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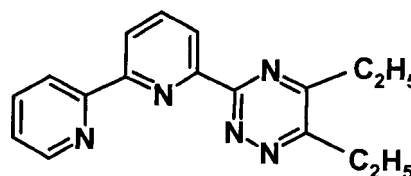
SEPARATION OF Am(III) FROM Eu(III) BY MIXTURES OF TRIAZINYLBIPYRIDINE AND BIS(DICARBOLLIDE) EXTRACTANTS. THE COMPOSITION OF THE METAL COMPLEXES EXTRACTED

Jerzy Narbutt, Jadwiga Krejzler

Reprocessing of spent nuclear fuels by the PUREX process leads to the formation of high active raffinates which contain nuclear wastes, *i.e.* fission products and minor actinides (MAs). In the future, the wastes will be vitrified and disposed of into deep underground repositories. The most important radiotoxicity of the waste, still significant even after more than 10^4 years, is related to the presence of MAs. Therefore, the elimination of these MAs from the nuclear wastes will simplify the selection of geological sites for the underground repositories. After partitioning from the fission products, the MAs can be transmuted into stable or short-lived fission products, using, for example, the future Accelerator Driven System facility. The research in Partitioning & Transmutation domain is an important programme in Europe and in several nuclear countries in the world [1]. The partitioning processes of MAs are the subject of an integrated project (IP) EUROPART realized in the 6th Framework Programme of EU within EURATOM [2]. The team from the Institute of Nuclear Chemistry and Technology (INCT) is one of 25 partners participating in the realization of the project.

The separation of trivalent actinides, in particular americium and curium, from lanthanides is an important step in an advanced partitioning process for future reprocessing of spent nuclear fuels. Since the trivalent actinides and lanthanides have similar chemistries, it is rather difficult to separate them from each other. The use of soft donor (N and S) ligands makes it possible to separate the two groups of elements, probably because of the more covalent character in the complexes with actinides compared to the lanthanides [3].

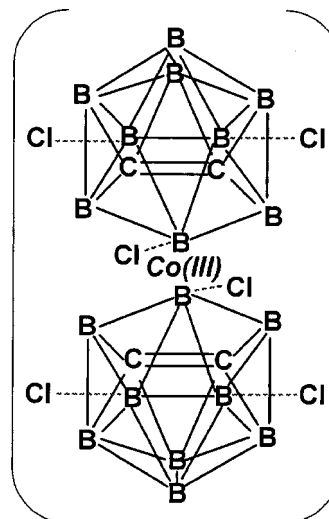
Very efficient polyheterocyclic extractants containing pyridine and triazine rings have been proposed for the partitioning of minor actinides from lanthanides [4,5]. Numerous extractants of this type were synthesized [6]. One of them, 6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (diethylhemi-BTP; Scheme 1), is the extractant studied in the present work. The diethylhemi-BTP was already



Scheme 1.

tested as an extractant of Am(III) and Eu(III) from nitric acid solutions, separating the metals in the presence of a co-extractant, 2-bromodecanoic acid [7]. Large hydrophobic anions of the carboxylic acid and neutral diethylhemi-BTP molecule(s) form extractable heteroleptic complexes with the metal ions. However, the rather high pK_a of this carboxylic acid (3.7) [8] requires its high concentration (1 M) to reach a significant extraction of Am(III) at higher acidities.

The aim of our work was to study solvent extraction of Am(III) and Eu(III) in a similar system with diethylhemi-BTP and COSAN: protonated bis(chlorodicarbollido)cobalt(III) or commo-3,3-cobaltabis(8,9,12-trichloro-1,2-dicarboclosododecaborane)ic acid (Scheme 2) – another hydrophobic



Scheme 2.

synergent of anionic character, more acidic than 2-bromodecanoic acid. The salts of chloroprotected COSAN – extremely hydrophobic, highly soluble in organic solvents, of high chemical and radiation stability, and completely dissociated in polar solutions – are able to co-extract the metals at low pH and at much lower concentrations [9]. The heterocyclic (pyridine/triazine) extractants with the chloroprotected COSAN were already tested for solvent extraction of alkaline earths [10], but the extraction of Am(III) and Eu(III) in systems of this type was not studied yet.

The present research was focused on both the determination of conditions for the separation of $^{241}\text{Am(III)}$ from ^{152}Eu in aqueous nitrate solution by using a synergistic extraction system diethylhemi-BTP–COSAN, and on the modelling of the

Table. The “best fit” parameters in Eq. (1), $b_i \pm s(b_i)$ (standard deviation).

Parameter	b_0	b_1	b_2	b_3
Am(III)	6.28 ± 1.03	0.70 ± 0.25	2.02 ± 0.27	1.99 ± 0.27
Eu(III)	4.53 ± 1.03	0.59 ± 0.24	1.98 ± 0.13	1.77 ± 0.13

process by slope analysis. The knowledge of the composition of the extracted metal species is crucial both for understanding the phenomena involved and for optimizing the process conditions. In order to conclude on the composition of the extracted complexes, we systematically studied the dependence of the distribution ratio, D , of Am(III) and Eu(III) on the concentration of diethylhemi-BTP (**B**) and of COSAN-H (**HA**) in the organic phase (1-octanol), the aqueous phase being 1 M NaNO_3 pH \approx 4, at 25.0°C. The initial organic-phase concentration of **B** varied from 0.010 to 0.025 M (series with the same initial $[\text{B}]$ values were used), while that of **HA** was always lower. The D_{Am} and D_{Eu} values were determined for the same aqueous solutions, pre-equilibrated with the proper organic phase. The drop in pH of the initial aqueous phase, caused by **HA** present in the organic phase, was balanced by adding small amounts of dilute NaOH solution. The final pH was in the range of 3.8–4.2, so the effect of pH on D had to be considered as well. The details of the experiment and the numerical data are available from the EUROPART reports [11,12].

Strong interactions between the co-extractants were observed: a yellow **BHA** adduct (1:1) precipitated upon contacting the liquid phases. This precipitate was removed, and the total concentrations of the co-extractants in the organic phase at equilibrium, $[\text{B}]_{\text{t.o}}$ and $[\text{A}^-]_{\text{t.o}}$, were determined by UV spectrophotometry [11,12]. The distribution ratios of both metal ions increased with increasing $[\text{B}]_{\text{t.o}}$ and $[\text{A}^-]_{\text{t.o}}$, and also changed with minute changes in pH, but the separation factor, $\text{SF}_{\text{Am/Eu}} = D_{\text{Am}}/D_{\text{Eu}}$, remained nearly constant, equal to 30–40, within the whole range of the concentrations studied. These interactions made the common slope analysis difficult, because we were not able to study the dependence of D on one parameter (concentration) at fixed values of the other parameters. This lack of full slope analyses in other studies on similar systems [7,10] was probably due to the same rea-

son. To overcome this difficulty, multi-regression analysis of the solvent extraction data was carried out.

Thermodynamic activities of the extractants (**B** and **HA**), necessary for the slope analysis, can be replaced by the concentrations of their free molecules in a given phase, but even the latter could not be directly determined under the conditions of the experiment. Therefore, we assumed that total concentrations in the organic phase, $[\text{B}]_{\text{t.o}}$ and $[\text{HA}]_{\text{t.o}}$, were good estimates.

The following function

$$\log D = b_0 + b_1 \cdot \text{pH} + b_2 \cdot \log[\text{B}]_{\text{t.o}} + b_3 \cdot \log[\text{HA}]_{\text{t.o}} \quad (1)$$

was fitted to 45 data points for Am(III) and 45 data points for Eu(III). The results are shown in Table. For all the data points: $|\log D_{\text{i,calc}} - \log D_{\text{i,exp}}| < 0.3$.

Figure 1 shows the distribution of the experimental $\log D_{\text{Am}}$ values (recalculated for pH=4) around the “best fit” plane (Eq. (1) pH=4). For a better clarity, the distribution has also been shown

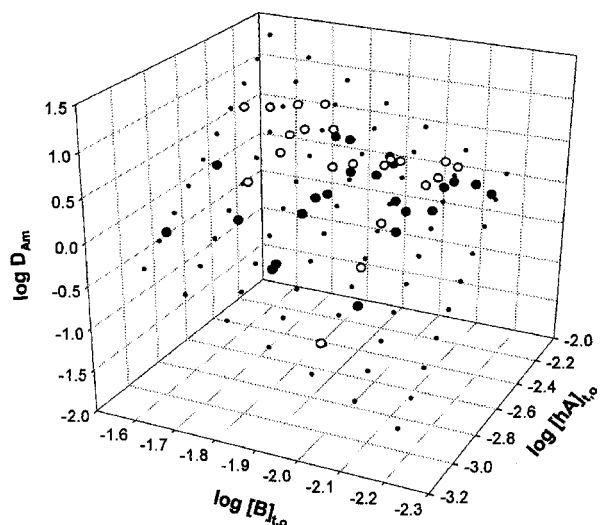


Fig.1. 3D dependence of $\log D_{\text{Am}}$ on the equilibrium total concentrations of the extractants, $\log[\text{B}]_{\text{t.o}}$ and $\log[\text{A}^-]_{\text{t.o}}$ for pH=4. Circles denote the pH-corrected experimental values and dots – the calculated “best fit” values. Open circles denote the values above the “best fit” plane, closed circles – the values below the plane.

in the form of 2D graphs, *i.e.* as functions of the concentration of only one extractant at a fixed concentration of the other (Fig.2). Similar graphs for the $\log D_{\text{Eu}}$ values are not shown.

Both stoichiometric coefficients b_2 and b_3 are close to the integer 2. It is noteworthy that b_3 is not equal to 3 as could be expected for the trivalent cations. In order to have the total charge zero on the extracted complexes with the two A^- anions only, which is an important condition for their efficient extraction, we assumed that one nitrate anion enters the coordination sphere of each metal ion. Similar structures were observed elsewhere [7].

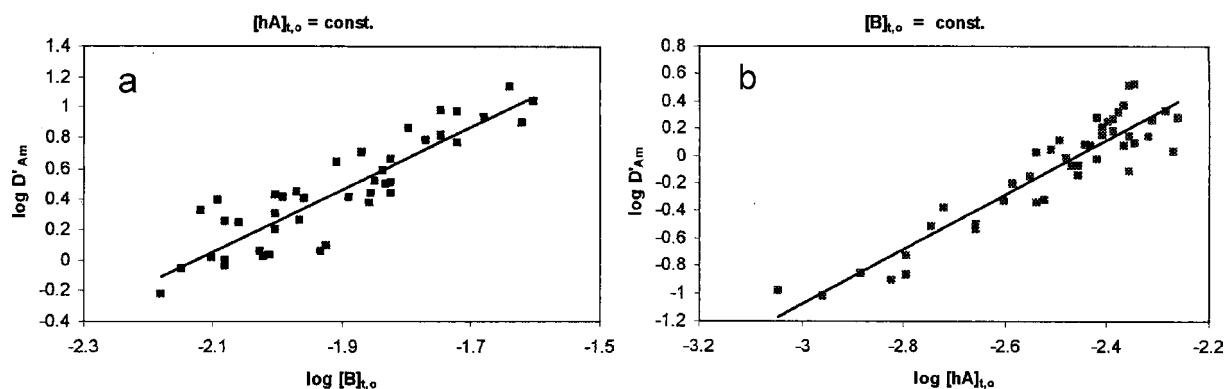
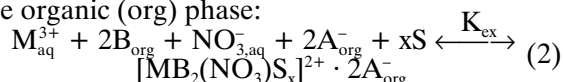


Fig. 2. 2D dependences of $\log D'_{Am}$ values: (a) on $[B]_{l,o}$ at $[A^-]_{l,o} = 0.004$ M and $\text{pH} = 4$, (b) on $[A^-]_{l,o}$ at $[B]_{l,o} = 0.015$ M and $\text{pH} = 4$. The points denote the experimental values corrected for: (a) pH and $[HA]$, (b) pH and $[B]$. Straight lines are the calculated "best fit" functions.

Assuming tridentate coordination by the **B** ligands, and bidentate – by NO_3^- , we can expect that with $\text{CN}_{Am, Eu} \approx 9$ no more than one molecule of solvent (water or octanol) enters the inner coordination sphere of the metal (M) ions, and the two large A^- anions remain in the outer sphere. The composition of the M(III) complexes extracted to the organic phase is $[\text{MB}_2(\text{NO}_3)_x\text{S}_x]^{2+} \cdot 2A^-$, where S denotes the solvent, and $x=0$ or 1.

The following equation describes extraction of the M(III) ions from the aqueous nitrate (aq) to the organic (org) phase:



In the presence of strong acid, HA , fully dissociated in the organic phase the base, **B**, in the same phase becomes protonated to a certain extent. This explains why the pH affects the equilibrium (2), therefore it also influences the D values as expected from Eq. (1). The detailed analysis of this problem will be done elsewhere.

In the synergistic system diethyl*hemi*-BTP–2-bromodecanoic acid [7], the distribution ratio, D , of the M(III) ions in the two-liquid-phase system decreased with the third power of HNO_3 concentration and increased with increasing concentration of **B**, and the observed SF_{Am-Eu} values at the concentration of **B** comparable to those studied in this work were about 18. Hudson *et al.* concluded that the extracted Am(III) and Eu(III) complexes contained three 2-bromodecanoate anions and one **B** molecule in the inner coordination sphere of the metal ion [7]. On the contrary, in the present system, the COSAN anion, A^- , does not enter the inner coordination sphere and acts only as a counter anion – the phase transfer reagent which neutralizes the charge of cationic complex(es) by formation of ion-pair species. We conclude that the higher SF_{Am-Eu} values in the system studied than those observed in the system with the three inner-sphere carboxylate ligands, which allow only one **B** ligand to coordinate the metal ions, are due to the greater number of the specific diethyl*hemi*-BTP ligands in the inner coordination sphere of the metal ions in the extracted complexes.

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