

## Use of Electrospray Ionization Mass Spectrometry (ESI-MS) for the characterization of complexes 'ligand - metallic cations' in solution

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**Abstract** – In the framework of nuclear waste reprocessing, separation processes of minor actinides from fission products are developed by the CEA. In order to understand the mechanisms involved in the extraction processes, the "ligand/metallic cation" complexes, formed in the organic phases are characterized by electrospray-mass-spectrometry (ESI-MS). This paper deals with the extraction of lanthanides (III) and americium (III) cations by an organic phase composed of a malonamide or / and a dialkyl phosphoric acid, diluted in an aliphatic diluent.

For the dialkyl phosphoric acid,  $\text{Ln}(\text{DEHP})_3(\text{HDEHP})_3$  complexes are observed and in the presence of a large excess of  $\text{Ln}(\text{NO}_3)_3$ , dinuclear species are also observed. For the malonamide extractant, it appears that the complexes formed in the organic phase are of the  $\text{Nd}(\text{NO}_3)_3\text{D}_x$  type, with  $2 \leq x \leq 4$ : their distributions depend on the ratio  $[\text{Ln}]/[\text{DMDOHEMA}]$ . When the two extractants are present in the organic phase, mixed 'Ln-malonamide-dialkyl phosphoric acid' species are observed.

The influence of several parameters, such as extractant concentration, solute concentration, aqueous acidity and the nature of the cations (lanthanides or americium) are studied.

## INTRODUCTION

Electrospray ionization mass spectrometry (ESI-MS) was introduced in the 1980's by Yamashita and Fenn [1,2] and applied to the analysis of large organic molecules. More recently, ESI-SM has been shown to be an appropriate technique to characterize metal-ligand complexes in solution [3-7]. 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 the time frame of electrospray ionization (milliseconds) is sufficiently short to prevent any equilibrium shift during the ionization process [8]. Though, the use of this technique for solvent extraction studies remains still rare [9-13].

This paper deals with the application of the ESI-SM technique to analyze metallic complexes in organic solutions of the DIAMEX (Diamide Extraction) – SANEX (Selective Actinide Extraction) solvent extraction process developed by the French Commissariat à l'Énergie Atomique (CEA) to separate the minor actinides An(III), from the high level liquid waste [14-17]. The separation of An(III) from the lanthanides (III) is an essential step, and is accomplished by using a mixture of a diamide and a

dialkylphosphoric acid dissolved in an aliphatic diluent. Under the highly acidic conditions of the aqueous phase, both An(III) and Ln(III) are extracted by the diamide. The separation/recovery of An(III) is then accomplished by contacting the loaded organic phase with an aqueous phase containing a complexing agent of actinides(III) in a low acidity aqueous phase. Under these conditions the diamide is completely ineffective as an extractant for metal cations, while the organophosphoric acid exhibits efficient extraction and significant selectivity for Ln(III) over An(III). The *N,N'*-dimethyl-*N,N'*-dioctyl hexylethoxy malonamide (DMDOHEMA, Figure 1) and the di(2-ethyl hexyl) phosphoric acid (HDEHP, Figure 1) are among the possible choices for the extractant mixture for the DIAMEX-SANEX process. The extraction of Ln(III) and Am(III) by the two single extractants and their mixtures in *n*-dodecane under a variety of aqueous and organic phase conditions has recently been investigated [16].

For HDEHP, the extraction reaction at tracer concentration level of the metal ions from  $\text{HNO}_3$  aqueous solutions can be written as:



where  $M^{3+}$  stands for either  $Eu^{3+}$  or  $Am^{3+}$ , HA represents HDEHP, A is the deprotonated acid ( $DEHP^-$ ) and bars indicate organic phase species.

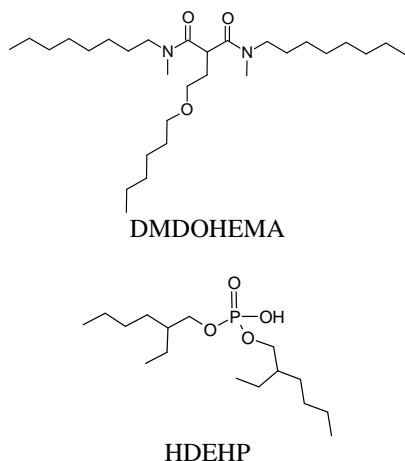
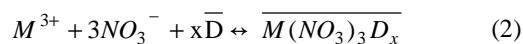


Fig 1. Structures of DMDOHEMA and HDEHP

In equilibrium 1, HDEHP is assumed to be dimeric in alkane diluents [18-21].

For the diamide, it is usually admitted that the extraction mechanism of actinides(III) and lanthanides(III) by malonamides is of solvation type with a solvation number between 2 and 5 depending on the initial conditions of temperature, acidity, extractant and solute concentrations [16,17,22,23]. Using X-ray absorption spectroscopy, stoichiometries and structures of trivalent actinide and lanthanide complexes formed with the DMDOHEMA extractant have been proposed [24]: they consist of two bidentate malonamides and three nitrates around the extracted metal. The general extraction reaction can be written:



where D stands for DMDOHEMA and x: 2 to 5.

The extraction of  $M^{3+}$  by DMDOHEMA, however, can be more complex than that shown in equilibrium 2, since in acidic media, nitric acid is coextracted by the diamide. A further complication in the solvent extraction chemistry of diamide extractants in alkane diluents, is the tendency of these extractants to form small aggregates of the reverse micelle type [16,17,22,25-27].

The extraction of Ln(III) and An(III) by mixtures of the two extractants indicate antagonism at low acidity (*i.e.* pH=1) and synergism at 1M nitric acid concentration. (Fig 2.) [Erreur ! Source du renvoi introuvable.]. Moreover, Gannaz *et al.* interpreted the extraction data as resulting from the formation of mixed 'dialkyl phosphoric acid - malonamide' species in the organic phase [16].

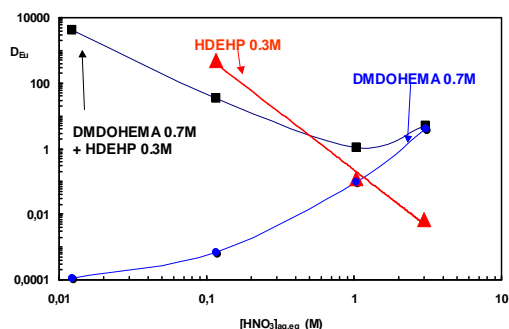


Fig 2. Europium extraction ( $D_{Eu}$ ) *v.s.* aqueous nitric acid concentration. Organic phases: red 0.3M HDEHP in dodecane, blue 0.7 M DMDOHEMA in dodecane, black 0.7 M DMDOHEMA + 0.3 M HDEHP in *n*-dodecane.

The objectives of this work are to characterize the complexes in organic phase by ESI-SM, and to determine their stoichiometry and their evolution when changing experimental conditions. The extraction of metallic solute by the two single extractants and their mixtures in *n*-dodecane have been investigated.

## EXPERIMENTAL

### Extraction conditions:

The organic and aqueous solutions were mixed together at 25°C during 15 minutes, then centrifuged during 5 minutes and separated.

Organic phase were diluted 1/10 in ethanol and 1/100 in acetonitrile/water before analysis by ESI-MS.

### Electrospray ionization mass spectrometry:

A Bruker Esquire LC mass spectrometer was used (Fig. 3.).

Experimental conditions: positive ion mode, nebuliser gas ( $N_2$ ): 5 L/min, 25 psi, 300°C, ionspray voltage: 4000V, capexit offset: 60V, skimmer 1: 30V, trapdrive 90.

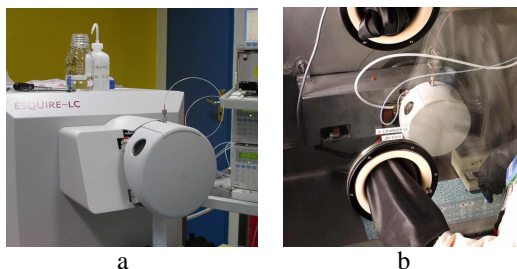


Fig. 3. Electrospray ionization mass spectrometer Bruker Esquire LC.  
a: before nuclearisation, b: after setting up in a glove box.

## RESULTS

### Extraction of $M^{3+}$ by HDEHP

The extraction of neodymium by HDEHP was studied in presence of pH 1 aqueous phase. In these conditions, organophosphoric acid exhibits efficient extraction for Ln(III). From the ESI-MS data (Fig. 4.), three Nd- HDEHP species have been identified:  $[\text{LnA}_2(\text{HA})_2]^+$ ,  $[\text{LnA}_2(\text{HA})_3]^+$  and  $[\text{LnA}_2(\text{HA})_4]^+$  (where HA and A represent the non dissociated dialkylphosphoric acid and its anionic form, respectively), with  $[\text{LnA}_2(\text{HA})_2]^+$  being the most stable species in the gas phase.

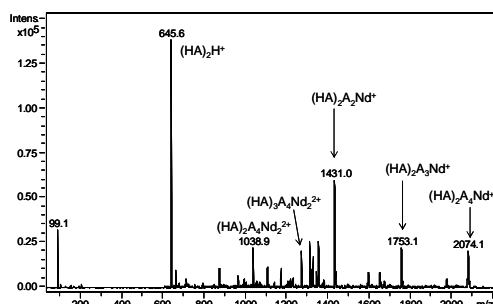


Fig. 4. Positive ESI-MS of 0.3M HDEHP in dodecane after contact with 0.1 M  $\text{Nd}(\text{NO}_3)_3$  in 0.1 M nitric acid. AH represents HDEHP

From these results, it appears that the neutral complexes formed in the organic phase are probably  $\text{LnA}_3(\text{HA})_3$  complex. During the ionization process and the transfer into the gas phase, this neutral species is transformed into  $[\text{LnA}_2(\text{HA})_4]^+$  by the addition of a proton to form a positive ion. The fragmentation of this ion shows that two ligands are less strongly bonded to the metal and the more stable species in the gas phase is  $[\text{LnA}_2(\text{HA})_2]^+$  [13].

To supplement this study, an experiment was performed in which a 0.1 M HDEHP solution in *n*-dodecane was equilibrated with a 0.1 M  $\text{HNO}_3$  aqueous solution containing a large excess of  $\text{Nd}(\text{NO}_3)_3$  in order to achieve organic phase saturation. The ESI-MS results (Fig. 5.) show new peaks. In this case, the most abundant species was the  $[\text{NdA}_2(\text{HA})_2]^+$  ion, however, the presence of  $[\text{NdA}_2(\text{HA})_3]^+$ , of  $[\text{NdA}_2(\text{HA})_4]^+$  (with a lower intensity), and of dinuclear species such as  $[\text{Nd}_2\text{A}_4(\text{HA})_x]^{2+}$  with  $x = 2$  or 3, was also observed.

These results are consistent with the solution studies carried out by liquid-liquid extraction, vapor pressure osmometry and EXAFS showing the formation of  $\text{LnA}_3(\text{HA})_3$  complex and the formation of dimeric species in extraction of Nd(III) by HDEHP at high loading of the organic phase [17,28,29].

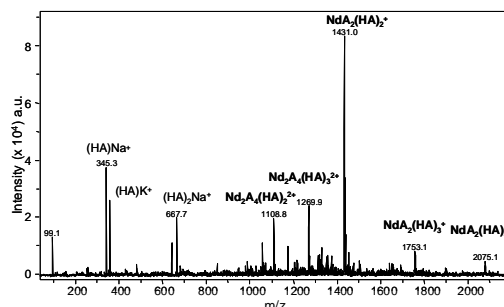


Fig. 5. Positive ESI-MS of 0.1M HDEHP in dodecane after contact with 1M  $\text{Nd}(\text{NO}_3)_3$  in 0.1 M nitric acid. AH represents HDEHP.

### Extraction of $M^{3+}$ by DMDOHEMA

The extraction of neodymium by DMDOHEMA was studied from 1 M  $\text{HNO}_3$  and 2 M  $\text{LiNO}_3$  aqueous solutions. In these conditions, Am(III) and Ln(III) are extracted by DMDOHEMA. The ESI-MS data for a 0.65 M DMDOHEMA solution in *n*-dodecane, after contact with an aqueous solution containing 0.1 M  $\text{Nd}(\text{NO}_3)_3$  exhibit peaks corresponding to several Nd-diamide species, with 2 to 7 diamide molecules for each metal center (Fig. 6A.). To gain information about the stability of these species, energy resolved mass spectrometry experiments with cone voltage variation were performed (Fig. 6B.). The results showed that the most abundant and stable species is  $[\text{NdD}_4]^{3+}$ . Indeed, the intensity of ions such as  $[\text{NdD}_x]^{3+}$  with  $x \geq 5$  strongly decreases with the increase of the cone voltage (Figure 5B) and the latter are probably

formed during the ionization process. The intensity of the  $[\text{NdD}_4]^{3+}$  species is maximum for a skimmer voltage of 50 V. Further increase of the cone voltage leads to its fragmentation by the loss of a malonamide molecule and the formation of  $[\text{NdD}_3]^{3+}$ .

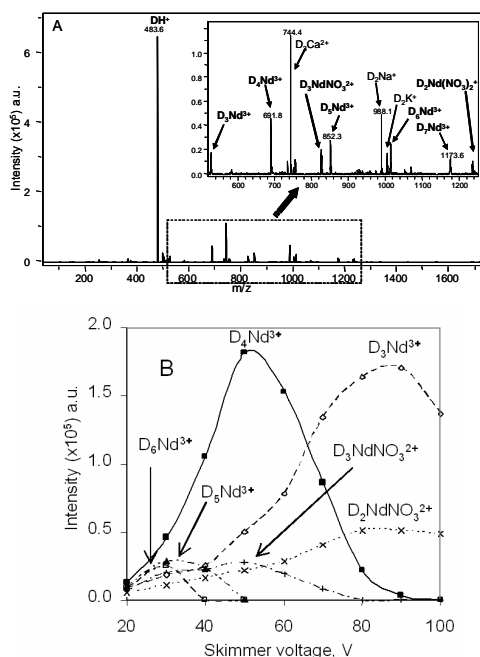


Fig. 6. 0.65 M DMDOHEMA in *n*-dodecane after contact with 0.1 M  $\text{Nd}(\text{NO}_3)_3$  in 1 M  $\text{HNO}_3$  + 2 M  $\text{LiNO}_3$ . A. Positive ESI mass spectrum. B. Intensity of Nd-diamide ions as a function of cone voltage. D stands for DMDOHEMA.

From these results it appears that the neutral complexes formed in the organic phase are of the  $\text{Nd}(\text{NO}_3)_3\text{D}_x$  type with  $2 \leq x \leq 4$ , the most abundant being the  $\text{Nd}(\text{NO}_3)_3\text{D}_4$  species. During the ionization process and transfer into the gas phase, the following ions are formed:  $[\text{Nd}(\text{NO}_3)_2\text{D}_x]^+$ ,  $[\text{Nd}(\text{NO}_3)\text{D}_x]^{2+}$ , and  $[\text{NdD}_x]^{3+}$ . Otherwise, it has been shown that malonamide extractants form aggregates in solution in alkane, and the aggregation number depends on the metallic solute concentration [30]. In order to link the stoichiometry of the complex in organic solution with the aggregation number, the ESI-MS experiments are performed for two 0.5 mol/L DMDOHEMA solutions in *n*-heptane contacted with two 3 mol/L  $\text{LiNO}_3$  solutions containing respectively 0.1 and 0.4 mol/L of europium nitrate (Fig. 7.) corresponding to a ratio [diamide] / [europium] in organic phase  $> 5$  and  $< 4$  respectively.

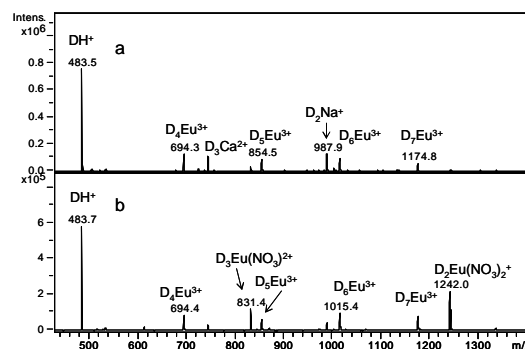


Fig. 7. Positive ESI mass spectrum for 0.5 mol/L DMDOHEMA in *n*-heptane organic phases after equilibration with (a) 0.1 mol/L or (b) 0.4 mol/L  $\text{Eu}(\text{NO}_3)_3$  in  $\text{LiNO}_3$  solutions.

The spectra show that the stoichiometry of complexes depends on the [diamide]/[europium] ratio. When [diamide]/[europium]  $> 5$ , the most abundant species correspond to a stoichiometry  $\text{Eu}(\text{NO}_3)_3\text{L}_4$  whereas when [diamide]/[europium]  $< 4$ , the most abundant species contains only 2 malonamides around europium. Several complexes are probably formed with the stoichiometries  $\text{Eu}(\text{NO}_3)_3\text{L}_x$  ( $x = 2, 3$  and  $4$ ), and their abundance depends on the experimental conditions.

These results agree with the solution studies by small angle neutrons or X-rays scattering, vapor pressure osmometry or liquid-liquid extraction showing the formation of aggregates containing about 4-5 malonamides [17,22, 23,30]. Thus, each aggregate can extract one Ln cation to form  $\text{Ln}(\text{NO}_3)_3\text{D}_x$  complex (with  $x=4$ ). Thus, when the lanthanide concentration increases, other species can be formed:  $\text{Ln}(\text{NO}_3)_3\text{D}_x$  (with  $x = 2$  or  $3$ ), leading to a change in the organization of the aggregates in the organic phase [30].

#### Extraction of $\text{M}^{3+}$ by HDEHP-DMDOHEMA mixtures

The extraction of neodymium by solutions containing 0.3 M HDEHP and 0.65 M DMDOHEMA in *n*-dodecane was studied in presence of two different aqueous solutions:  $\text{Nd}(\text{NO}_3)_3$  (0.1 M) in 0.1 M  $\text{HNO}_3$  or in 1 M  $\text{HNO}_3$  + 2 M  $\text{NaNO}_3$  which represent the efficiency domains for di-alkylphosphoric acids and malonamide, respectively. The ESI-MS results show that the species formed in the

organic phases are essentially the same for the two aqueous phases used to extract  $\text{Nd}^{3+}$ . The assignment of the species is reported in Table 1, Nd-D and mixed Nd-D-HA species are observed (Fig. 8A) (where D stands for the malonamide and A for the anion of the organophosphoric acid, respectively).

TABLE 1: m/z ratio and species assignment in the positive ESI-MS data for the HDEHP-DMDOHEMA system after extraction of  $\text{Nd}^{3+}$  from I: 0.1 M  $\text{Nd}(\text{NO}_3)_3 + 0.1$  M  $\text{HNO}_3$ , or II: 0.1 M  $\text{Nd}(\text{NO}_3)_3 + 1$  M  $\text{HNO}_3 + 2$  M  $\text{NaNO}_3$  (D stands for DMDOHEMA and HA for HDEHP)  
+: observed species, -: absent species

Species	m/z	I	II
$[\text{D}_3\text{Nd}]^{3+}$	530.9	+	+
$[\text{D}_4\text{Nd}]^{3+}$	691.8	+	+
$[\text{D}_5\text{Nd}]^{3+}$	852.3	+	+
$[\text{D}_2\text{Nd}(\text{NO}_3)]^{2+}$	585.4	-	+
$[\text{D}_3\text{Nd}(\text{NO}_3)]^{2+}$	826.9	-	+
$[\text{D}_2\text{Nd}(\text{NO}_3)_2]^+$	1232.8	-	+
$[\text{D}_2\text{NdA}]^{2+}$	715.0	+	+
$[\text{D}_3\text{NdA}]^{2+}$	956.2	+	+
$[\text{DNdA}_2]^+$	1268.8	+	+
$[\text{D}_2\text{NdA}(\text{NO}_3)]^+$	1492.0	-	+
$[\text{DNd}(\text{HA})\text{A}_2]^+$	1591.0	+	+
$[\text{D}_2\text{NdA}_2]^+$	1751.2	+	+

The main difference is the absence of nitrate-species at the lower acidity (0.1 M  $\text{HNO}_3$ ) in the aqueous phase. Since nitrate-species are formed when the metal nitrate is extracted by the malonamide (see equilibrium 2), this result suggests that the malonamide by itself does not contribute to neodymium extraction at low aqueous acidity. Indeed, under the conditions of low acidity and nitrate ion concentration, the diamide is a poor extractant of lanthanide cations. The  $[\text{D}_x\text{Nd}]^{3+}$  species (with  $x = 3$  or 4) in the ESI-MS spectrum can arise from mixed complexes.

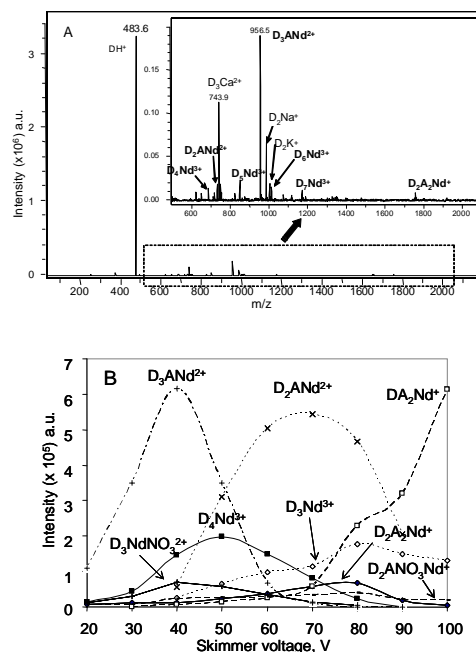


Fig. 8. 0.65 M DMDOHEMA + 0.3 M HDEHP in n-dodecane after contact with 0.1 M  $\text{Nd}(\text{NO}_3)_3$  in 0.1 M  $\text{HNO}_3$ . A. Positive ESI mass spectrum. B. Intensity of Nd-species ions as a function of cone voltage. D and A represent DMDOHEMA and DEHP, respectively. To simplify the plot, the species  $[\text{D}_5\text{Nd}]^{3+}$ ,  $[\text{D}_2\text{Nd}(\text{NO}_3)]^{2+}$ , and  $[\text{DNd}(\text{HA})\text{A}_2]^+$  are not shown.

At higher aqueous acidity and  $\text{NO}_3^-$  concentrations, the complexes formed in the organic phase can be written as  $\text{D}_x\text{Nd}(\text{NO}_3)_3$  for Nd extraction by the malonamide alone, and as  $\text{D}_y\text{NdA}_2(\text{NO}_3)$  or  $\text{D}_y\text{NdA}_3$  (with  $y \leq 5$ ) for the mixed complexes. During the ionization process and the transfer into the gas phase, the following ions are formed:  $[\text{D}_y\text{Nd}]^{3+}$  (with  $y \leq 5$ ),  $[\text{D}_3\text{NdA}]^{2+}$ ,  $[\text{D}_2\text{NdA}(\text{NO}_3)]^+$ ,  $[\text{D}_2\text{NdA}_2]^+$  and  $[\text{DNd}(\text{HA})\text{A}_2]^+$ .

An energy resolved mass spectrometry experiment with cone voltage variation showed that the Nd-D-HA mixed complexes predominate over the metal complexes containing only the diamide for both aqueous phase conditions. Fig. 8B presents the results obtained with the 0.1 M  $\text{Nd}(\text{NO}_3)_3 + 1$  M  $\text{HNO}_3 + 2$  M  $\text{NaNO}_3$  aqueous phase. Increasing the cone voltage induces fragmentation of  $[\text{D}_3\text{NdA}]^{2+}$  leading to  $[\text{D}_2\text{NdA}]^{2+}$  by the loss of one malonamide. This fragmentation has been confirmed by MS<sup>2</sup> experiments. In the same way, the  $[\text{DNdA}_2]^+$  species, only observed at high cone voltage, is probably formed by fragmentation of other ions.

To summarize, mixed species are formed whatever the aqueous phase acidity, and Nd-DMDOHEMA complexes are also formed at higher acidity. This is consistent with the fact that, at high aqueous phase acidities, the diamide is a good extractant for Ln(III). These results agree with aggregation studies of malonamides – dialkyl phosphoric acid mixture by vapour pressure osmometry and liquid-liquid extraction. Indeed, to interpret extraction data, Gannaz proposed a mixed extractant species containing two alkylphosphoric acid and five malonamide molecules. [16,17].

To supplement this study, Am(III) complexes formed with the mixture HDEHP-DMDOHEMA was carried out. To analyze metal-ligand complexes by ESI-MS, their relative concentration in solution must be sufficient (*i.e.* > 1% of the total ligand concentration). Otherwise, the decrease of the ligand concentrations leads to a decrease of the distribution ratio, and then a decrease of the complex proportion in the organic phase. Consequently, to avoid the handling of concentrated americium solution and get information about Am complexes, experiments were performed in homogeneous phase. Solution containing  $2.7 \cdot 10^{-4}$  M HDEHP,  $5.3 \cdot 10^{-4}$  M DMDOHEMA,  $2.4 \cdot 10^{-3}$  M  $\text{HNO}_3$  and  $2.7 \cdot 10^{-4}$  M of  $^{241}\text{Am}$  in ethanol was prepared and diluted  $1/3^\circ$  in acetonitrile/water before analysis by ESI-MS. The mass spectra show as for Nd extraction, the presence of DMDOHEMA-Am and mixed DMDOHEMA-HDEHP-Am complexes (Fig. 9.). 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. Energy resolved mass spectrometry experiment with cone voltage variation showed that these Am-D-HA mixed complexes predominate. From MS data, the complexes formed can be written as  $\text{D}_x\text{Am}(\text{NO}_3)_3$  for Am extraction by the malonamide alone, and as  $\text{D}_y\text{AmA}_2(\text{NO}_3)$  or  $\text{D}_y\text{AmA}_3$  (with  $y \leq 5$ ) for the mixed complexes. Am and Ln complexes seem to have the same stoichiometry which is consistent with liquid-liquid extraction data [16].

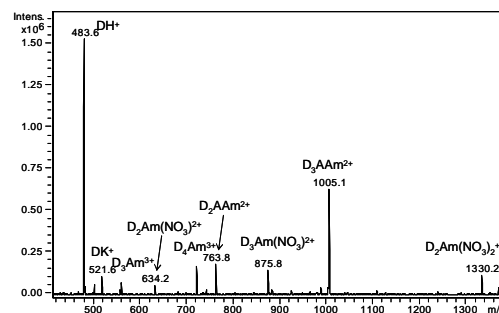


Fig. 9. Positive ESI mass spectrum of solution containing  $5.3 \cdot 10^{-4}$  M DMDOHEMA,  $2.7 \cdot 10^{-4}$  M HDEHP,  $2.4 \cdot 10^{-3}$  M  $\text{HNO}_3$  and  $2.7 \cdot 10^{-4}$  M of  $^{241}\text{Am}$  in ethanol. D and A represent DMDOHEMA and DEHP<sup>-</sup>, respectively.

TABLE 2: m/z ratio and species assignment in the positive ESI-MS data for the HDEHP-DMDOHEMA -Am<sup>3+</sup> system in ethanol. (D stands for DMDOHEMA and HA for HDEHP)

+: observed species, ε: low intensity peak

Species	m/z	
$[\text{D}_3\text{Am}]^{3+}$	563.3	+
$[\text{D}_4\text{Am}]^{3+}$	724.1	+
$[\text{D}_5\text{Am}]^{3+}$	884.2	+
$[\text{D}_2\text{Am}(\text{NO}_3)_2]^{2+}$	634.2	ε
$[\text{D}_3\text{Am}(\text{NO}_3)_2]^{2+}$	875.8	+
$[\text{D}_2\text{Am}(\text{NO}_3)_2]^{+}$	1330.2	+
$[\text{D}_2\text{AmA}]^{2+}$	763.2	+
$[\text{D}_3\text{AmA}]^{2+}$	1005.1	+
$[\text{DAmA}_2]^{+}$	1366.1	ε
$[\text{D}_2\text{AmA}(\text{NO}_3)]^{+}$	1106.8	ε
$[\text{D}_2\text{Am}(\text{HA})\text{A}_2]^{+}$	1588.4	ε
$[\text{D}_2\text{AmA}_2]^{+}$	1847.9	ε

## CONCLUSION

In conclusion, we note that electrospray ionization - mass spectrometry is a valuable approach to obtain structural information on the complexes formed during solvent extraction experiments. The predominant species in gas

phase are consistent with the complexes observed by other techniques in solution.

Thus, the formation of  $\text{Ln}(\text{DEHP})_3(\text{HDEHP})_3$  complex and the dinuclear species at high loading of the organic phase is observed in extraction of Nd(III) by HDEHP in alkane.  $\text{Ln}(\text{NO}_3)_3(\text{DMDOHEMA})_x$  complexes (with  $x=2, 3$  or  $4$ ) are proposed for the extraction of Ln(III) cations by DMDOHEMA in alkane and their extraction yields depend on the ratio  $[\text{Ln}]/[\text{DMDOHEMA}]$ .

The formation of mixed species containing 2 organophosphorus acid and several diamide molecules per metal center is observed after extraction or complexation of Am(III) and Ln(III) by a mixture of the two extractants HDEHP and DMDOHEMA.

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