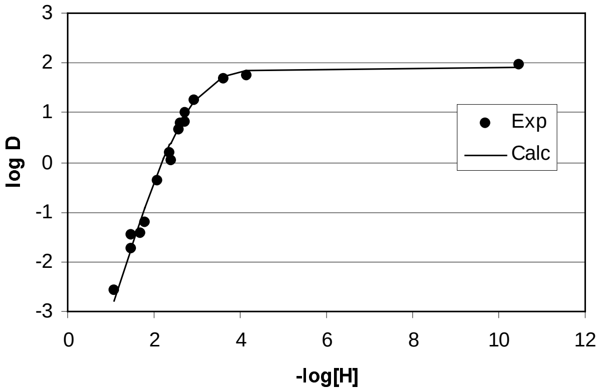

***Figure 2-1.*** *Calculated and experimental distribution coefficients for Tp (298 K, 1 M NaNO$_3$) [AND 02].*

Figure 2-1 gives as typical result from this kind of studies the distribution of Tp between an organic phase (*tert*-butylbenzene) and an aqueous 1 M NaNO$_3$ phase at varying pH. The D-value, used in the figure as a measure of the distribution ratio of the extracting agent, is defined as

$$D = \frac{[Tp_{tot}]^{org}}{[Tp_{tot}]^{aq}} \qquad (5)$$

$[Tp_{tot}]^{org}$ and $[Tp_{tot}]^{aq}$ are the total concentrations of the extracting agent in the organic and aqueous phases, respectively. By introducing the protonation constants, Equation (4), and the distribution of non-charged Tp, $\lambda$ (defined as the concentration ratio of the non-protonated species of the extracting agent between the organic and aqueous phases), into this equation, the D-value can be expressed as

$$D = \frac{\lambda}{1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3} \qquad (6)$$

A precise value of $[H^+]$ is crucial for the determination of the protonation constants. The free hydrogen ion concentration $[H^+]$ can be determined either by measuring the pH in the aqueous phase (after contact with the organic phase) or by calculating it as a part of the data treatment. The latter method is preferred owing to uncertainties in determining the activity coefficients needed to recalculate a measured hydrogen ion *activit*y on the conventional pH scale to a hydrogen ion *concentration.*

The following equations must be used in an iterative procedure in modelling:

$$\left[H^+\right] = \frac{\left[H_{tot}\right]}{1 + \beta_1\left[Tp\right] + 2\beta_2\left[Tp\right]\left[H^+\right] + 3\beta_3\left[Tp\right]\left[H^+\right]^2} \qquad (7)$$

where

$$\left[Tp\right] = \frac{\left[Tp_{tot}\right]}{\lambda + 1 + \beta_1\left[H^+\right] + \beta_2\left[H^+\right]^2 + \beta_3\left[H^+\right]^3} \qquad (8)$$

The total concentration of hydrogen ions in the system, $[H_{tot}]$, is determined through titrations of the aqueous phases before the solvent extraction experiments are done. No calibration of the electrode is needed, since the inflection point, regardless of the actual pH of the system, gives the equivalence volume in the titration, as described below. The total concentration of Tp, $[Tp_{tot}]$, is also known from the solution preparation. The results can be found in Table 2-1.

**Table 2-1. Protonation constants of terpylog**

| | |
|---|---|
| log $\beta_1$ | 3.2 ± 0.2 |
| log $\beta_2$ | 2.8 ± 0.2 |
| log $\beta_3$ | 1.8 ± 0.5 |

This method is a good example of the difficulties involved in using pH for this kind of work. Instead of using a measured pH, the free hydrogen ion concentration is determined using Equations (6-8).

Estimating the error in protonation constants, $\beta_i$, is complicated. It can be done either by estimating the uncertainties in every step of the experimental chain, or by giving the data used in the calculation of the protonation constants a lower weight in regions where an error in the hydrogen ion concentration has the greatest affect on the results.

In estimating the uncertainty through experimental statistics, different sources of input uncertainties must be defined. The total concentration of hydrogen ions in each aqueous phase has been determined by at least three titrations (with uncertainties in amount and concentrations of base *etc.*). When the two phases have been contacted, triple samples are taken from each phase for further concentration determination of the extracting agent (with uncertainties in quantities taken, several dilutions and spectrophotometric evaluation). One method that can be used is the chi-square method [MEI 00].

The iterative manner in which eqn:s 5-8 are used to determine the unknown protonation constants complicates the estimation of the sensivity of the D-value relative to $H^+$ concentration. Expressing the log$[H^+]$ derivative of logD Equation (6), one can calculate where a small change in $[H^+]$ results in a large change in D. The expression can be written as:

$$\frac{\partial \log D}{\partial \log\left[H^+\right]} = \frac{\beta_1\left[H^+\right] + 2\beta_2\left[H^+\right]^2 + 3\beta_3\left[H^+\right]^3}{1 + \beta_1\left[H^+\right] + \beta_2\left[H^+\right]^2 + \beta_3\left[H^+\right]^3} \qquad (9)$$

Plotting the derivative against -log[$H^+$] with constant values of $\lambda$ (80) and $\beta_i$ ($10^{3.2}$, $10^{6.1}$ and $10^{7.9}$ respectively) gives Figure 2-2.

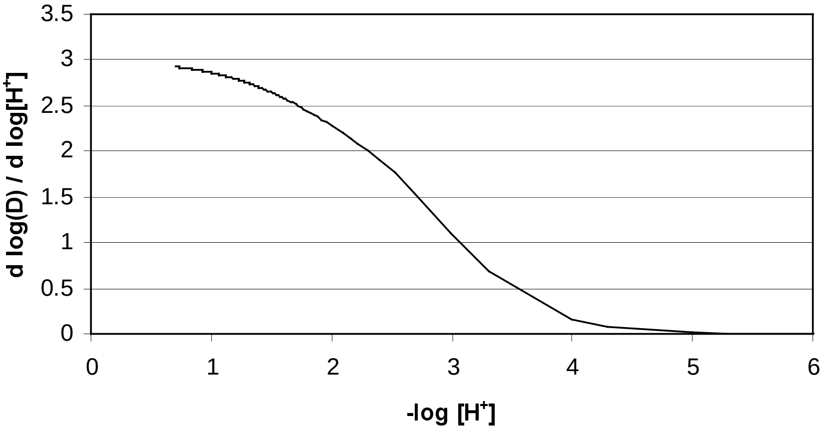

***Figure 2-2.*** *The derivative of log D with respect to log[$H^+$], plotted against -log[$H^+$]. Constant values of lambda and the protonation constants have been assumed.*

From this it can be determined that a small change in [$H^+$] affects the D-value most at high [$H^+$]. The same procedure was repeated with Equation (8) in order to be able to see how a change in [$H^+$] affects [Tp], see Figure 2-3.

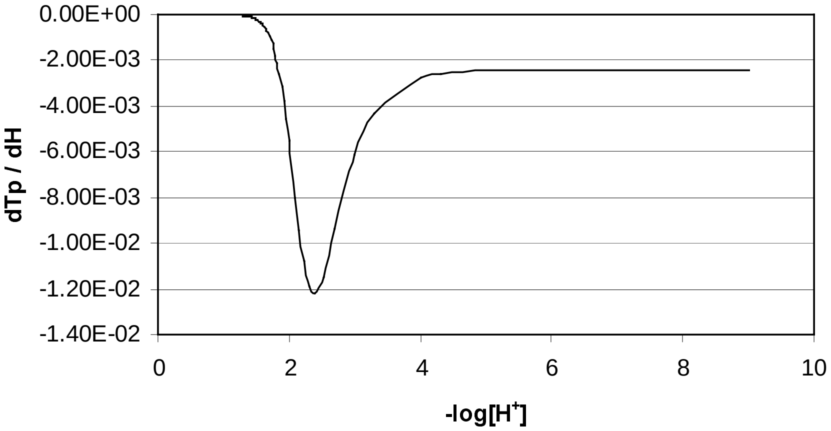

***Figure 2-3.*** *The derivative of Tp with respect to [H+] plotted against -log[H+]. Constant values of lambda and of the protonation constants have been assumed.*

The concentration of Tp does not affect the D-value very much at [$H^+$] > 0.04. Low concentrations of Tp in the organic phase at low pH will make it experimentally difficult to determine the concentration of Tp, and thus the D-value. This contributes to higher uncertainties in the data obtained in this pH-region.

### 2.1.2 Protonation of 2,4,6-tri-(2-pyridyl)-1,3,5-triazine

The aim was to calculate the protonation constants of 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (TPTZ) in nitric acid medium. The extraction method used for the determination of protonation constants for terpy does not work as well with TPTZ due to the low solubility of the neutral TPTZ molecule in water. Instead a liquid/liquid extraction method and a solubility method has been used. The originally low solubility of TPTZ increases with acidity. This phenomenon is believed to be caused by the formation of water soluble protonated forms of TPTZ in acid media.

Two series of experiments have been performed. In series 1, TPTZ powder was mixed with nitric acid solutions ($1.61 < -\log([H^+]) < 5.7$) and the total concentration of TPTZ determined in the resulting aqueous solution. In series 2 the concentration in the aqueous phase was determined after stripping of TPTZ from an organic phase (0.05 M TPTZ in nitrobenzene) to nitric acid ($1.61 < -\log([H^+]) < 5.7$).

The total TPTZ concentrations in the aqueous phase after filtration through a 0.1 μm filter were measured by spectrophotometry at 290 nm.

The protonation reactions considered can be written as:

$$TPTZ + iH^+ \Leftrightarrow H_iTPTZ^{i+}$$

And we define the constant of protonation, $\beta_i$, as follows:

$$\beta_i = \frac{[TPTZ] \times [H^+]_f^i}{[H_iTPTZ^{i+}]} \times \frac{\gamma_{TPTZ} \times (\gamma_{H^+})^i}{\gamma_{H_iTPTZ^{i+}}}, \qquad (10)$$

where:

$[H^+]_f$: concentration of free $H^+$ in aqueous solution,
$[H_iTPTZ^{i+}]$: concentration of protonated form of TPTZ,
[TPTZ]: concentration of TPTZ neutral (solubility of TPTZ in distilled water).

We assume that $\gamma_{TPTZ} = 1$ for unprotonated TPTZ because it is a neutral molecule and assume that $\gamma_{H_iTPTZ^{i+}}$ does not change considerably (within 20%) in the interval where each $\beta_i^{'}$ is determined:

$$\beta_i^{'} = \beta_i \times \gamma_{H_iTPTZ^{i+}} = \frac{[TPTZ] \times ([H^+]_f \times (\gamma_{H^+}))^i}{[H_iTPTZ^{i+}]} \qquad (11)$$

Because the ionic strength, I, is lower than 0.1 M, the activity coefficient of $H^+$, $\gamma_{H^+}$, is calculated from the Debye-Hückel equation considering the dimension of the ion.

A mass balance of TPTZ gives:

$$[TPTZ]_t = [TPTZ]_0 + \sum_i [H_iTPTZ^{i+}] \qquad (12)$$

Where:

$[TPTZ]_0$ =solubility of TPTZ in distilled water ($S_0$),
$[TPTZ]_t$ = solubility of TPTZ in aqueous solution (S).

Finally, by expressing the solubility S using Equation 11 and 12 we get:

$$S = S_0 \times (1+\sum_{i=1}^{m} \frac{([H^+]_f \times \gamma_{H^+})^i}{\beta'_i}) \qquad (13)$$

The TPTZ was dissolved in (series 1) or stripped into (series 2) aqueous media of varying acidity to form the protonated and neutral species. At any investigated acidity, the solubility of TPTZ obtained by both methods is the same within error limits (Figure 2-4).

When modelling the solubility we have considered 2 protonated species: $HTPTZ^+$, $H_2TPTZ^{2+}$ in a range 2.7 < -log($[H^+]$) < 5.5, in order to explain the shape of the experimental curves (Figure 2-5). The protonation constants used in Equation 13, are shown in Table 2-2.

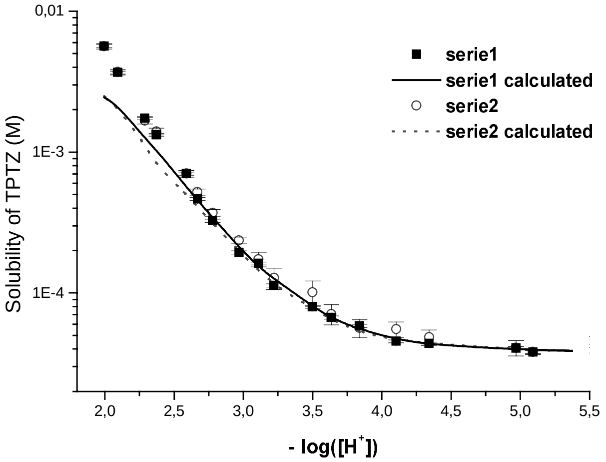

***Figure 2-4.*** *Experimental and calculated solubility curve of TPTZ (serie 1 + serie 2) vs. –log([H+]) between 2 and 5.5. The lines are calculated from the protonation constants given in Table 2-2.*

The difference between the calculated and experimental curves for both series at –log([H+]) below 2.7 indicates the existence of at least one other species in the aqueous solution. Such species could be either a triple protonated TPTZ or a polymer form, e.g $H_2TPTZ_2^{2+}$, or possibly both.

**Table 2-2. Protonation constants of TPTZ in nitric acid medium, I < 0.05 M, at room temperature.**

*this work I<0.03 M $HNO_3$, I=0.1 M (K,H)Cl [PAG 68], I=0.23 M (Na,H)Cl [PRA 70], I=1 M (K,H)Cl [VIT 84]

| Ref. | $pK'_1$ | $pK'_2$ |
|---|---|---|
| This work | 3.6 ± 0.2 | 2.7 ± 0.2 |
| Pagenkopf and Margerum [PAG 68] | 3.53 | 2.73 |
| Prasad and Paterson [PRA70] | 2.9 ± 0.3 | 2.82 ± 0.01 |
| Vitorge [VIT 84] | 3.8 ± 0.2 | 2.7 ± 0.3 |

The fitting calculations have been made in Matlab R12 by minimising the squared sum of residuals between experimental and calculated solubilities.

The values of the two protonation constants determined by us are comparable to those given in the literature [PAG 68, PRA 70, VIT 84].

To check our assumptions, Figure 5 shows a comparison between the measurements of $[H^+]_f$ using $[H^+]_f$ calculated from equation 13 with experimental values of the solubility and the two calculated protonation constants (Table 2-2). It can be seen that at $-\log([H^+]) < 2.7$ the calculated values overestimate free $H^+$. This proves that we have at least one other species in aqueous phase.

If the third protonation is considered, we obtain a third protonation constant ($pK'_3 = 2.5 \pm 0.3$) by fitting the corresponding model to our data. The agreement between calculated and measured $[H^+]$ in Figure 2-5 is improved in the range $2 < -\log([H+]) < 2.7$, but the difference in $-\log([H+]) < 2$ is still not explained. Consequently, a polymer form of TPTZ seems to exist. This has also been observed previously by P.Vitorge [VIT 84].

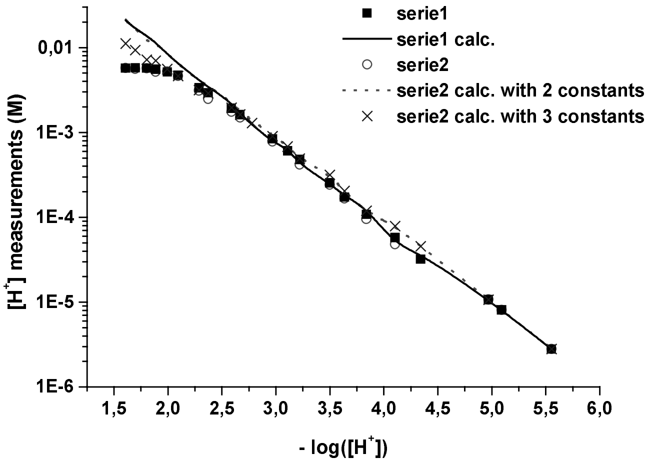

***Figure 2-5.*** *Comparison between measured $[H^+]$ and $[H^+]$ calculated from our protonation constants. The difference is higher for $-\log([H^+]) < 2$ indicating a polymer form of TPTZ.*

To check the assumption of the existence of a polymer form we calculate ñ, the number of $H^+$ divided by the number of molecules of TPTZ. If we consider that only the protonated species exist at $-\log([H^+]) < 2$, the equation for ñ is:

$$\tilde{n} = \frac{[H^+]_t - [H^+]_f}{[TPTZ]_t} \cong \frac{\Sigma\, y[H_y TPTZ_x^{y+}]}{\Sigma\, x[H_y TPTZ_x^{y+}]} \qquad (14)$$

Where

x: number of TPTZ,
y: number of $[H^+]$,
$[H^+]_t$: $[H^+]$ initial.

If we consider only one major species, Equation 14 becomes:

$$\tilde{n} = \frac{y}{x} \qquad (15)$$

The number ñ is lower than 1 at $-\log([H^+]) < 2$ (Figure 2-6). This means that there are more TPTZ than $H^+$ per molecule (x > y) or in other words, a polymer form.

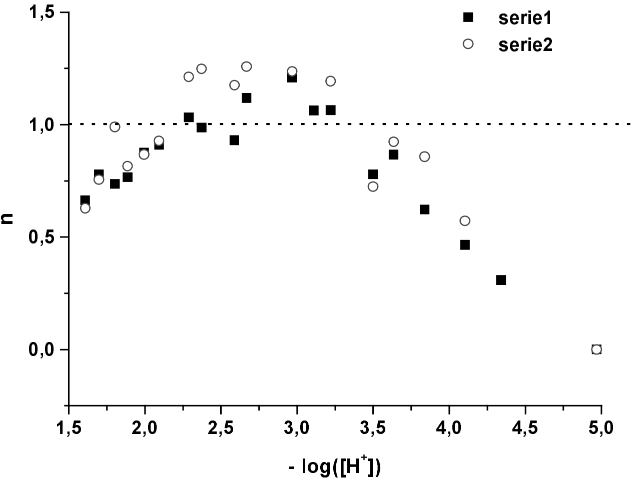

***Figure 2-6.*** *The number ñ (the number of $H^+$ divided by the number of TPTZ) vs. $-\log([H^+])$. The polymer form appears at $-\log([H^+]) < 2$.*

For $-\log([H^+]) > 3.2$, ñ is also lower than 1, but here the explanation is the existence of neutral TPTZ.

For $2 < -\log([H^+]) < 3.2$, the ñ value is always lower than 1.5, so the third protonation seems less likely and the hypothesis about the existence of polymer form may be a better explanation. Indeed for $2 < -\log([H^+]) < 2.7$, ñ is close to 1, i.e. x = y (equation 15), so a possible major species could be $H_2TPTZ_2^{2+}$.

To conclude we found that the solubility curve of TPTZ is not fully described by a model using two constants of protonation, where the considered species are TPTZ, $HTPTZ^+$, $H_2TPTZ^{2+}$. We have to assume at least one other species like a triple protonated one or a polymer form. Further investigations are underway in order to better determine which species are present.

Complementary studies by for example NMR should also be made in order to confirm and supplement these results.

## 2.2 Modelling the influence of organic phase composition on the extraction of trivalent metals

Extraction of americium, curium and promethium was investigated using 0.1 M 2,2':6,2''-terpyridine (terpy) and 1.0 M 2-bromodecanoic acid as complexing agents in different combinations of organic diluents. Extraction data was used to develop a model for predicting distribution ratios for Am, Cm and Pm from a standard aqueous phase without performing any laboratory work. The separation factor between the actinides (Am, Cm) and the lanthanide (Pm) was about 10 regardless of which organic solvents was used as organic phase. No significant separation was observed between Am and Cm. The model used is derived from an equation describing the activity of a component in a regular solution [WAK 64] and can be expressed as:

$$\ln(D_A) = V_{m,A}\left[\frac{1}{V_{m,org}} - \frac{1}{V_{m,aq}} + \frac{1}{RT}\left(K - \Delta_{d,A,org} - \Delta_{p,A,org} - \Delta_{h,A,org}\right)\right] \qquad (16)$$

where

$$K = \Delta_{d,A,aq} + \Delta_{p,A,aq} + \Delta_{h,A,aq}$$

and

$$\Delta_{d,A,aq} = \left(\delta_{d,A} - \delta_{d,aq}\right)^2,\ \Delta_{p,A,aq} = \left(\delta_{p,A} - \delta_{p,aq}\right)^2 \text{ etc...}$$

where index A denotes the extracted metal complex, $V_m$ is the molar volume [$cm^3$/mole] and δ Hansen solubility parameters for dispersion (d), polar (p) and hydrogen bonding (h) contributions [$(cal/cm^3)^{½}$]. Unknown constant parameters in Equation 16 are $V_{m,A}$, K, $\delta_{dA}$, $\delta_{pA}$ and $\delta_{hA}$. K is constant since the aqueous phase used in the extraction experiments was the same in all cases and hence parameters regarding the aqueous phase are considered constant. Three sets of parameters were developed, one for each of the elements. Results indicate that the extracted complexes have no hydrogen bonding character ($\delta_{hA} = 0$), as expected.

**Tabell 2-3. Constants used in Equation 16, obtained by fitting extraction data**

| Constants for equation 16 | | A = Am-complex | A = Cm-complex | A = Pm-complex |
|---|---|---|---|---|
| $V_{m,A}$ ($cm^3$/mole) | | 331.0 | 389.5 | 402.8 |
| K | ($cal/cm^3$) | 42.29 | 43.54 | 37.63 |
| $\delta_{dA}$ | $(cal/cm^3)^{½}$ | 6.10 | 5.82 | 6.19 |
| $\delta_{pA}$ | $(cal/cm^3)^{½}$ | 1.82 | 1.82 | 1.60 |
| $\delta_{hA}$ | $(cal/cm^3)^{½}$ | 0 | 0 | 0 |

The model was found to give a good agreement with experiments for most of the extraction cases tested (Figure 2-7). However, the model does not work well with nitrobenzene. An explanation to this disagreement could be that nitrobenzene is a fairly strong polar substance. Polar substances can induce dipoles in other non-polar substances and Hansen's solubility parameters do not take such dipole-induced dipole interactions into consideration.

A fourth component was included in the model in an attempt to compensate for dipole-induced dipole interactions. By introducing this fourth component the model works better with for instance nitrobenzene and isopropylbenzene among others (see Figures 2-7 and 2-8). However the new model is also more accurate with n-hexane, a non-polar solvent, which might indicate that the fourth component does not only compensate for dipole-induced dipole but also for something else.

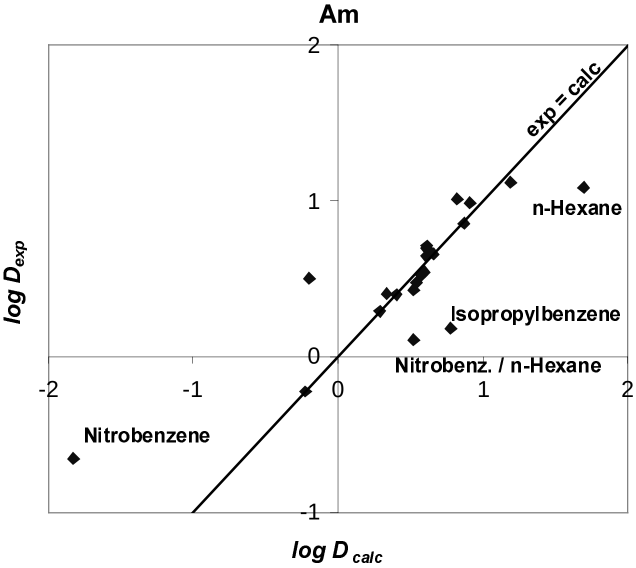

***Figure 2-7.*** *Comparison between experimental and calculated distribution ratios using older model, similar results with Cm and Pm.*

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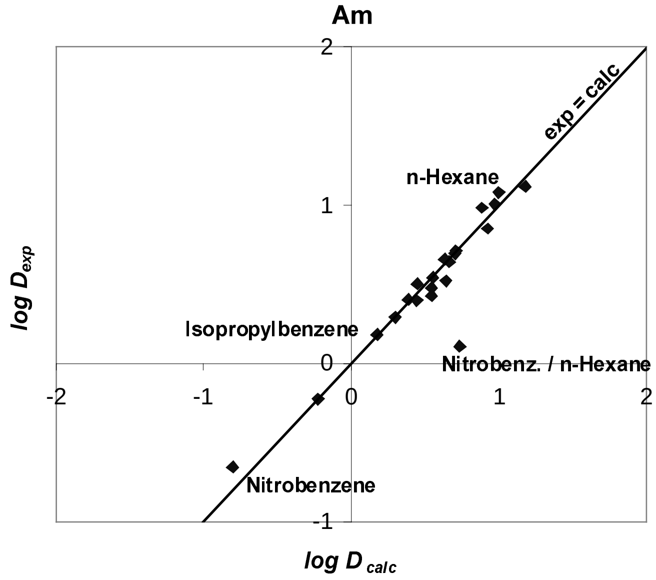


*Figure 2-8.* *Comparison between experimental and calculated distribution ratios using new model.*

A model like this might be used as a tool for reducing the time, and thus the funding, needed to find a suitable separation system for the partitioning of spent nuclear fuel. Of course, interesting results must be verified experimentally.

## 2.3 Physical properties of 2,2':6,2''-terpyridine

### 2.3.1 Density

The density of terpy has been measured using a multivolume pychnometer 1305 from Micromeritics. The terpy-powder was dried in an exsiccator before measurement to make sure that all water was purged from the powder. The density was found to be 1.324 ± 0.006 g/cm$^3$. This density was used when calculating the refractive index.

### 2.3.2 Refractive index

The refractive index for 2,2':6',2''-terpyridine (terpy) has been determined. By dissolving terpy in *tert*-butylbenzene (TBB) and measuring the refractive index and density of the solution and using Equations 17 and 18 the refractive index of pure terpy can be calculated.

The molar refraction of a substance *i* is calculated from the refractive index, *n*, molar mass, *M* and density, *ρ* of the substance [GLA 62].

$$R_i = \frac{n_i^2 - 1}{n_i^2 + 2} \cdot \frac{M_i}{\rho_i} \tag{17}$$

For a homogenous mixture of two substances *i* and *j* the molar refraction of the mixture should obey the following equation:

$$R_{ij} = x_i R_i + x_j R_j \tag{18}$$

Plotting the molar refraction of a solution of two substances against different molar fraction should thus yield a linear correlation. This was tested using mixtures of terpy and TBB, see Figure 2-9. If the plot is linear and the molar refraction of one substance is known the molar refraction of the other substance can be calculated from eqn. 18.

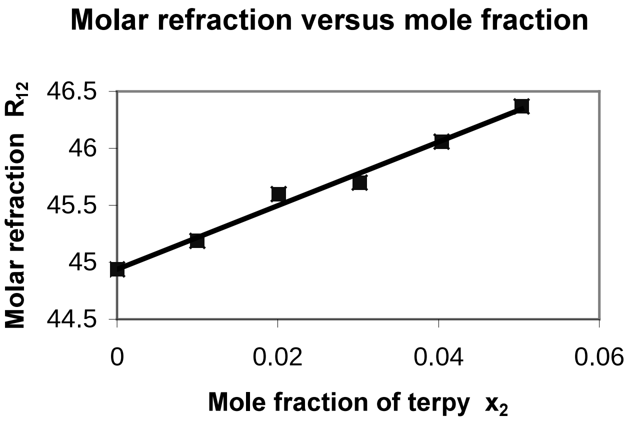


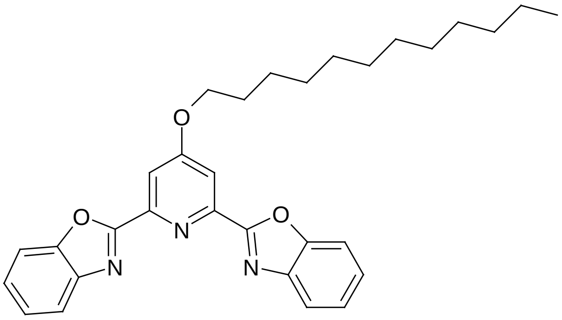
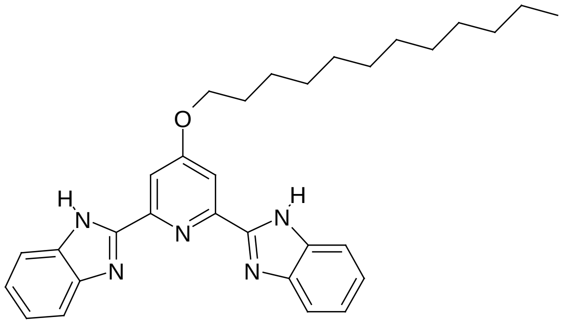
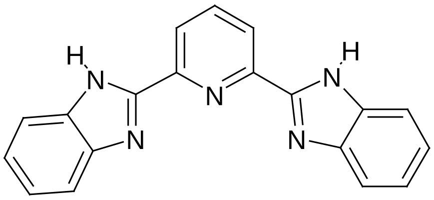
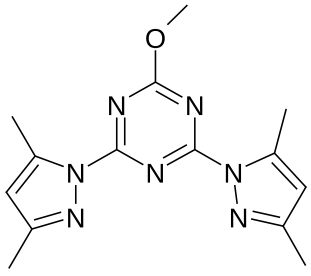
***Figure 2-9.*** *The molar refraction of a mixture of TBB(1) and terpy(2) against different mole fractions of terpy in TBB.*

A preliminary value for the refractive index of terpy has been found to be 1.75. This method is easy to use on any substance that can be dissolved in a diluent with known molar refraction. The method will be used to find the refractive index for new ligands in order to calculate the polar contribution to the solubility parameters used in the model described in paragraph 2.2 above.

## 2.4 New Ligands

During this year some different ligands, containing the same active site as the previously studied oligopyridines and triazines, have been investigated. The new ligands are listed in Table 2-4.

**Table 2-4. New nitrogen containing molecules studied this semester. All provided by the University of Reading except 2,6-bis-(benzimidazolyl)-pyridine provided by Aldrich Chem Co.**

| | |
|---|---|
|  |  |
| 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine (BODO) | 2,6-bis-(benzimidazol-2-yl)-4-dodecyloxylpyridine (BIDO) |
|  |  |
| 2,6-bis-(benzimidazolyl)-pyridine (BIP) | 2,4-bis-(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine (DIMPMO) |

Of the new ligands only BODO could be dissolved in *tert*-butylbenzene (TBB), to a concentration of 0.01M, without the addition of 2-bromodecanoic acid. At 0.1M 2-bromodecanoic acid a concentration of 0.02M could be obtained with all substances examined.

### 2.4.1 Extraction behaviour of the new ligands

The extraction of americium and europium from nitric acid was examined for all ligands but for all of them (except BODO) precipitation limited the nitric acid concentration. For BIP no results have been obtained because of precipitate formation even at very low nitric acid concentration. For BIDO there are no results for nitric acid concentrations above 0.01M. The previously studied terpyridine/2-bromodecanoic acid system was used as reference system when evaluating the results for the new molecules.

Extraction with BODO gave higher D-values for americium and higher Am/Eu separation than terpyridine, see Figure 2-10. At 0.01M $HNO_3$ the D-value for americium was 11 for BODO and 5 for terpyridine and the separation factor ($SF=D_{Am}/D_{Eu}$) was 36 for BODO compared to about 7 for terpyridine. The slope of the nitric acid dependence, on a log-log scale, is approximately -3 for the whole concentration range studied. Constant ion strength in the aqueous phase of 1 M H,$NaNO_3$ was used in all extraction experiments.

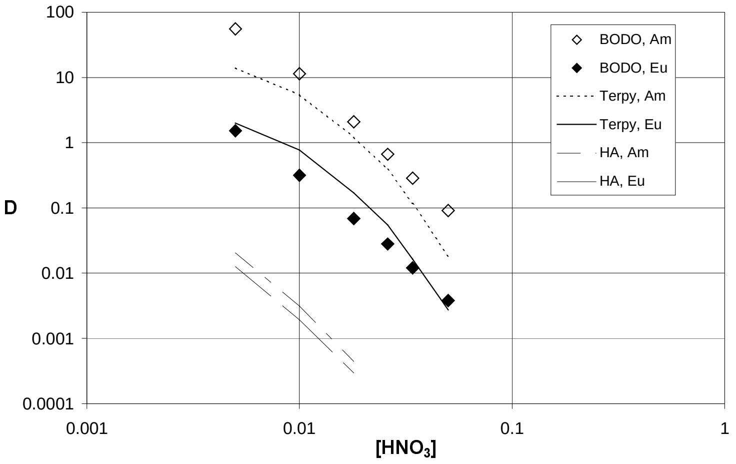


***Figure 2-10.*** *Metal extraction from nitric acid with 0.02M BODO and 1M 2-bromodecanoic acid (HA) in tert-butylbenzene (TBB). Curves for extraction with 0.02M terpyridine/1M HA in TBB and 1M HA in TBB added for comparison.*

In the terpyridine system, distribution ratios and the separation factor decrease as the nitric acid concentration increases due to protonation and transfer of reagent into the aqueous phase. This is apparently not the case with BODO since the metal extraction decreases linearly with nitric acid concentration in a log-log plot.

For the other molecules, BIDO and DIMPMO, the distribution ratios are lower ($D_{Am}$ is 0.06 and 1, respectively, at 0.01M $HNO_3$ compared to 5 for terpy) and the Am/Eu separation slightly better than with terpyridine (7.2 and 13 compared to 7), see Figure 2-11.

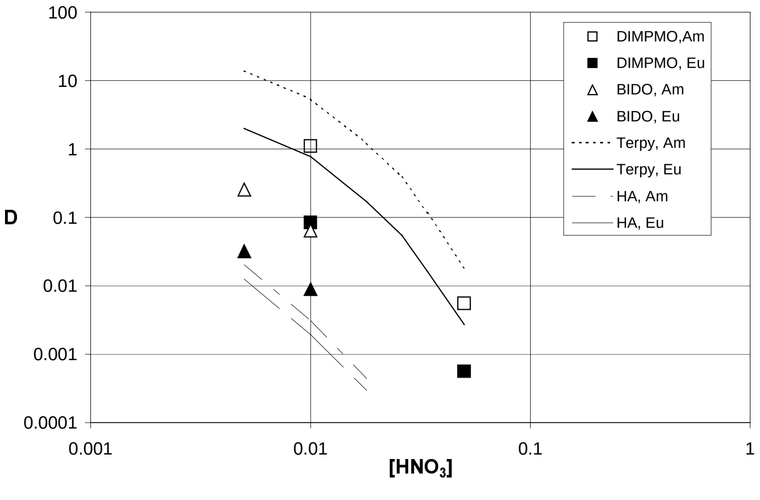


***Figure 2-11.*** *Metal extraction from nitric acid with 0.02M ligand and 1M 2-.bromodecanoic acid (HA) in tert-butylbenzene (TBB). Curves for extraction with 0.02M terpyridine/1M HA in TBB and 1M HA in TBB added for comparison.*

The fact that the solubility, americium extraction and americium/europium separation is higher for BODO than for BIDO is interesting because the introduction of more oxygens in the active site of the molecule was expected to give a lower separation. The question is whether the oxygens coordinate directly to the metal or if the difference in extraction behaviour is due to the change in electron configuration on the coordinating nitrogens. This needs to be studied further.

### 2.4.2 Physical and chemical properties of new ligands

If the investigations of the basic thermodynamic properties of terpyridine were easily performed, some problems arose when applying the same method for BODO. It was not possible to dissolve the molecule in TBB in a desirable concentration. In finding a better solvent different factors have to be 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. Nitrobenzene, dichlorobenzene and trichloroethylene (TRI) all worked and did not (or only partially) absorb at the same wavelengths as BODO.

In contacting 0.01M BODO (dissolved in TRI) with aqueous phases (1M H,$NaNO_3$ at different pH), no transfer of BODO into the aqueous phase was observed. Using a ~7M $HNO_3$ solution as aqueous phase, made something happen (change of colour of the aqueous phase and some transfer of BODO (or part of BODO) into the aqueous phase). What really happened will be further investigated, but hypotheses involve ion pair extraction and/or oxidation of the molecule itself.

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

A few measurements of the density of BODO has been performed and more will follow. The refractive index and subsequently the polarity of BODO, will also be calculated as soon as a good value of the density has been determined.

## 2.5 Temperature dependence of synergic extraction with 2-bromodecanoic acid and nitrogen bearing ligands

Synergistic extraction experiments have been performed using combinations of 2-bromodecanoic acid with terpyridine and TPTZ respectively in different organic solvents. The extraction/separation of Am and Eu was investigated at 8 different temperatures ranging from 15 to 45 degrees centigrade. Results so far indicate that the extraction is temperature-dependant. Further results will be published early next year (2002).

# 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 (D)
- 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)

# 4 Meetings and lectures

**Educational visit to Oskarshamn and Äspö,** Sofie Andersson and Mikael Nilsson visited (with other PhD students from the department) CLAB and Äspö.

**EU Cluster Meeting on Partitioning,** Madrid 3-8 April. Jan-Olov Liljenzin and Sofie Andersson attended.

**Symposium on Separation,** Stockholm 19 April, Jan-Olov Liljenzin and Sofie Andersson attended as invited speakers. Christian Ekberg, Åsa Enarsson, Mikael Nilsson and Gunnar Skarnemark also attended.

**ITU Summer school on Actinides,** Karlsruhe 19-24 June. Sofie Andersson and Mikael Nilsson attended a summer school on actinides.

**166th PTB Seminar: Importance of Traceable pH Measurements in Science and Technology,** Braunschweig 24-25 September. Sofie Andersson and Mattias Olsson (PhD student from the department of Nuclear Chemistry, Chalmers) attended as invited speakers.

**Educational visit to Studsvik,** 5 October**.** Sofie Andersson, Mikael Nilsson and Gunnar Skarnemark visited (with other PhD students from the department) Studsvik.

**EU Cluster Meeting on Partitioning,** Marcoule 9-12 October. Jan-Olov Liljenzin attended.

**EURATOMs 6th Framework Program,** Stockholm 30 November. Sofie Andersson, Mikael Nilsson and Gunnar Skarnemark attended.

# 5 Articles and publications

Sofie Andersson and Mikael Nilsson have been working with articles to ISEC 2002, but they will not be published until next year [AND 02][NIL 02].

Christian Ekberg, Sofie Andersson and Mattias Olsson have written the following article on the uses of pH-electrodes in the field of nuclear chemistry:

- Ekberg, C., Andersson, S., Olsson, M., *Uses of pH electrodes in Nuclear Chemistry*, invited for publication in Analytical and Bio Chemistry, 2002.

Åsa Enarsson has finished her studies and published her licentiate thesis with the following title:

- Enarsson, Å., *Studies of Extraction and Separation of Am(III) and Eu(III) using Synergistic Extraction with Nitrogen Coordinating Ligands and 2-Bromodecanoic Acid*, 2001

An abstract is given in appendix I. One copy of the thesis will be attached to the original of this report.

# 6 Future work

Investigation of new ligands.

Further investigation of what happens with BODO at low pH.

Determination of the density of BODO.

The effect of nitrate concentration of the extraction properties of BODO.

Temperature dependence of the extraction properties of BODO.

Results from temperature-experiments with terpyridine will be published.

Mixer-Settler, process testing. A French diploma worker will join the group on this subject.

Alternatives to alfabromodecanoic acid.

Regeneration of terpyridine.

Goodness numbers for extracting agents.

# 7 References

[AND 02] **Andersson S, Ekberg C, Liljenzin J-O, Skarnemark G, 2002.** Determination of Acidity Stability Constants of 2,2':6',2''-terpyridine from Liquid-Liquid Distribution Data, proceedings from ISEC'2002, in press.

[EKB 99] **Ekberg C, 1999.** Uncertainties in Actinide Solubility Calculations. Illustrated Using the Th-OH-$PO_4$ System. PhD thesis, Dept of Nuclear Chemistry, Chalmers University of Technology, Göteborg, Sweden.

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[MEI 00] **Meinrath G, Ekberg C, A. Landgren and J-O. Liljenzin, 2000.** Talanta 51(2) 231-246.

[NIL 02] **Nilsson M, Liljenzin J-O, Ekberg C, 2002.** Modelling the Influence of Organic Phase Composition on the Extraction of Trivalent Actinides, proceedings from ISEC'2002, in press.

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# Appendix

### Studies of Extraction and Separation of Am(III) and Eu(III) using Synergistic Extraction with Nitrogen Coordinating Ligands and 2-bromodecanoic acid*

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## Abstract

Transmutation of the long-lived actinides in spent nuclear fuel to short-lived or stable nuclides will greatly reduce the long-term radiotoxicity of the waste. For the transmutation to be effective the actinides have to be separated from the rest of the waste.

The separation of trivalent actinides from lanthanides is a somewhat cumbersome step in the separation process because of the similarities in their chemical behaviour. However, the trivalent actinides have a stronger tendency to form complexes with soft donor ligands, e.g. ligands coordinating to the metal through nitrogen or sulphur, than the lanthanides and this property can be used to separate the two groups.

In this work the extraction of americium and europium from nitric acid by a number of nitrogen coordinating heterocyclic ligands in synergy with 2-bromodecanoic acid in *tert*-butylbenzene has been studied. Am(III) and Eu(III) has been used as representatives for the trivalent actinides and lanthanides respectively.

The ligands studied all share the same active site with three aromatic nitrogens, oligopyridines or triazines, to which the metal is assumed to coordinate. Ligands with four and five aromatic nitrogens were also studied. The basicity of the ligands were measured and compared to the extraction experiments.

At low acidities the ligands with four and five pyridine rings showed higher metal extraction and Am/Eu separation but the effect was lost as the nitric acid concentration was increased probably due to protonation. The quinolinyltriazines examined showed no enhancement in extraction compared to 2-bromodecanoic acid alone. For the ligands with three aromatic nitrogens the metal extraction decreased with the basicity of the ligand.

*Keywords*: solvent extraction, separation, transmutation, synergism, actinide, lanthanide, Am, Eu, oligopyridines, triazines, basicity

*Licenciate Thesis, Chalmers Univerity of Technology, Department of Nuclear Chemistry, Göteborg 2001