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Use of electrospray ionization mass spectrometry for the characterization of actinide complexes in solution

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Abstract. In order to understand the mechanisms involved in the extraction processes developed to separate minor actinides, the “ligand/metallic cation” complexes formed in the organic phases are characterized by electrospray ionization-mass-spectrometry (ESI-MS). This paper deals with the application of the ESI-MS technique to analyze americium complexes in organic solutions. Two extractant systems are investigated: 1/ organic solutions of nitrogen polydentate extractants such as 6,6’-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBPs) and 2/ organic solutions composed of mixture of a malonamide and a dialkylyphosphoric acid.

1. Introduction
Electrospray ionization mass spectrometry (ESI-MS) was introduced in the 1980’s by Yamashita and Fenn [1]-[2] and applied to the analyses of large organic molecules. More recently, ESI-MS has been shown to be an appropriate technique to characterize metal-ligand complexes in solution [3]-[8]. ESI-MS is a fast and sensitive technique, which allows direct and continuous introduction of liquid samples. A notable difference from solution-phase methods is, however, that analytes must be charged and then transferred to the gas phase prior to their detection. It has been demonstrated recently, that no shift in equilibrium occurs during the electrospray ionization upon evaporation down to troplets size of about 1 μm [9]. Though, the use of this technique for solvent extraction studies remains still rare [10]-[14].

This paper deals with the application of the ESI-MS technique to analyze americium complexes in the organic phase of the solvent extraction processes developed to separate minor actinides An(III) from high level liquid waste. Two extraction systems are studied: 1/ organic solutions of nitrogen polydentate extractants such as 6,6’-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridines (BTBPs) [15]-[20] and 2/ organic solutions composed of mixtures of a malonamide and a dialkylyphosphoric acid dissolved in an aliphatic diluent [21]-[23]. The objectives of this work are to characterize the complexes existing in the organic phases by ESI-MS in order to understand the mechanisms involved in the extraction processes.

2. Experimental
2.1. Extraction/complexation conditions

2.1.1. **BTBP extractants.** Organic solutions consisted of either 0.005 M CyMe\textsubscript{4}-BTBP or 0.005 M C5-BTBP dissolved in cyclohexanone, nitrobenzene, or octanol. The organic solutions were pre-equilibrated with 1 M HNO\textsubscript{3} before the experiments. The aqueous solution consisted of 8.7x10\textsuperscript{-4} M \textsuperscript{241}Am in 1 M HNO\textsubscript{3}. The organic and aqueous solutions were mixed together in vials for 2h at 20\textdegree C in a thermostated shaking device to reach equilibrium of extraction. After mixing, the vials were centrifuged for 10 minutes at 6200 g and samples were taken from each phase.

Aliquots of 20 μL from each phase were diluted 1/50\textsuperscript{th} in acetonitrile/water (50/50) or (80/20) in the case of nitrobenzene before analysis by ESI-MS.

2.1.2. **DMDOHEMA-HDEHP extractants.** A solution containing 2.7x10\textsuperscript{-4} M HDEHP, 5.3x10\textsuperscript{-4} M DMDOHEMA, 2.4x10\textsuperscript{-3} M HNO\textsubscript{3} and 2.7x10\textsuperscript{-4} M of \textsuperscript{241}Am in ethanol was prepared and diluted 1/3\textsuperscript{rd} in acetonitrile/water (50/50) before analysis by ESI-MS.

2.2. Electrospray ionization mass spectrometry

The mass spectrometric measurements were recorded in positive ionization mode using a Bruker Esquire-LC quadrupole ion trap equipped with an electrospray interface installed in a glove box (Figure 1). A syringe infusion pump (Cole Palmer) delivered the sample at 90 μL/h to the electrospray source. Experimental conditions were positive ion mode, drying gas (N\textsubscript{2}): 5 L/min, nebulizer gas 5 psi, 250\textdegree C, ion spray voltage of 4000V, cap exit offset of 60V, skimmer 1 of 30 V (lower settings would have led to a loss of sensitivity and a higher setting would have led to fragmentation of the ions coming from the complexes), skimmer 2 of constant 10 V, trapdrive 50 for Am-BTBP complexes and 90 for Am-DMDOHEMA-HDEHP complexes. Spectra were acquired over a mass range of m/z 45-2200.

![Figure 1](image1.png)  
**Figure 1.** Electrospray ionization mass spectrometer Bruker Esquire LC.  
(a): before nuclearisation, (b): after setting up in a glove box.
3. Results

3.1. Extraction of Am(III) by nitrogen polydentate ligands

The nitrogen polydentate extractants were investigated in order to separate An(III) from Ln(III). Among these extractants, the BTBPs act as tetradentate ligands and show good selectivity towards trivalent actinides over lanthanides [15]-[20]. Complexes formed between BTBPs and actinides and lanthanides have been investigated using various experimental approaches such as crystal structures [24]-[25], UV-visible spectrophotometry [17], and liquid-liquid extraction [16] -[20]. Several different types of complexes have been discussed in the literature as being involved in the extraction of actinides and lanthanides by BTBPs in nitrate media. Am$^{3+}$ and Eu$^{3+}$ have the possibility to coordinate up to two BTBPs each, but it has been shown in solution that 1:1 and 1:2 (metal:extractant) complexes are formed [16]-[20] depending on the experimental conditions (nature of the diluent, extractant concentration, etc.).

The extraction of americium (III) from nitrate media by two BTBP molecules (2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]triazin-3-yl)-[2,2']bipyridine, CyMe$^4$-BTBP, and 6,6'-bis(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridine, C5-BTBP, Figure 2), diluted in three different diluents: nitrobenzene, octanol, and cyclohexanone, was investigated by ESI-MS in positive ionization mode.

![Figure 2. Structures of the BTBPs](image)

An example of the typical spectra obtained for each extractant is given in Figure 3, where complexes identified with Am are shown. The assignments of the americium complexes are reported in Table 1. Similar spectra for the other diluents selected are observed. The resulting species of interest are for both extractants, regardless of the diluent: L$_2$Am$^{3+}$ and L$_2$Am(NO$_3$)$_2^{2+}$, the latter being the main species.

<table>
<thead>
<tr>
<th>Based peak m/z</th>
<th>C5-BTBP-Am</th>
<th>CyMe$^4$-BTBP-Am</th>
</tr>
</thead>
<tbody>
<tr>
<td>[L$_2$M]$^{3+}$</td>
<td>476.7</td>
<td>436.6</td>
</tr>
<tr>
<td>[L$_2$M(NO$_3$)]$^{2+}$</td>
<td>746.0</td>
<td>685.8</td>
</tr>
</tbody>
</table>

These results show that, as for europium [26], americium is surrounded by two extractants, both in the case of C5-BTBP and CyMe$^4$-BTBP, which agrees with previous studies carried out by liquid-liquid extraction using octanol or cyclohexanone as the diluent [16]-[19]. This suggests that, in octanol, cyclohexanone, or nitrobenzene, the dominant complex is L$_2$M(NO$_3$)$_3$. During the ionization process and the transfer in the gas phase, this species is modified and transformed into L$_2$M(NO$_3$)$_2^{2+}$.
and \( L_2M^{3+} \) to form positive ions. The absence of \( L_2M(NO_3)_2^{2+} \) could suggest that one or two nitrate ions are probably in the outer coordination sphere. Indeed, if all nitrate ions were in the inner coordination sphere, a singly charged species (generally preferred in the gas phase) should be observed in the mass spectrum. On the other hand, the very low intensity of \( L_2M^{3+} \) in the mass spectra could suggest that at least one nitrate is bonded to the metal ions. If all nitrate ions were in the outer coordination sphere, the \( L_2M^{3+} \) ion should be the main ion detected in the mass spectra. Otherwise, the crystal structure of \( (C_2-BTBP)Ln(NO_3)_3 \) shows that europium is in 10-coordinate environment: it is bonded to three bidentate nitrates and a tetradentate BTBP [20]. Then, in \( (C_5-BTBP)_2M(NO_3)_3 \) or in \( (CyMe_4-BTBP)_2M(NO_3)_3 \), we could imagine that the metal ions should be bonded to two tetradentate BTBP ligands and one nitrate, the two others nitrates should be probably in outer coordination sphere. Thus, the ionization of these species would lead to a formation of the main ions: \( L_2M(NO_3)_2^{2+} \).

**Figure 3.** Positive ESI mass spectra of organic phase of BTBP in octanol after extraction. L stands for BTBP. Aqueous phase: \(^{241}\)Am \( 8.7 \times 10^{-4} \) M in HNO\(_3\) 1M. Organic phase: BTBP 0.005 M in octanol. Organic phase is diluted 1/50 th in acetonitrile/water before analysis. A. C5-BTBP, B. CyMe\(_4\)-BTBP. The peak at m/z =614.5, 622.4 and 626.4 (Fig. A) and 554.4; 562.4 and 566.3 (Fig. B) are assigned to parasite complexes formed in solution with Ca, Fe, and Zn due to the high complexing power of the BTBPs.

3.2. Extraction of Am(III) by DMDOHEMA-HDEHP solution

In the DIAMEX (Diamide Extraction) – SANEX (Selective Actinide Extraction) solvent extraction process [21]-[22], developed by the French Commissariat à l’Energie Atomique (CEA), the separation of the trivalent actinide ions, An(III), from the trivalent lanthanide ions, Ln(III), is accomplished by using a mixture of a diamide and a dialkylphosphoric acid dissolved in an appropriate aliphatic diluent. The \( N,N'\)-dimethyl-\( N,N'\)-dioctylhexylethoxymalonamide (DMDOHEMA, Figure 4) and the di-n-ethyl-2hexylphosphoric acid (HDEHP, Figure 4) are among the possible choices for the extractant mixture. Under the highly acidic conditions of the aqueous phase, both Am(III) and Ln(III) are co-extracted by the diamide. The separation/recovery of the An(III) is then accomplished in a subsequent step where the An(III) are selectively stripped from the organic phase. The extraction of Ln(III) and Am(III) either by the two extractants alone, or by their mixtures in \( n\)-dodecane has recently been investigated under a variety of aqueous and organic phase conditions [14],[23],[27]-[28].
The extraction of Ln(III) and An(III) by mixtures of the two extractants indicates a synergism at 1M nitric acid (Figure 5). Gannaz et al. interpreted the extraction data as resulting from the formation of mixed 'dialkyl phosphoric acid – malonamide' species in the organic phase [23].

To investigate the possible formation of a mixed DMDOHEMA-HDEHP species, the extraction of neodymium by solutions containing the mixture 0.3 M HDEHP and 0.65 M DMDOHEMA in n-dodecane was previously studied in the presence of two different aqueous solutions: Nd(NO₃)₃ in 0.1 M HNO₃ or in 1 M HNO₃ + 2 M NaNO₃ [14]. The ESI-MS results showed that the species formed in the organic phases were essentially the same for the two aqueous phases used to extract Nd³⁺. Two types of species were observed: Nd-DMDOHEMA and mixed Nd-DMDOHEMA-HDEHP species.

![Figure 4. Structures of the DMDOHEMA and HDEHP](image)

**Figure 4.** Structures of the DMDOHEMA and HDEHP

![Figure 5. Americium extraction (Dₐm) vs. aqueous nitric acid concentration. Organic phases: red 0.3M HDEHP in dodecane, blue 0.7 M DMDOHEMA in dodecane, black 0.7 M DMDOHEMA + 0.3 M HDEHP in n-dodecane.](image)

**Figure 5.** Americium extraction (Dₐm) vs. aqueous nitric acid concentration. Organic phases: red 0.3M HDEHP in dodecane, blue 0.7 M DMDOHEMA in dodecane, black 0.7 M DMDOHEMA + 0.3 M HDEHP in n-dodecane.

To pursue this study, Am(III) complexes formed with the mixture HDEHP-DMDOHEMA were investigated by ESI-MS. However, in order to analyze metal-ligand complexes by ESI-MS, their relative concentrations in solution must be sufficient (i.e. > 1% of the total ligand concentration). Otherwise, the decrease of the ligand concentration leads to a decrease of the distribution ratio, and subsequently to a decrease of the complex proportion in the organic phase. To avoid the handling of concentrated americium solutions and to get information about Am complexes, experiments were performed in homogeneous phase. Solutions containing HDEHP, DMDOHEMA, HNO₃ and ²⁴¹Am in ethanol were prepared and analyzed by ESI-MS. The mass spectra show, as for Nd extraction, the presence of DMDOHEMA-Am and mixed DMDOHEMA-HDEHP-Am complexes (Figure 6). The assignment of the species is reported in Table 2, where D stands for the malonamide and A for the anion of the organophosphoric acid, respectively.
As for Ln extraction, mixed Am-HDEHP-DMDOHEMA complexes are observed. From MS data, the complexes formed can be written as $D_yAmA_3(NO_3)$ or $D_yAmA_3$ (with $y \leq 5$) for the mixed complexes. Thus, Am and Ln complexes seem to have the same stoichiometry which is consistent with liquid-liquid extraction data [23].

**Figure 6.** Positive ESI mass spectrum of solution containing $5.3 \times 10^{-4}$ M DMDOHEMA, $2.7 \times 10^{-4}$ M HDEHP, $2.4 \times 10^{-3}$ M $HNO_3$ and $2.7 \times 10^{-4}$ M of $^{241}Am$ in ethanol. D and A represent DMDOHEMA and DEHP, respectively.

**Table 2.** $m/z$ ratio and species assignment in the positive ESI-MS data for the HDEHP-DMDOHEMA-Am$^{3+}$ system in ethanol. (D stands for DMDOHEMA and HA for HDEHP)

<table>
<thead>
<tr>
<th>Species</th>
<th>Base peak m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[D_3Am]^{3+}$</td>
<td>563.3</td>
</tr>
<tr>
<td>$[D_4Am]^{3+}$</td>
<td>724.1</td>
</tr>
<tr>
<td>$[D_5Am]^{3+}$</td>
<td>884.2</td>
</tr>
<tr>
<td>$[D_2Am(NO_3)]^{2+}$</td>
<td>634.2</td>
</tr>
<tr>
<td>$[D_2Am(NO_3)]^{3+}$</td>
<td>875.8</td>
</tr>
<tr>
<td>$[D_2Am(NO_3)_2]^+$</td>
<td>1330.2</td>
</tr>
<tr>
<td>$[D_4AmA]^+$</td>
<td>763.8</td>
</tr>
<tr>
<td>$[D_2AmA]^+$</td>
<td>1005.1</td>
</tr>
<tr>
<td>$[DAmA]^+$</td>
<td>1366.1</td>
</tr>
<tr>
<td>$[DAmA(NO_3)]^+$</td>
<td>1106.8</td>
</tr>
<tr>
<td>$[D_2AmA(NO_3)]^+$</td>
<td>1588.4</td>
</tr>
<tr>
<td>$[D_3AmA]^+$</td>
<td>1847.9</td>
</tr>
</tbody>
</table>

**4. Conclusion**

Electrospray ionization - mass spectrometry was used to investigate actinide complexes in organic solutions of the solvent extraction processes. ESI-MS is a valuable approach for obtaining structural information about the complexes formed during solvent extraction experiments and can give information about the stability of the complexes in gas phase.

In the studied system, the predominant species in gas phase are consistent with the complexes observed by other techniques in solution. Nevertheless, although some features of the solution
structure may be preserved by the gas-phase ions such as complex stoichiometry, the nature of the coordination in the gas phase species ‘inner’ vs. ‘outer’ may be different than in the solution species, and rearrangement may occur between the solution and bare gas ion species. Thus, the correlation between gas phase ions and solution phase species is a topic of ongoing research.

Acknowledgments
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References
[27] Gannaz B 2007 CEA Report R6159