Interaction study between two extractants involved in the DIAMEX-SANEX process.

B. Gannaz(1), C. Hihi(1), X. Heres(1), F. Testard(2), G. Cote(3)

(1) CEA Valrô, DEN/DRCP/SCPS/LCSE, BP 17171, 30207 Bagnols-sur-Cèze Cédex, France
(2) CEA Saclay, DEN/DRECAM/SCM/LIONS, 91191 Gif-sur-Yvette Cédex, France
(3) ENSCP, Laboratoire d’Electrochimie et de Chimie Analytique (UMR 7575)
11, rue Pierre et Marie Curie, 75231 Paris Cédex 05, France
benoit.gannaz@cea.fr

Abstract – In the frame of nuclear spent fuel reprocessing researches, separation of lanthanides(III) from actinides(III) is a key step. Among the R&D programs dealing with this step, currently developed by the CEA, one is based on separation by selective back-extraction of actinides(III) in DIAMEX-SANEX process. Trivalent actinide aqueous complexing agents are generally efficient in low acidic medium, but lanthanides are not extracted by malonamides in these conditions. To enhance the extractive capacity of the DIAMEX-SANEX solvent at low acidity, and avoid nitrate salt addition, an organo-phosphoric acidic extractant is added to the malonamide in Hydrogenated Tetra-Propylene (TPH). The extraction properties of the malonamide and alkyphosphoric acid mixture were investigated, as well as interactions between these extractants. In fact, the difficulties to explain synergism or antagonism observed in liquid-liquid extraction experiments, emphasize the need for both approaches, at molecular and supramolecular scales.

INTRODUCTION
The CEA has undertaken the development of the DIAMEX-SANEX process, which separates minor actinides from fission products in High Level Liquid Waste (PUREX raffinate). DIAMEX leads to the co-extraction of actinides(III) and lanthanides(III), the separation of which, achieved by selective back-extraction of An(III), takes place in the SANEX process. The latter requires an organic layer containing an acidic extractant in addition to the malonamide used in DIAMEX. Selective back-extraction of An(III) is enabled by a complexing aqueous system consisting of polyaminocarboxylic and hydroxycarboxylic acids. The diamide, which co-extracts metallic cations and nitrate anions from the aqueous phase, is the NN’-dimethyl-NN’-dioctyl-hexyl-ethoxy-malonamide (DMDOHEMA). Different dialkylphosphoric acids, which extract cations by proton exchange, were studied, such as bis-1,3-dimethylbutylphosphoric acid (HBDMBP) or dihexylphosphoric acid (HDPH). Liquid-liquid extraction of americium(III) and europium(III) traces from diluted nitric acid showed that pH variation induced synergism or antagonism. As this mix did not have a course behavior, a better understanding of its component interactions seemed essential. The study especially focused on liquid-liquid extraction, supra-molecular structure, aggregation and micellization.

EXPERIMENTAL PROCEDURE

Liquid-liquid extraction
DMDOHEMA, HBDMBP, and the mixture DMDOHEMA-HBDMBP were diluted in TPH, and their respective concentrations were measured by titration. Pre-equilibrated organic phases were contacted with low nitric acid aqueous solutions containing traces of 152Eu(III) and 241Am(III), at 25°C. Phase activities were checked by gamma counting of aliquots. Initial pH was adjusted by HNO3 addition and variable ionic strength was obtained by LiNO3 addition.

Infrared (IRTF)
IRTF spectra were recorded on a Brucker Equinox 55 spectrophotometer.

Small Angle Neutron Scattering (SANS)
Experiments were performed at the LLB (Laboratoire Léon Brillouin, Saclay). All samples were diluted in deuterated dodecane. First adjustments of experimental data were obtained in collaboration with LIONS’s scientists.
LIQUID-LIQUID EXTRACTION RESULTS

Results are given here, as a preliminary study, without supramolecular consideration.

Extraction by DMDOHEMA-HBDMBP

$^{152}$Eu(III) and $^{241}$Am(III) extraction was performed by mixtures of DMDOHEMA and HBDMBP in TPH, with respective concentrations as 0.36 mol.L$^{-1}$ and 0.31 mol.L$^{-1}$ or 0.72 mol.L$^{-1}$ and 0.31 mol.L$^{-1}$. Figure 1 jointly presents results obtained for $^{241}$Am(III) extraction with a mixed system (HBDMBP 0.31 mol.L$^{-1}$ plus DMDOHEMA 0.72 mol.L$^{-1}$ in TPH) and with solely extractant systems (HBDMBP 0.3 mol.L$^{-1}$ and DMDOHEMA 0.65 mol.L$^{-1}$, in TPH).

Fig. 1. Effect of equilibrium proton concentration in the aqueous phase on the distribution ratios of $^{241}$Am(III) for different extracting systems, at variable ionic strength, at 25°C.

As appearing on Fig. 1, the mixed extractant system presents an antagonism for $^{241}$Am(III) extraction at low nitric acidity but a synergism at higher acidity. The same tendencies were observed for $^{152}$Eu(III) extraction.

In these preliminary studies, the following general reaction was investigated step by step.

$$M^{3+} + x[(\text{L})_b] + y[(\text{HP})_b] + z\text{NO}_3^- + w\text{HNO}_3 \longrightarrow M(x[(\text{L})_b])_y[(\text{HP})_b]_{y-3}[\text{NO}_3]_z[(\text{HNO}_3)_w] + (3-z)\text{H}^+$$  \hspace{1cm} (1)

where L is DMDOHEMA, and HP is HBDMBP.

A first approach consisted in trying to get the reaction parameters from simple systems. Below is presented an attempt based on single extractant systems.

Extraction by DMDOHEMA

For a given concentration of nitric acid (3.1 mol.L$^{-1}$), the log-log variation of the distribution ratios ($D_{\text{M}(\text{III})} = [\text{M}]_{\text{org}}/[\text{M}]_{\text{aq}}$) of $^{152}$Eu or $^{241}$Am with the initial concentration of DMDOHEMA followed a linear relationship with a slope close to 2. This is in agreement with former extraction studies on DMDOHEMA analogues [1,2]. In the case of metal trace extraction by DMDOHEMA up to [XNO$_3$]$^-$=3 mol.L$^{-1}$ (X=H$^+$ or Li$^+$), the plot of log(D$_{\text{M}(\text{III})}$) versus log([XNO$_3$]$^-$) is linear with a slope of 3, indicating the involvement of 3 nitrate anions in the extracted complex. Without considering the aggregation of DMDOHEMA, the following equilibrium is proposed:

$$M^{\text{III}} + 2\text{NO}_3^- + w\text{HNO}_3 \longrightarrow M(\text{NO}_3)_w(\text{HNO}_3)_zL_z$$  \hspace{1cm} (2)

So far, experimental results did not allow w to be determined, but it is probably not null in binary media (HNO$_3$-XNO$_3$).

In equilibrium (1), $x=2$ and $\alpha=1$ (even if dimers and tetramers are present in concentrated DMDOHEMA solutions).

Extraction by HBDMBP

For an initial HBDMBP concentration of 0.31 mol.L$^{-1}$ in TPH, log variation of D$_{\text{M}(\text{III})}$ ($^{152}$Eu, $^{241}$Am) with the pH exhibited a linear behaviour with a slope of 3. This result agrees with the cation extraction mechanism by proton exchange for trivalent cations. At this concentration, HBDMBP exists under both monomer (HP) and dimer (HP)$_2$ forms so that the general following reaction may occur [3]:

$$M^{3+} + \frac{3 + v}{\beta}[(\text{HP})_b] \longrightarrow MP_v[(\text{HP})_b] + 3\text{H}^+$$  \hspace{1cm} (3)

where $\beta=1$ and $v=0$ for monomers and $\beta=2$ and $v=1$ for dimers, respectively.

Using the parameters provided by this preliminary study, as a first approach, the general reaction becomes:

$$M^{3+} + 2\text{NO}_3^- + \frac{3 + v}{\beta}[(\text{HP})_b] + w\text{HNO}_3 \longrightarrow M[(\text{HP})_b]_{y-3}[\text{NO}_3]_z[(\text{HNO}_3)_w] + (3-z)\text{H}^+$$  \hspace{1cm} (4)

where $\beta=1$ and $v=0$ for monomers and $\beta=2$ and $v=1$ for dimers, respectively.

Experiments in progress seem to confirm the existence of mixed complexes containing DMDOHEMA, BDMBP and NO$_3^-$ anions. Thus z is probably equal to 1. This would give the best explanation for the -2 pH dependency of log(D$_{\text{M}(\text{III})}$) observed (Fig. 1)
Dealing with such a complicated system, liquid-liquid extraction results were not easily interpreted and called for complementary studies, like supramolecular ones [4].

SUPRAMOLECULAR STRUCTURE AND INTERACTIONS BETWEEN EXTRACTANTS

Infrared Spectroscopy
Systems such as DMDOHEMA/HNO₃/Eu(III), HBDMBP/HNO₃/Eu(III) and DMDOHEMA-HBDMBP/HNO₃/Eu(III) were investigated. The main information resulting from this study was that no strong interaction between HBDMBP and DMDOHEMA was discernible (Fig. 2).

Fig. 2 Stacked zooms of IRTF spectra showing no strong interaction in the extractants mixture but new bands in case of gel formation.

Absorption bands showed that europium was linked to oxygen atoms of P-O (P=O or P-O ⋯ H) when bonded to HBDMBP and of C=O when bonded to DMDOHEMA. Consequently, this enabled to discriminate the implication of one extractant from the other, in the extraction process. Gelification of organic phase occurred when increasing the concentration of extracted europium(III). The gel structure was significantly different from the solution one (Fig. 2) and seemed to be a tridimensional network of HBDMBP molecules, swollen by DMDOHEMA.

Small Angle Neutron Scattering
SANS experiments allowed the structure of organic phases to be determined. The first fit ever published of DMDOHEMA SANS experiments (Fig. 3) was realized and showed that DMDOHEMA aggregates into inverted micelles of 19 Å diameter, made up of 4 DMDOHEMA molecules, surrounding an aqueous core. Results obtained by SAXS show the same organization [5].

Fig. 3. Calculated (—) and experimental (o) SANS data of DMDOHEMA 0.7 mol.L⁻¹ in deuterated dodecane, contacted with water.

Other results are being analyzed, but yet we can presume that HBDMBP, and HDHP, form small aggregates in dodecane contacted with water. Apart from the gelification zone, europium does not seem to alter this organization. In case of mixed systems, phosphoric acids appeared to be weak modifiers of DMDOHEMA inverted micelles, when kept at lower concentration than the malonamide. Further exhaustive SANS and SAXS studies will confirm supramolecular organization.

CONCLUSION

As revealed by the liquid-liquid extraction experiments, such mixed extractant systems have a complicated behaviour. In our system conditions (selective back-extraction of Am(III) in the DIAMEX-SANEX process), extraction of Ln(III) is mainly due to HBDMBP. However DMDOHEMA seems to organize the organic solution into inverted micelles, not modified by HBDMBP. Thus, both molecular and supramolecular scale approaches are needed to understand the extractive behaviour of this system. Further experiments will aim at linking supramolecular organization of an organic phase to its liquid-liquid extraction properties.

REFERENCES

1. L. Nigond, Propriétés extractantes des N,N,N',N'-tetraalkyl-alkyl-2
propanediamides-1,3, *Thèse de doctorat*, Université de Clermont-Ferrand II. (1992)


3. see poster P2 31, E. Leclerc et al.
