

Electrospray-mass spectrometric studies of selectivity of alkali metal cations extraction by calix[4]arene crowns

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Abstract. Electrospray Ionization Mass Spectrometry (ESI/MS) has quickly become a versatile method of qualitative analysis of a wide variety of host–guest complexes formed in solution. However, considerable controversy exists on how ESI spectra quantitatively reflect and compare to the results obtained on these complexes. The extraction of alkali cations from acidic aqueous solutions by nine various calix[4]arenes-crown-6 diluted in NPOE, was studied by using ESI/MS. The stoichiometry of cesium complex and Cs⁺/Na⁺ selectivity were evaluated.

Keywords: Calixarene crown, alkali metal cations, electrospray, complexation, selectivity

1. Introduction

Since the first studies of D. Gutsche, calix[n]arenes [1], simple and relatively inexpensive polyaromatic compounds, are considered as a particularly interesting family of potential host–guest receptors for ions [1]. These properties for ion recognition, one of the new trends in organic, bio-organic and analytical chemistry, are offered by both the rigid and lipophilic calix[n]arene cavity and the possibility of addition of ligands on phenolic oxygens or in substitution of para tert butyl groups, in order to obtain compounds displaying high efficiency and important selectivity. Nuclear fuel reprocessing operations produce both high and medium level activity liquid wastes. The removal of different radionuclides and volume reduction of these wastes are important scientific and economical goals. For instance, the minor actinides and other long lived fission products such as trace level ⁹⁰Sr and ¹³⁷Cs, have to be removed from high salinity acidic medium (NaNO₃ 4 M-HNO₃ 1 M), allowing most of the waste to be disposed of, after conditioning, in surface site, and the remaining small part containing the long live radio elements to be sent, after vitrification, to an interim repository before transmutation or disposal in geological formations.

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The specific design of 1,3-alt-calix[4]arenes modified by addition of one or two complexing crown-6 ether bridge(s), leads to a promising way for solving difficult problems such as the removal of cesium cation from radioactive liquid waste [2,3]. These aqueous solutions contain several other alkali metal cations which could be co-extracted and competitively complexed by calixcrowns. The evaluation of extraction potential and selectivity toward the target cation of any given calixcrown should be done using a specific, reliable and fast analytical technique for complex mixture study. The solvent extraction of alkali metal cations (Cs^+ , Rb^+ , K^+ , Na^+) by 1,3-alt-calix[4]arenes-crown-6 have been extensively studied by liquid-liquid extraction [4]. These compounds show a high selectivity toward Cs^+ in the alkali cation series. The *o*-nitrophenyl octyl ether, (NPOE), has been often chosen as solvent for calixarenes because it has demonstrated good property in liquid-liquid extraction and in transport through supported liquid membranes [2,4]. Several Molecular Dynamic (MD) simulations performed on the calix[4]arene crown compounds [5–11], enabled to study alkali complexes structures *in vacuo* and in various solvents, and allowed to deduce their respective selectivity in the alkali cation series.

The selectivity and the specific stability constants K_s , needed to provide an approximation of equilibrium conditions in aqueous solution, were experimentally measured using UV absorption spectrophotometry [12] together with extensive structure studies by NMR spectrometry and X-ray techniques [5, 6]. In particular, the evaluation of complexation of crown ethers with alkali cations were reported first by FAB/MS [13–16], LSIMS [17] and then by LD/ITMS [18]. More recently, host-guest chemistry [19, 20] of crown ethers were studied by PD/MS [21], ESI/FTICR [22] and ESI/ITMS [23]. Conventional chemical (CI) and electron impact (EI) [24] ionization mass spectrometry were used to enhance host-guest cluster but the complexes are difficult to detect by these methods. However with FAB/MS [25], SIMS [26–28], FTICR [29], PDMS [30] and MALDI [31], calixarene-cation complexes (Fig. 1) were studied with much more success.

Electrospray ionization [32] (ESI) mass spectrometry, a soft ionization desorption technique [33,34] using polar solvents such as water, methanol or acetonitrile, was used for direct measurement of cations in solutions and a more critical approach to the stability constant values of complexes [35] already established. This ionization/desorption mode, despite some controversies concerning the formation of ions from droplets, is believed to better represent the equilibrium between cation and host calixcrown in solution. The presence of the liquid matrix during the ionization [36] process, although not completely representative of the solution fingerprints, is the closest approximation to the equilibrium state in solution. The gas phase processes [35,37] are certainly affecting the results of the final analysis (e.g., because of the difference in stability of desolvated ions in the gas phase). Using the ESI technique, Liu [37,38]

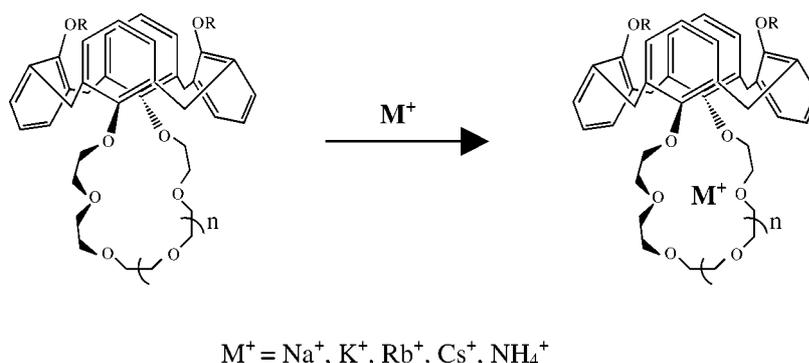


Fig. 1. Complexation of calixarenes by alkali metal cations.

successfully studied the selectivity of different crown ethers [39,40] toward the alkali cations, proposed a calibration curve methodology and determined stability constants.

To our knowledge, little work on calixarene complexes of alkali cations has been done using the ESI/MS. Electrospray has been mainly used to characterize the synthesis [41–48] of calixarenes. In this work, we report the use of ESI/MS to the qualitative analysis of the extraction of alkali cations from an acidic aqueous phase by nine calix[4]crowns (Fig. 2) diluted in NPOE, focusing on the stoichiometry

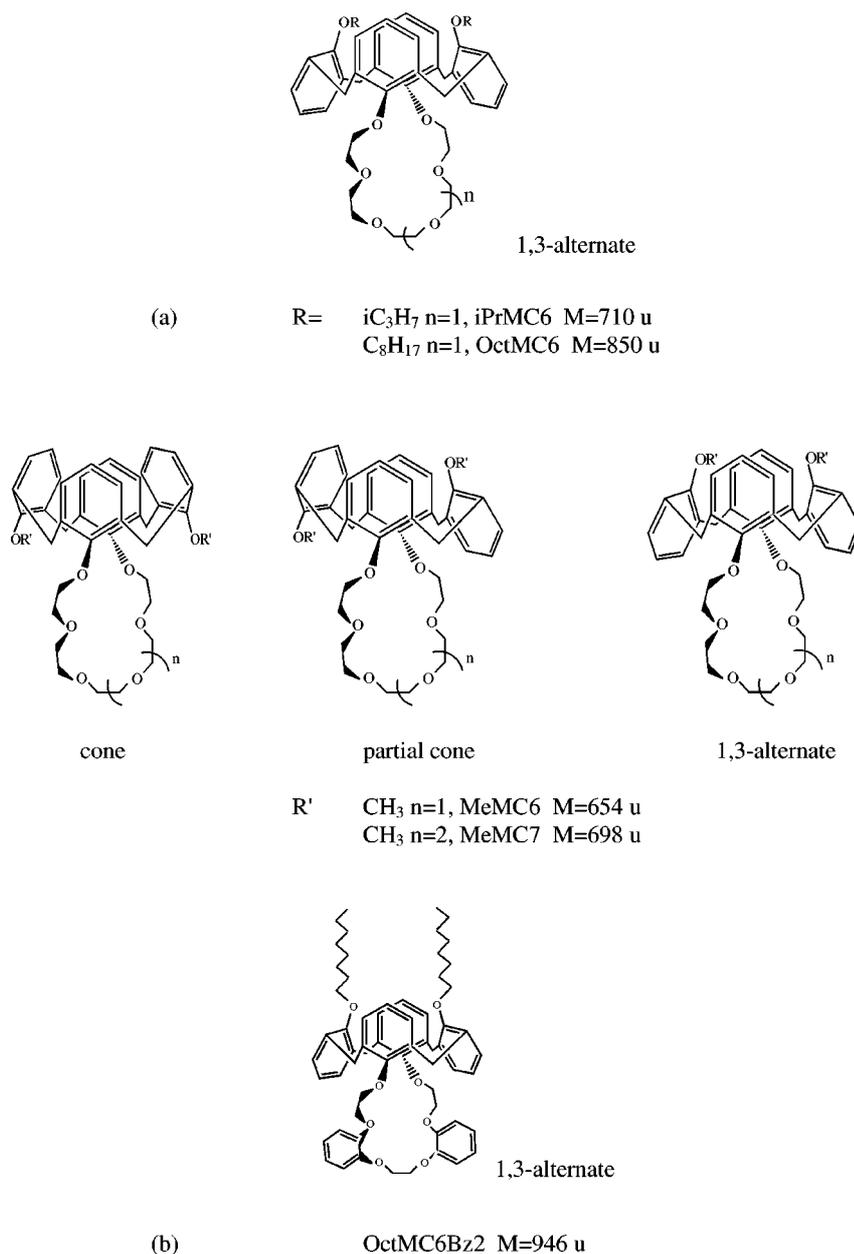


Fig. 2. Structure of calixarenes.

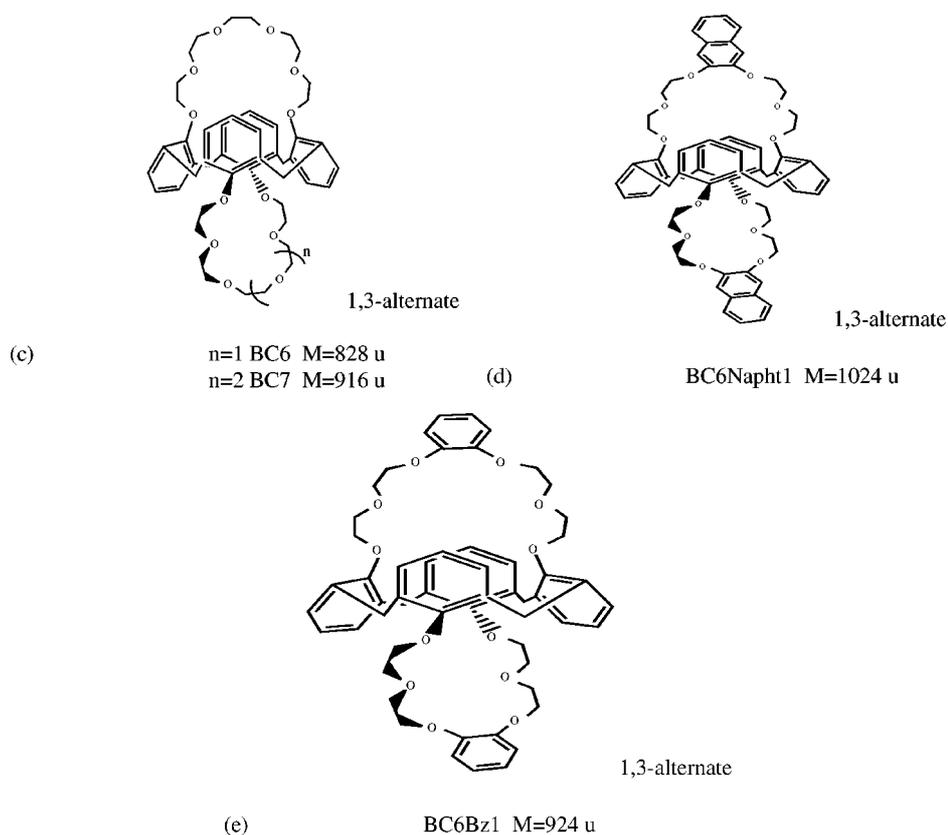


Fig. 2. (Continued).

of cesium complex and the selectivity of extraction in the whole alkali metal kation series. From ESI spectra, a preliminary estimation of the stability constant K_s is done assuming that ESI spectra obtained in gas phase directly reflect equilibrium of host-guest complexes present in solution.

2. Experimental

2.1. Mass spectrometry

The ESI mass spectra were performed on single quadrupole Nermag R10-10 (Quad Service, France) equipped with an ESI source (Analytica of Branford, USA) with a mass to charge ratio range from 80 to 2000 and a Spectral-30, version 3.7 data system. The ESI source was used without modification and typical operating conditions were as follow: the sample was introduced through a syringe pump (Harvard Apparatus 11, Cambridge, MA, USA) at a rate of $3 \mu\text{l}/\text{min}$. ESI was performed in the positive ion mode and the electrospray needle was fixed at $+3.5$ kV. The nitrogen stream (10 l/min), heated at 150°C , was circulated as a counter-current gas for producing efficient desolvation. The electron multiplier was set at ca -0.5 V (from -0.49 V to -0.52 V). The lens and quadrupole voltages were optimized to obtain maximum ion current for electrospray.

The preliminary ESI analysis were also performed on a triple quadrupole Quattro II (Micromass, UK) in similar conditions (sample injected at $10 \mu\text{l}/\text{min}$, source temperature: 80°C). ESI was performed in

the positive ion mode and the tension of the capillary was maintained at +3.35 kV. The cone voltage was set at 20 V and the skimmer voltage at 1.9 V. Ions were detected by scanning the first quadrupole and the scans were monitored over the mass range m/z 80–1200 in 5 s. At least 30 scans were averaged to obtain representative spectra.

2.2. Material

All calixarenes (Fig. 1) and *o*-nitrophenyl octyl ether (NPOE) used in this work were supplied within the CEA network. The synthesis of calix[4]arene crown was performed by Vicens [42] and Ungaro [43]. The compounds were not purified prior to the extraction processes. Inorganic salts were purchased from Merck Chemicals (Darmstadt, Germany) (NaCl) and Johnson-Matthey Chemicals (Royston, England) (RbCl and CsCl). The 65% nitric acid used for extraction also comes from Merck. The ESI solvent acetonitrile (HPLC grade, 99.8%) was purchased from Carlo Erba (Val de Reuil, France). All other solvents used in this work were from Merck.

2.3. Extraction: general procedure

To the 500 μl of 10^{-2} M solution of calix[4]arene crown in NPOE, 500 μl of solution of salt in 1 M nitric acid was added. The combined solutions were shaken for 30 min and then centrifuged for 15 min. The 5 μl sample of organic phase, diluted with 1 ml of acetonitrile, was used for ESI/MS measurements.

2.4. Successive extraction of Cs^+ and Rb^+

Equimolar Cs^+ and Rb^+ salts were dissolved in 500 μl of aqueous nitric acid (1 M) then treated with 500 μl of BC6 10^{-2} M solution in NPOE. Both cations and BC6 were in equimolar ratio during the first extraction, the combined solutions followed then the general procedure. In the second extraction of the aqueous nitric phase, the same volumes of the solution of 10^{-2} M BC6 in NPOE were used (v/v). This procedure was repeated in a series of four successive extractions.

2.5. Selectivity evaluation procedure

The equimolar nitric acid solution of cesium and sodium chlorides (1 : 1) was treated with any given calix[4]arene solution (10^{-2} M in NPOE) according to the extraction procedure previously described. The alkali ion/calix[4]crown ratio was maintained at 2 : 1 ratio. The organic phase, diluted with acetonitrile was studied by ESI without further treatment.

The selectivity was expressed as a ratio of the intensity of a given metal complex calix[4]crown-cation (e.g., $[\text{MC}+\text{Cs}]^+$) to the corresponding sodium (e.g., $[\text{MC}+\text{Na}]^+$) ion complex.

3. Results and discussion

Selective complexation between crown ethers and different cations has been largely studied using FAB/MS [14,16] and then ESI/MS [38,39,44]. The complexation of calix[4]arene crown-6 with alkali metal cation (Cs^+ , Rb^+ , Na^+) studied by liquid-liquid extraction [4], MD simulations [5–11] and NMR [6], shows a highly selective complexation toward Cs^+ . Complexation of calixarene crown with alkali metal cations can form mono or dicationized complexes which are named mono or binuclear species, respectively.

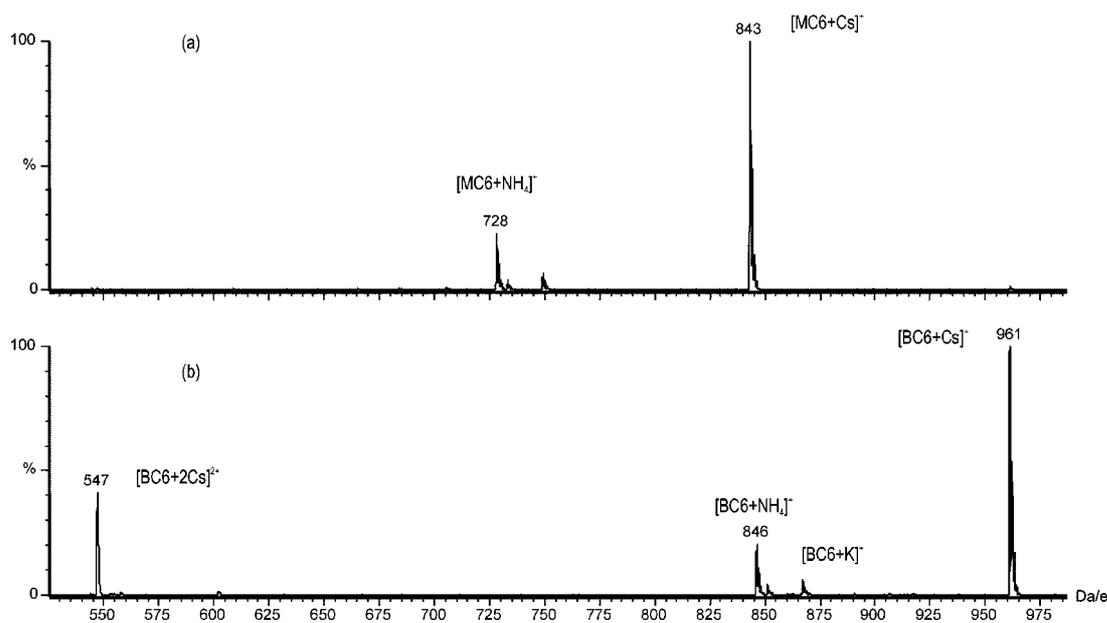


Fig. 3. Complexation of cesium by calixarene crowns: (a) extraction of cesium by the iPrMC6 (equimolar ratio cesium-calixarene); (b) extraction of cesium by the BC6 (equimolar ratio cesium-calixarene).

3.1. Stoichiometry studies in the extraction process

In this two part study, we would like to present the qualitative estimation of extraction of alkali cations as seen by ESI technique.

The first part of this study concerns the stoichiometry of cesium complexes obtained by extracting cesium cation from an aqueous nitric phase to an organic phase constituted of a calixarene monocrown (iPrMC6) or biscrown (BC6) diluted with NPOE (Fig. 3). When the cesium cation is specifically extracted by iPrMC6 from the equimolar cation-extractant mixture, the ESI mass spectra shows the mononuclear ion: [iPrMC6+Cs]⁺ at m/z 843 (Fig. 3a). In the similar extraction with BC6 (Fig. 2c), both mononuclear and binuclear species are present as shown in Fig. 3b ([BC6+Cs]⁺ at m/z 961 and [BC6+2Cs]²⁺ at 547). This result confirms that biscrown systems may complex up to two Cs⁺ cations which should be located in the crown rather than in calixarene cavity, indeed, no multi charged complex like [BC6+3Cs]³⁺ appear. These results are in agreement with those obtained by X-ray and molecular dynamics simulations [6] showing that the size of the cavity is too small for trapping cesium cation, in contrast with the crown part which is suitable for the cesium complexation. Hence, electrostatic interactions between crown oxygen atoms and cesium cations form stable complexes. In liquid-liquid extraction [4], only the mononuclear species is formed with BC6 due to an excess of calixarene compared to cations. The formation of binuclear species with BC6 depends on the ratio of calixarene to cation as will be confirmed thereafter. It should be noted that in all the experiments, the presence of K⁺, Na⁺ or NH₄⁺ complexes with calix[4]arene should be considered as artifacts provided from salt impurity present in solution or dispersed on the 'pepperpot' surface.

The second part was to study the relative concentration of the binuclear species with respect to the BC6-Cs⁺ ratio (Fig. 4). When BC6 is in excess over cesium (Fig. 4a), the major species is the mononuclear (m/z 961) complex (100%), and the binuclear (m/z 547) species represents only 12%.

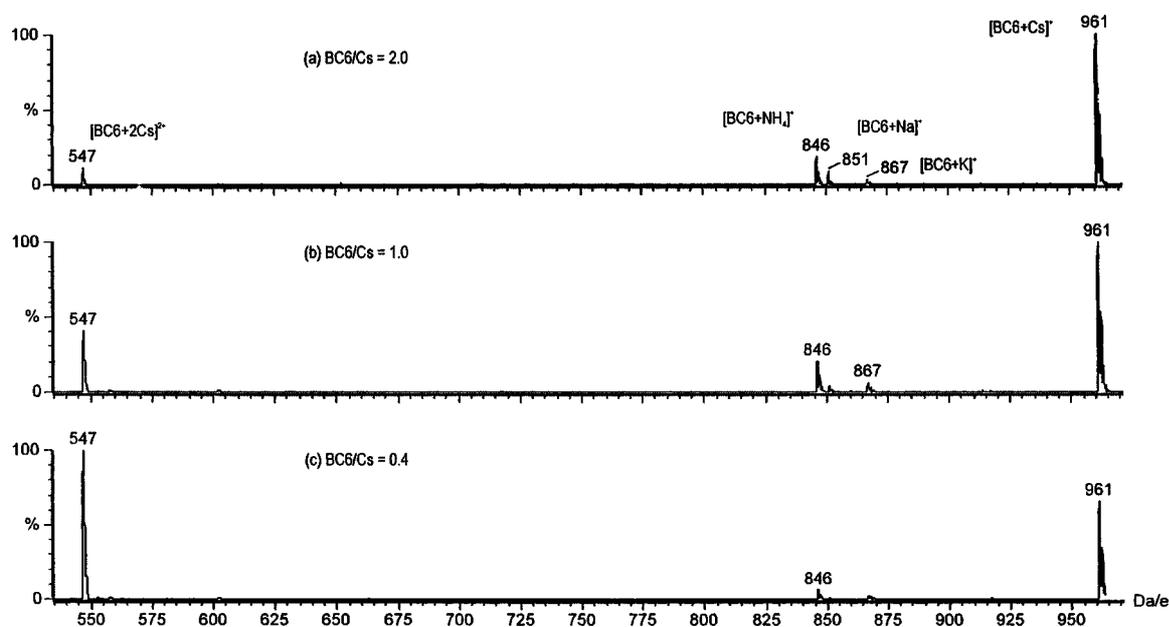


Fig. 4. Extraction of cesium by the calixarene biscrown, variation of the cesium cation to BC6 ratio.

For the same concentration of cesium and BC6, the binuclear species (m/z 547) appeared clearly but the mononuclear is still preponderant (Fig. 4b). Finally, when there is an excess of cesium compared to BC6, as in Fig. 4c, the binuclear complex (composed of two Cs^+ cations) is observed as a major species (100%) and the mononuclear m/z 961 species is reduced to 65% of the base peak. This abundance dependence indicates that the mononuclear complex formation as expected precedes the formation of binuclear one in solution and that the complex evolution is easily followed by ESI/MS. The same observation stands for, e.g., Rb^+ studies. Rubidium cation is smaller than cesium cation (cesium: atomic radius: 3.34 Å, rubidium: atomic radius: 3.04 Å) and results observed are identical for both cations (spectra available on request). In another way, under our conditions, formation of 1 : 2 metal–ligand complexes or ‘sandwiches’ is not detected, although they are seen when the cavity size is too narrow for the cation as with 18 crown-6 [45] or as noted by Shinkai [26] and Takumi [46] for calix[8]arene and crown ether acetal, respectively.

3.2. Selectivity experiments

A first evaluation of selectivity in the alkali series was performed for close molecular radius cations cesium (present in nuclear waste) and rubidium, using BC6 calixarene. Several consecutive extractions of a Cs^+ and Rb^+ equimolar mother solution were performed according to the procedure presented in the experimental part. Figure 5 shows ESI mass spectra of the solutions after each extractions. Several comments can be made: ESI allows to display as expected both calixarene complexes formed with each one of the rubidium isotopes (^{85}Rb and ^{87}Rb with respective abundance of 72% and 28%). The formation of the following monocharged ions was observed in Fig. 5: $[\text{BC6}+\text{Cs}]^+$: m/z 961, $[\text{BC6}+\text{Rb}]^+$: m/z 913, $[\text{BC6}+\text{K}]^+$: m/z 867, $[\text{BC6}+\text{Na}]^+$: m/z 851, $[\text{BC6}+\text{NH}_4]^+$: m/z 846, as well as the corresponding doubly-charged ion, both leading to the formation of ions at: $[\text{BC6}+2\text{Cs}]^{2+}$ m/z 547, $[\text{BC6}+\text{Cs}+\text{Rb}]^{2+}$ m/z 523, $[\text{BC6}+\text{Cs}+\text{K}]^{2+}$ m/z 500 and $[\text{BC6}+2\text{Rb}]^{2+}$ m/z 499.

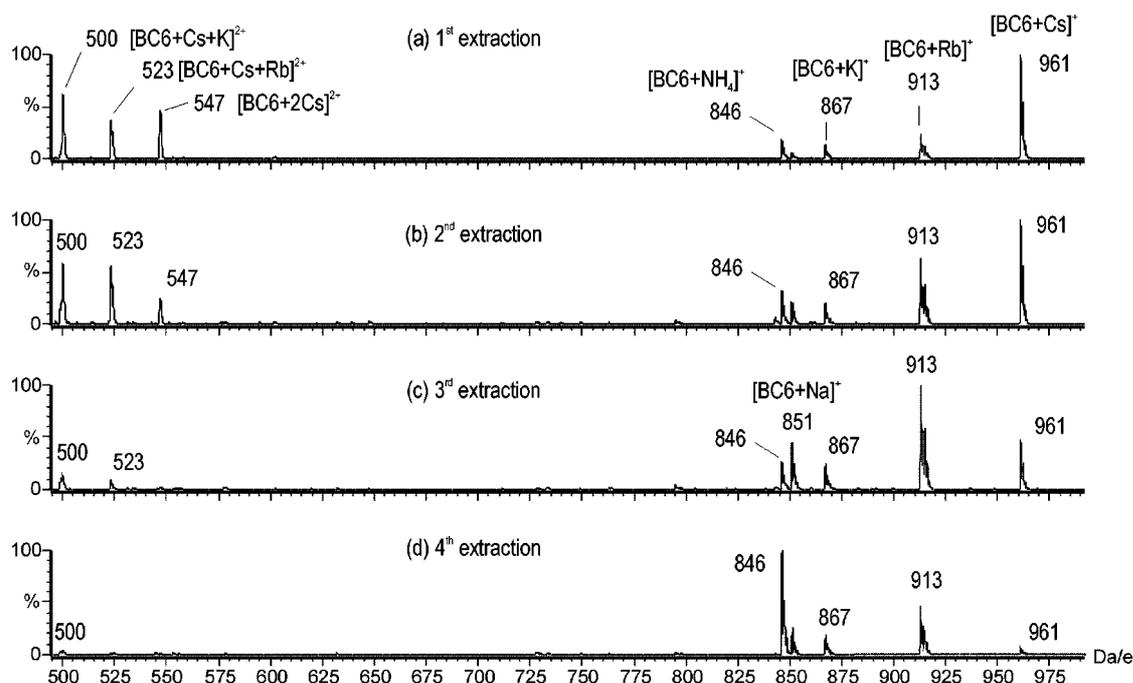


Fig. 5. Successive extractions of Cs^+ and Rb^+ cations mixture by BC6: (a) 1st extraction: equimolar ratio of both cations and BC6 (10^{-2} M in NPOE); (b) 2nd extraction of the aqueous nitric phase containing Cs^+ and Rb^+ cations by BC6 (10^{-2} M in NPOE) (v/v); (c) 3rd extraction of the aqueous nitric phase containing Cs^+ and Rb^+ cations by BC6 (10^{-2} M in NPOE) (v/v); (d) 4th extraction of the aqueous nitric phase containing Cs^+ and Rb^+ cations by BC6 (10^{-2} M in NPOE) (v/v).

Direct comparison of abundance of cesium and rubidium complex ions, as displayed in the mass spectra, showed that during the first extraction (Fig. 5a), Cs^+ is more efficiently extracted than Rb^+ . In a second extraction, after the removal of the main portion of Cs^+ (Fig. 5(a, b)), the rubidium complex ions are preferentially eliminated (Fig. 5c). In the last extraction, both Cs^+ and Rb^+ cations are almost absent and the BC6 starts to complex all other trace cations present in the acetonitrile solution or coming from the ESI source. This behavior suggests that cesium cation size is better adapted than slightly smaller rubidium for the BC6 size whose crown radius is estimated from the X-ray data at 3.1–3.5 Å [6]. In summary, ESI method shows the preferential extraction of cesium cation compared to rubidium cation by BC6 from solution mixture.

In this study, the results concerning the comparison of the complexation selectivity of BC6 or i-PrMC6 toward Cs^+ and K^+ were not presented. However, in agreement to the molecular dynamic studies the ESI/MS confirmed that calixarenes BC6 and i-PrMC6 are preferentially complexing Cs^+ (comparing to K^+). These detailed results will be published later.

The last part consists in evaluating the potential of ESI/MS for selectivity measurements of several calixarene crowns toward cesium and sodium cations. While selectivity of crown ethers toward alkali cations has been currently studied by FAB [14], SIMS [28] and ESI [39], selectivity of calixarene toward cesium was mainly studied by liquid-liquid extraction [4], stability constants determination in “classical” solvents like acetonitrile [12] and MD simulations [5–11] which demonstrated that 1,3-altconformation-calix[4]crown-6 preferentially complex and extract cesium. To evaluate the behavior of a whole family of nine calix[4]arenes toward cesium cation, selectivity of extraction of each one has been systematically studied by comparing the extraction of a standard Cs^+ and Na^+ mixture. Experiments have been

Table 1

Selectivity of calixarene monocrowns and bis-crowns towards cesium and sodium cations

Calixarene monocrowns	Selectivity β^*
iPrMC6	60
OctMC6	>1000
OctMC6Bz2	>1000
MeMC6	0.1
MeMC7	0.05
Calixarene biscrowns	Selectivity β
BC6	40
BC7	0.1
BC6Napht1	>1000
BCBz1	>1000

*Selectivity $\beta = I_{[\text{calixarene}+\text{Cs}]^+} / I_{[\text{calixarene}+\text{Na}]^+}$.

performed with the cesium and sodium cations because both are present in nuclear waste at very different concentration. The intention is to extract preferentially cesium, radionuclide of interest compared to sodium largely present in all matrices of the nuclear reprocessing. So, a search for a calixarene with a very good Cs^+/Na^+ selectivity is absolutely mandatory.

The extraction differences within this family will emphasize the complexation ability of calix[4]arene for these two ions with regards to abundance of their corresponding complexes. The selectivity parameter (β) is defined by using the intensity ratio of Cs^+ to Na^+ complexes (used as a standard). Hence, it is well known that the peak intensities in ESI can be related to the gas phase ion stabilities, but they do not represent the absolute amounts of these species in solution [47] (as it has been shown for crown ethers by Lui [38], Vouros [40] and Kebarle [36]). Even if different species have different cationization efficiencies [37,38], it was possible (without calibration) to obtain an estimation of the selectivity for different calixarenes present in solution.

The selectivity β parameter is measured by using the ratio:

$$\beta = I_{[\text{calixarene}+\text{Cs}]^+} / I_{[\text{calixarene}+\text{Na}]^+}$$

The peak intensities were used directly without any correction for gas phase and solution, as described by Liu [38] and Brodbelt [23] and because of liquid-liquid extraction [4], the selectivity Cs^+/Na^+ of these calixarenes was very different. Selectivity results (presented in Table 1) enabled to arrive to several observations: (i) calix[4]arenes family preferentially complexed Cs^+ compared to Na^+ and (ii) this preferential complexation is observed except for MeMC6, MeMC7 and BC7 for which, selectivity Cs^+/Na^+ is much lower (Fig. 2(a, c)).

The $[\text{calix[4]arene}+\text{Na}]^+$ ions are present in very low abundance compared to the Cs^+ complex, and the selectivity β was arbitrarily assigned as >1000 which corresponds to a strong extraction of cesium and very low extraction of sodium cation for the same voltage. In such a way, a discrimination between medium and low concentration of complexed $[\text{calix[4]arene}+\text{Cs}]^+$ was made. It is clear, that our method is less sensitive for calix[4]arene with $\beta > 1000$.

Examination of the structure of the high Cs^+ selectivity calix[4]arene leads to the conclusion that within the monocrown family, the presence of the long octyl chain (Fig. 2a) or/and the aromatic crown

ring residue (Fig. 2b) improves their selectivity. Similarly for biscrown, the additional aromatic moiety (Fig. 2(d, e)) in a skeleton improves the selectivity. These observations confirm results obtained in liquid-liquid extraction [4] and MD which are explained in terms of preorganization (1,3-alternate versus cone or mobile conformation [10]) and, in the case of benzocrown derivatives, increase of structural complementarity toward Cs^+ and rigidification, and of the hydrophobicity of the complexation site unfavorable for sodium cation [11]. Hence, when hydrophobicity increases (like for octMC6, octMC6Bz2, BC6Napht1 and BC6Bz1), less Na^+ is extracted and better is the Cs^+/Na^+ selectivity.

The conformation of calix[4]arene crowns (Fig. 2a) (e.g., cone, partial cone, 1,3-alternate) affects also their selectivity [10]. The octyl (in octMC6) or iso-propyl (in iPrMC6) chain which blocked the calixarene in 1,3-alternate conformation (Fig. 2a), is more suitable for selective extraction of Cs^+ cation. With smaller substituents located at this position (e.g., methyl, Fig. 2a), the 1,3-alternate conformation necessary for efficient complexation remained in equilibrium with the two other possible conformations (e.g., cone, partial cone) and decreased the extraction of cesium. For a relatively smaller sodium cation, the calixarene 1,3-alternate conformation is not well adapted for complexation but represents an ideal target for Cs^+ larger and well fitted kation. These observations were confirmed by modeling [7–11] studies in which 1,3-alternate conformation was found as being most favorable for the complexation of Cs^+ .

The influence of the crown size on the complexation is also significant. A crown with six oxygen atoms offered the most suitable arrangement for cesium cation. The crown with seven oxygen atoms is too large for cesium. These observations are in agreement with MD simulations [7].

Benzo or naphtho aromatic groups in the crown, which increases the hydrophobic character of the calixarene, improve the selectivity of Cs^+ over other alkali cations, for both mono or biscrown compounds (see Table 1). In this case the crown size is slightly decreased by participation of the C=C double bond of the additional aromatic ring. X-ray data and MD [9] showed that the sodium cation is stabilized in the crown by one molecule of water. However the ESI technique, under our condition does not show this [calix[4]arene+Na+H₂O]⁺ solvated ion structure. Again, Nguyen [48] has demonstrated the hydration of alkylammonium ions under nonanalytical electrospray ionization conditions. More than 20 water molecules are associated with the central ion. The addition of aromatic moieties on the crown structure increased the calixarene hydrophobic character, prevented the binding of one water molecule in the crown. For both series, bis or monocrown calix[4]arene complexes, the sodium complex is formed on a trace level. As we have shown, the enhanced selectivity toward Cs^+ of these calix[4]arenes, is related to both conformation and hydrophobic character (the octyl chain crown aromatic moieties calixarene support this conclusion). These observations were also confirmed via the liquid-liquid extraction [4], molecular dynamic [7–9] and thermodynamic [12] studies.

On the other hand, according to the Lui method described in details in reference 38 for determination of stability constants (K_s), an estimation of the log K_s can be obtained. This estimation could only be made assuming that the ESI spectra directly reflect presence of some species in solution and the solvation of different calixarenes in the NPOE is identical. The literature [12] log K_s value of BC6 with Na^+ in acetonitrile is 1.97. Using Lui's equation [38]:

$$K_{s(\text{Cs})}/K_{s(\text{Na})} \approx S^* (I_{[\text{BC6}+\text{Cs}]^+} / I_{[\text{BC6}+\text{Na}]^+}), \quad (1)$$

where S^* is the relative cationization efficiency equal to 1 (because no correction has been applied in our result on peak intensities), and $\beta = I_{[\text{BC6}+\text{Cs}]^+} / I_{[\text{BC6}+\text{Na}]^+}$. The Eq. (1) could be then simplified to:

$$K_{s(\text{Cs})}/K_{s(\text{Na})} \approx \beta \quad (2)$$

and then

$$\log K_{S(\text{Cs})} - \log K_{S(\text{Na})} = \log \beta.$$

Using the log K_S of BC6 with Na^+ as a standard, the log K_S value of BC6 with Cs^+ is calculated as 3.6 from Eq. (2) different than the literature value (5). The discrepancy is certainly due to the approximations that have been made (e.g., absence of calibration, dilution effect). Although in the ESI-MS method the ion intensities are not directly proportional to the concentration of species present in solution, in order to apply the Lui methodology we have considered that the ESI is directly reflecting the species presence in solution. This result shows that with ESI method, a rapid estimation of the log K_S can be made, however in order to get an exact value, it was necessary to use calibration method [38].

4. Conclusion

In the nuclear industry field, the selective extraction of cesium present at trace level in nuclear waste is one of the major goals. ESI method, with its soft ionization characteristic enabled to study non covalent complexes present in solution and represents a technique of choice to study calixarene-cation complexes.

ESI/MS has been successfully applied (Fig. 6), for the first time, for rapid estimation of calixarene selectivity towards some selected cations of interest such as alkali cations. Results obtained are in agree-

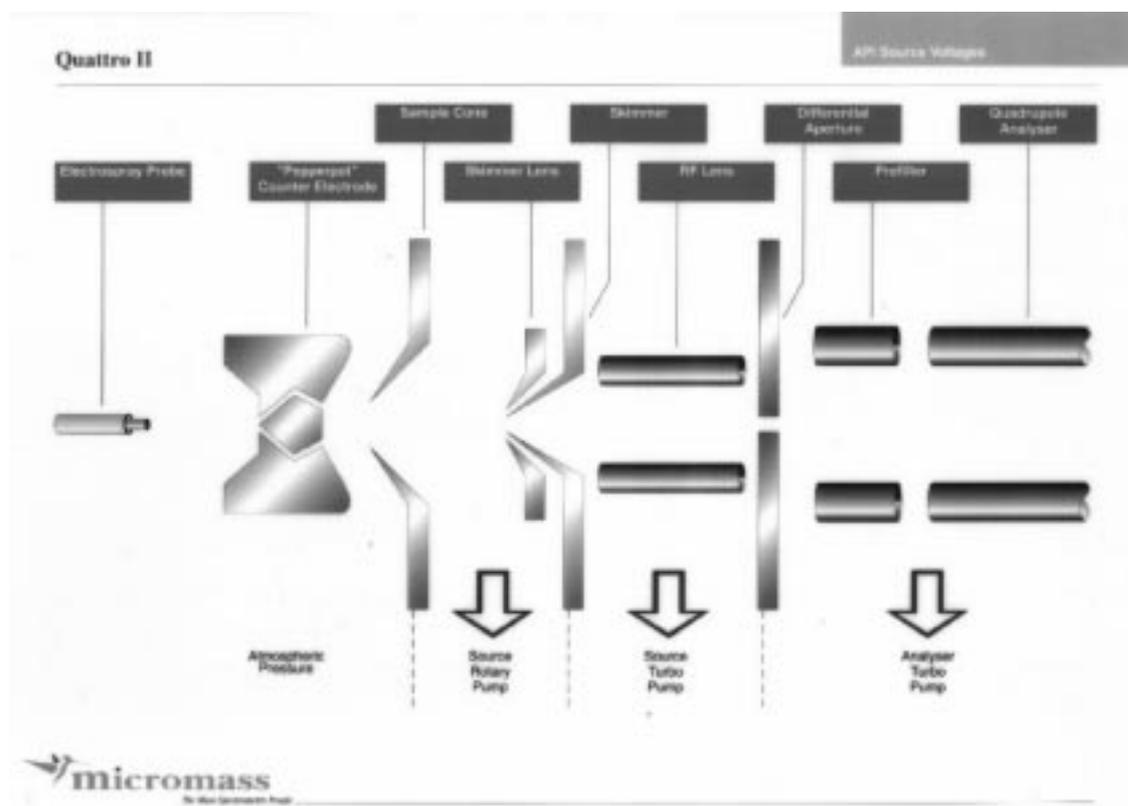


Fig. 6. ESI Quattro II mass spectrometer scheme.

ment with liquid-liquid extraction and therefore, ESI confirms the choice of the best calix[4]arene crown system for selective extraction of Cs⁺ with a possible nuclear waste disposal application.

It was also possible, by using this technique, to have a relative estimation of different complex concentrations present in solution allowing the tentative speciation of calixarene host-guest compounds. Finally, an estimation of the stability constant of complexes in solution using simple procedures is achievable. Still, better knowledge of the calixarene host-guest behavior when passing from solution to gas phase is needed (particularly of the stability of complexes in gas phase) and experiments in this direction are in progress.

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