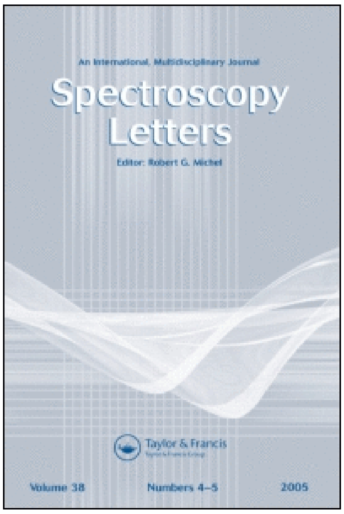

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Comparison of the Stability of Calix[4]arene-crown-6-cation Binary Complexes Under Electrospray Mass Spectrometry[‡]

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ABSTRACT

Electrospray/mass spectrometry ESI/MS analyses were performed to study the stability of calix[4]-arene-crown-6/alkali cation complexes in the gas phase, and in acetonitrile/water mixtures. This approach allowed a comparison with previous investigations by molecular-dynamic

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simulations,which demonstrated a complementarity between calculation and experiment. Experimental results obtained from ESI/MS confirm that the stability of calixarene/cation complexes depends upon the medium used. Indeed, the calixarene in solution presents a strong affinity for cesium, whereas in the gas phase, it has a stronger affinity for sodium. Similarly, the stability of [calixarene + Na]$^+$-type complexes in the solvent phase is increased by the presence of water in the dilution system (up to 40% in acetonitrile), whereas other alkaline complexes are destabilized by water in any proportion. Finally, calixarenes that bear benzo groups on their crowns have an affinity for sodium, which is weak in solution, but considerably stronger in the gas phase.

Key Words: Calix[4]arene; Cs$^+$ complexes of calix[4]-arene-crown-6; Complexes study via ESI.

INTRODUCTION

Many studies have been performed with the intent of reducing the volume and the residual toxicity of radioactive High Activity (HA) liquid waste resulting from the reprocessing of spent fuel from nuclear reactors.[1,2] Extractant molecules should have a high specificity, in order to separate radionuclei from the inactive remainder of the liquid waste.[3] One potential extractant, calix[4]arene, a macrocycle made of four phenolic moieties linked together via methylene groups, offers different sites of inclusion, to which specific chemical moieties can be linked.

Calix[4]-arene-crown-6, particularly in its 1,3-alternate conformation, allows the selective separation of cesium cation by liquid–liquid extraction, regardless of the pH of the liquid waste.[4,5] This makes it useful for the removal of cesium contamination from solutions of fission byproducts, and from strongly saline solutions in the presence of large amounts of alkaline ions such as Na$^+$ or K$^+$, which result from the dismantling of nuclear spent fuel operations.[6,7]

These selective extractants and their alkali cation complexes have been studied by molecular dynamics (MD) simulations so as to better understand their particular affinity for cesium cation, as well as their cesium/sodium selectivity. This selectivity is dependent on the nature of the substituents grafted to the crown ether.[8] In particular, two p-disubstituted benzene groups on the crown would favour the gas phase stability of the binary sodium complex.[9] However, this does not necessarily mean that the sodium cation is included inside the cavity of the host system, as can occur in solution with cesium cation.

The selectivity for cesium, as observed in liquid/liquid extraction and in complexation experiments, can then be explained by a lesser tendency for sodium to lose its hydration shell during complexation,[10,11] which thus inverts the selectivity of the alkali cation series. MD simulations of the aqueous phase show, as do available X-ray structures, that sodium is co-complexed in the crown with a water molecule.[12] The lesser stability observed for sodium complexes when aryl groups are grafted onto the crown, should then result from a more hydrophobic environment, which hinders the complexation of the hydrated sodium cation in solution.

To empirically verify these simulation results, electrospray ionization/mass spectrometry (ESI/MS) experiments were performed. This soft-ionization/desorption technique is useful for gaining insight into the properties of complexes in both solution and in the gas phase.[13] ESI-MS has proven to be very efficient for the study of complexation phenomena in the framework of speciation studies, since all species present, organic molecules, cations and complexes, can be observed either directly or via charged adduct ions.[14–16]

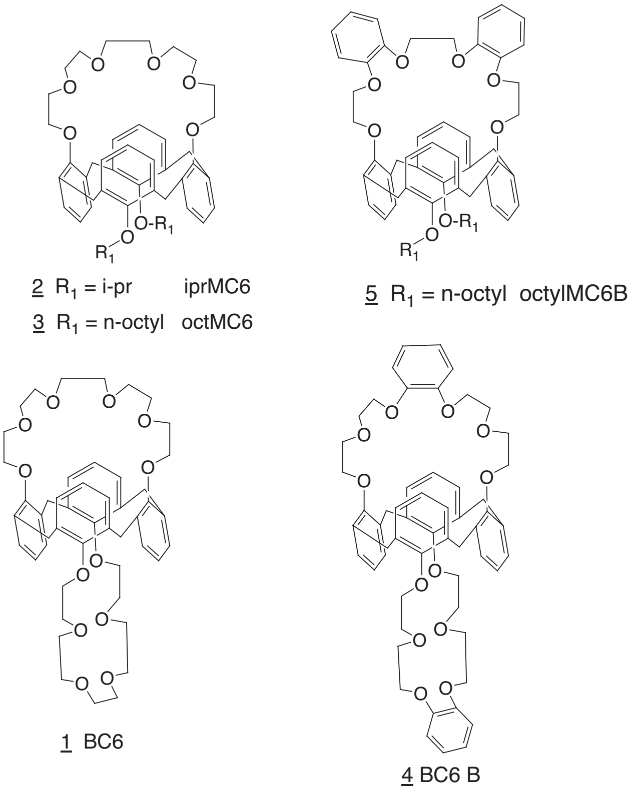
As described in a previous paper,[13] organic phases resulting from the extraction of alkali chlorides by various calixcrowns ethers diluted in NPOE (o-nitrophenyloctylether) solvent were analyzed by ESI/MS. In the case of the extraction of cesium by bis-crown-6 calix[4]arene (BC-6) ($\underline{1}$) (Figure 1), mass spectrometric analysis showed that, in addition to the mononuclear complex, whose presence has already been deduced, there was a small quantity of the binuclear species, which becomes the main extracted complex only when the cesium cation is introduced in excess (as in $(\underline{1} + 2Cs)^{+2}$).

The best calix[4]arene for this series of experiments was chosen by screening the family of monocrown iso-propyl mono-crown-6 calix[4]arene (ipr MC-6) ($\underline{2}$) and bis-crown $\underline{1}$ parent compounds with Cs^+, K^+ and Na^+ water solutions. In all cases the mono-crown-6 compound $\underline{2}$ was a better extractant for these cations, as its bis-crown-6 counterpart $\underline{1}$ had relative efficiencies of ~40, 45 and 25% for Cs^+, K^+, and Na^+ respectively.

The trend in Cs^+ extraction efficiencies observed for di-n-octyloxy mono-crown-6 calix[4]arene (oct-MC-6) ($\underline{3}$) and its dibenzo analogs (oct-MC-6B) ($\underline{4}$) was in favour of the calixarene $\underline{2}$. This same di-n-octyloxy calixarene $\underline{3}$, however, is a more efficient Cs^+ extractant than is calixarene $\underline{2}$.

ESI/MS detection was also used for the identification of degradation compounds resulting from the irradiation of the organic phase ($\underline{1}$ diluted in NPOE solvent). Our study showed that substitution products were formed from $\underline{1}$ when irradiation occurred in contact with nitric acid.[10,13]

This paper focuses first on different complexes of the sodium cation with two mono-crown calixarene 6 derivatives: di-iso-propoxy $\underline{2}$ and di-n-octyloxy



2 R$_1$ = i-pr iprMC6
3 R$_1$ = n-octyl octMC6
5 R$_1$ = n-octyl octylMC6B
1 BC6
4 BC6 B

Figure 1. Calixcrown-6.

3. In order to clarify the role of the solvent on the Cs$^+$/Na$^+$ selectivity in solution and in gas phase, we performed experiments to establish conclusively the stabilizing role of water on sodium binary complexes. In a second set of experiments, the cation reactivity of a calixcrown-6 was compared with that of its dibenzocrown derivative. The gas phase experiments were performed, using MS/MS together with collision-induced-dissocation (CID), so as to verify that the intrinsic (i.e. without solvent) stabilities of their sodium complexes were of the same order of magnitude. In turn they proved that the difference of stability of these complexes in acetonitrile was due only to cation solvatation.

In previous studies of calixarene complexes with alkali metal cations,[13,17,18] it was difficult to obtain complexes of the requisite stability, which we concluded was due to use of a two-step procedure—first complexation, followed by extraction of cationic species.

In order to avoid such discrepancies during the MS identification, we instead used the following procedure.

EXPERIMENTAL

Chemicals

The standard calix[4]arenes were purchased from Aldrich Chemicals. The dibenzo calix[4]arenes were obtained within the CEA network (Cadarache-Saclay, France). The solvents used were purchased from C. Erba (France).

ESI/MS Experiments

The detailed experimental procedure of complex-formation was described in Ref. [13]. The experiments were performed using a Quattro II (Micromass, Manchester, UK) triple quadrupole mass spectrometer. Either the first or the third quadrupole can be scanned for both the mass spectrum and various CID scanning.

In MS mode, the ions were introduced into the API source, where they dissolved at a rate dependent on the voltage applied to the lenses, and, in particular, to the cone. These ions were then analysed by scanning the first quadrupole. The mass spectra recorded give a reasonably faithful representation of the liquid phase, after addition in methanol in order to partition out the abundant NH_4^+ ion observation.[17] The relative peak intensities provided information about the complex stabilities. Thus, the greater the intensity of the peak of a complex in the mass spectrum, the more stable that complex was in solution in the afore mentioned conditions.

EXPERIMENTAL CONDITIONS

Typical Experimental Conditions

Stock solutions of calix[4]arenes (10^{-3} m/L) in acetonitrile were prepared. These were diluted to 1/10, then to these solutions equal volumes of aqueous solution containing Na^+, K^+, Cs^+ (1/3, 1/3, 1/3, total 1 equivalent) were added and the spectra were then recorded at different proportions of water in these solutions (Figures 2, 3).

The CID experiments were run in 100% acetonitrile for selected ions only (cone voltage—50V) with variation of collision energy as shown in Figures 4 and 5.

CID Experiments

Tandem-mass spectrometry was used to study partial fragmentations of ion previously-selected by the first quadrupole, by collision with inert gas in the collision chamber, Rf only, on the second quadrupole. This mode provides information about the structure of the selected ion, and about its stability in the gas phase toward the alkali cation that was released. Ions resulting from this fragmentation were analyzed by scanning of the third quadrupole.

Low energy CID experiments showed both the selected parent ion and the fragment ions, whose intensities varied as a function of the collision laboratory energy E_{Lab} which is the difference in potential between the source and the second quadrupole. As the collision energy increases, so

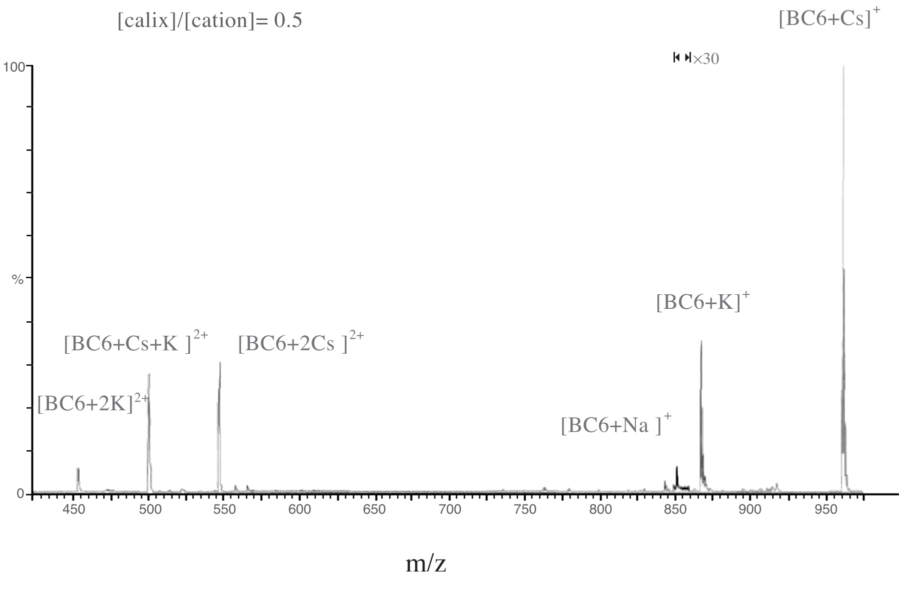


Figure 2. ESI/MS analysis of the complexation of Na^+, K^+, and Cs^+ by 1 (calixcrown BC-6, m/z 828 + kation, in acetonitrile).

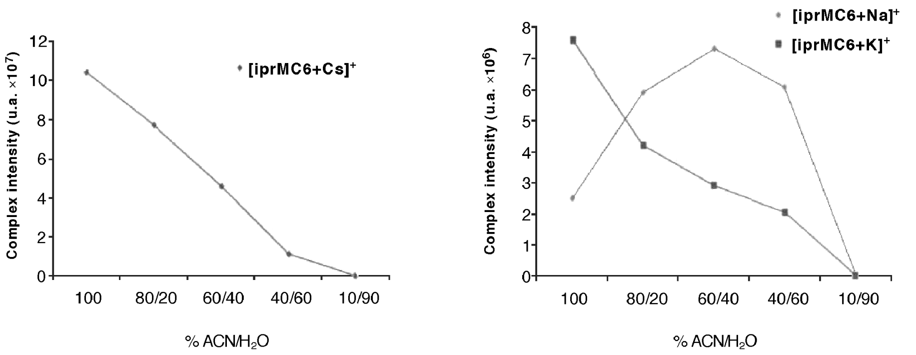


Figure 3. Influence of water content on the stability of complexes of 2 (iprMC-6, m/z 710, $[\text{iprMC-6} + \text{Cs}]^+$ (m/z 843), $[\text{iprMC-6} + \text{K}]^+$ (m/z 749), $[\text{iprMC-6} + \text{Na}]^+$ (m/z 733) prepared in acetonitrile from stoechiometric $[\text{Na}^+] = [\text{Cs}^+] = [\text{K}^+]$ mixture.

does the likelihood of an ion fragmenting according to the higher rate constant. Comparison of the $V_{1/2}$ values, measured at half of the parent ion's disappearance, allows us to compare the stability of the selected parent ion.

RESULTS AND DISCUSSION

Our first objective was to verify, via mass spectrometry, the yield of ion desorption and/or stability as a function of the preformed complexes that existed in solution, according to the proportion of water introduced into the solvent mixture.

Influence of Water on the Stability of Sodium Complexes

Before considering the influence of an addition of water to the dilution solvent, we first studied the competitive complexation of cesium, potassium and sodium cations by calix[4]arene bis-crown-6, 1, in acetonitrile used as solvent (Figure 2).

As seen in Figure 2, the ESI mass spectrum for calixarene 1 displays both singly charged species, e.g., $[\text{BC-6} + \text{Cs}]^+$, $[\text{BC-6} + \text{K}]^+$, and $[\text{BC-6} + \text{Na}]^+$, at m/z 961, 867, and 851—and doubly-charged species, e.g., $[\text{BC-6} + 2\text{Cs}]^{2+}$, $[\text{BC-6} + \text{Cs} + \text{K}]^{2+}$, $[\text{BC-6} + 2\text{K}]^{2+}$, at m/z 547, 500 and 453 respectively. This variation in behavior suggests that both bis-crown

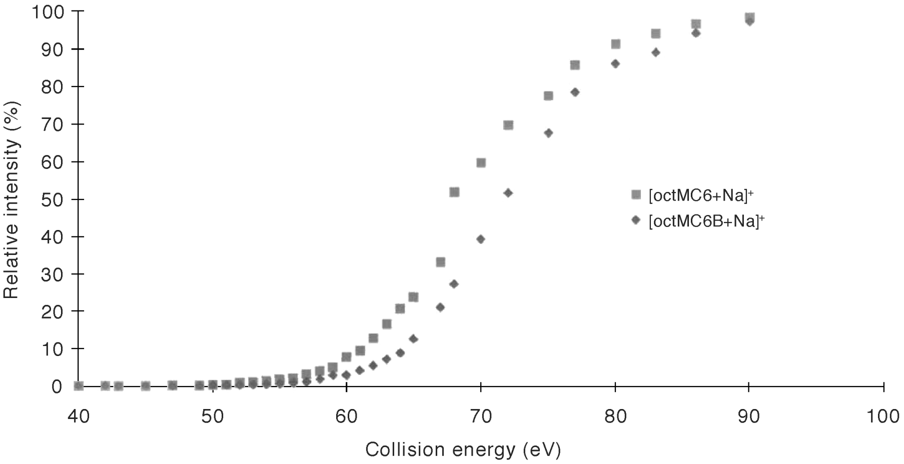


Figure 4. MS/MS study of the gas-phase stability of complexes of 1 $[BC\text{-}6 + Cs]^+$ (m/z 961), $[BC\text{-}6 + K]^+$ (m/z 867), and $[BC\text{-}6 + Na]^+$ (m/z 851) according to the E_{Lab} value (eV). In Figures 4, 5, 6 the collision energy is given in E_{Lab} (eV).

cavities may host two cations, one per crown, in contrast to the monocrown. A similar experiment done with a calixarene having but a single crown leads to the appearance of only singly-charged species. The ESI spectrum displays that, in acetonitrile, the cesium complex is the most stable of the monocharged cationised complex species. However, the effect is lower than the doubly charged complex, because 1 solvated Cs^+ and K^+ with similar yield. This indicates that, most likely, the Cs^+ cation induced in the first crown modified the conformation and thus the second Cs^+ cation is in the second crown with K^+, the latter being more easily complexed under this modified conformation. This reflects the greater stability in the gas phase, rather than that in a solution of the ternary complex, compared to both the potassium and sodium complexes.

Since the stability of the complex is a function of the nature of the dilution solvent,[7] greater or lesser solvation of the cation, addition of water can induce modifications in the mass spectrum. Figure 3 shows the variation of intensity of each complex as a function of the dilution of the solvent.

In the case of cesium and of potassium complexes, the proportion of water in the solvent varies inversely with the intensity of the specific ion, because the ion generated in solvent is destroyed via the cation solvation induced by water. The sodium complex reacts differently. This result means that Na^+ is less solvated by water.

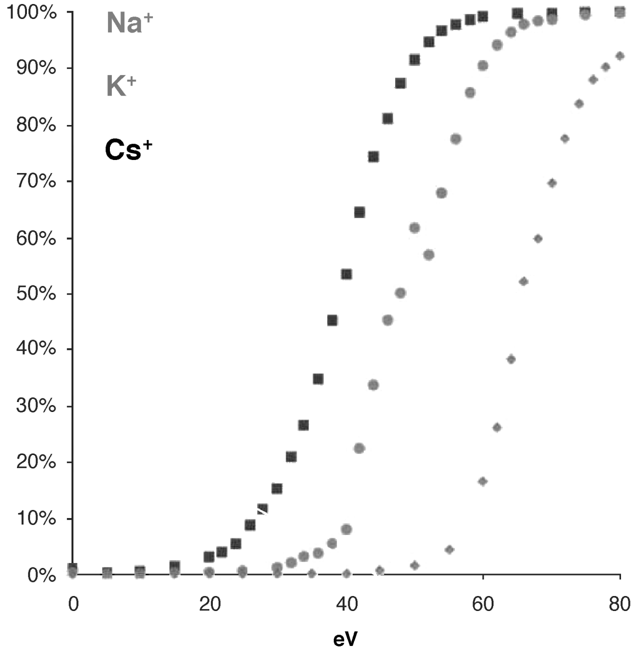


Figure 5. MS/MS study of the gas-phase stability of complexes of 3 [octMC-6 + Na]$^+$ (m/z 874) and [octMC-6B + Na]$^+$ (m/z 970) according to the E_{Lab} value (eV) of 5.

The abundance of the diagnostic binary complex decreases as the water ratio in the solvent system increases. Addition of water induces an increase in the stability of the Na^+ complex. This last phenomenon most likelycorresponds to the introduction of a water molecule to the crown of the calixarene; however, for calixarene *2* a [iprMC-6 + Na + H_2O]$^+$ complex was not detected by ESI/MS, which may be a result of its rather low stability during ion desolvation. When the proportion of water increases, there is solvation of the cation and destruction of the complex in solution, as is the case with [iprMC-6 + Cs]$^+$ and with [iprMC-6 + K]$^+$ ions.

Stability of Complexes in the Gas Phase

A second objective of this study was to compare the affinity of the gas-phase of 1 toward cesium, potassium, and sodium, as well as the relative affinities of two other studied calixarenes for sodium. In this case, the investigation was performed on naked binary complex, free of solvent, which is not the case at the cone where ions undergo solvatation. These experiments were performed using tandem-mode CID. The breakdown curves which were thereby obtained by raising collision laboratory energy, are shown in Figures 4 and 5.

In the case of calixarene-cation complexes, both the parent ion, and the cation produced during the collision, are observed in the mass spectrum. The breakdown curves show that, in the gas phase, the cesium complex is the least stable, and the sodium complex is the most stable. The $V_{1/2}$ values (measured in E_{Lab} values) observed for the breakdown were 35 eV, 45 eV and 68 eV for calixarene 1 $[BC\text{-}6\text{-}Cs]^+$, $[BC\text{-}6\text{-}K]^+$ and $[BC\text{-}6\text{-}Na]^+$ respectively. The complexes with Cs^+ and K^+ are relatively close, compared to the one with Na^+. In single-mode MS, the mass spectrum (Figure 2) showed that, in acetonitrile, the cesium complex was more stable than the sodium complex, which is the converse of its behaviour in solution. Thus the relative order of the stabilities of the complexes in solution is thus the opposite of that in the gas phase.

In the second part of the investigation, we sought to determine the role of water on the Na^+-calixarene complex stability, as observed from modelling studies. Finally, we compared the behaviour of 1 (with its weak selectivity towards Na^+) to that of dibenzo-crown-6 calix[4]arene (BC-6B) (4) and dibenzo crown-6 din-octyl calix[4]arene (octMC-6B) (*5*) (Figure 5), whose selectivities are much greater.

As for the affinity of the two calixarenes for sodium, liquid–liquid extraction has shown that the calixarene which bears two benzo groups on its crown is that which presents the weaker affinity for sodium.[19,20] Under CID, the sodium affinities of these two calixarenes are very close with curves shifted by only a few eV. The complex formed from the calixarene bearing the benzo groups have a greater stability.

Three types of qualitative experiments performed showed that:

i) when the water ratio varies, loss of sensitivity is observed for calixarene 1 $[BC\text{-}6 + K]^+$ and $[BC\text{-}6 + Cs]^+$. However, an increase in the ratio of water in the solvent system leads to greater stability of the $[BC\text{-}6 + Na]^+$ complex.

ii) CID analysis was performed on calixarene 1 $[BC\text{-}6 + K]^+$, $[BC\text{-}6 + Cs]^+$, and $[BC\text{-}6 + Na]^+$ quasimolecular cations. An important difference was observed between their stabilities in water solution, and in gas-phase. Not only is a consistent difference observed in the order of the stabilities, but this order is, in gas-phase MS, the opposite of that in solution.

iii) Finally, CID analyses performed on calixarene 1 $[BC\text{-}6 + Na]^+$ ion and, on both the analogous dibenzo crown-6 calixarene *4* and

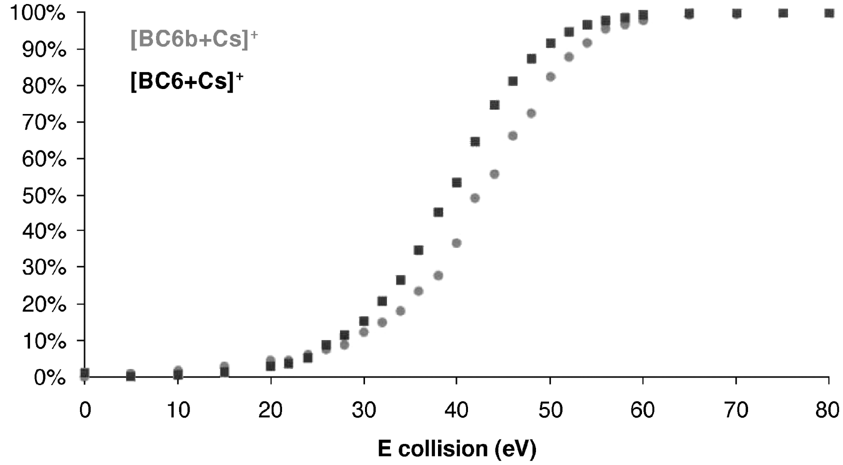


Figure 6. MS/MS study of the gas-phase stability of complexes of 1 [BC-6 + Cs]$^+$ (m/z 961) and of 4 [BC-6B + Cs]$^+$ (m/z 1058) according to the E_{Lab} value (eV).

5 ions ([BC-6B + Na]$^+$, and [dibenzo-BC-6 + Na]$^+$) show that both ions behave completely differently than in water-containing solvent systems (Figure 6). Modelling studies indicate that their gas phase stabilities should be quite close; however, under CID conditions, the dibenzo-biscrown calixarene is so strongly selective towards Cs$^+$ that study of analogous Na$^+$ complexes is almost impossible.[21–26]

CONCLUSION

Experimental results obtained from ESI/MS confirm that the stability of calixarene/cation complexes depends upon the medium used. Indeed, the calixarene in solution presents a strong affinity for cesium, whereas in the gas phase, it has a stronger affinity for sodium. Similarly, the stability of [calixarene + Na]$^+$-type complexes in the solvent phase is increased by the presence of water in the dilution system (up to 40% in acetonitrile), whereas other alkaline complexes are destabilized by water in any proportion. Finally, calixarenes that bear benzo groups on their crowns have an affinity for sodium, which is weak in solution, but considerably stronger in the gas phase. In this study, the water/acetonitrile solvent system was chosen so as to resemble as closely as possible the conditions under which Cs is extracted industrially. Alcohol addition, as suggested by one of the referee of this paper decreases the doubly-charged ions intensities, countering the increase of intensities which typically accompanies a rise in solvent polarity of solvent rise. When the acetonitrile-methanol system was used, we did not observe any significant variation of the calixarene-Cs^+/calixarene-K^+ complex ratio, which remains in the 10:1 range, and independent of the relative concentration of methanol in this binary solvent system.[27] Although benzocrown bearing calixarenes were not specifically tested with radioactive $^{22}Na_4$ in liquid–liquid extraction experiments,[28] as we previously did for calixarenes $\underline{1}$ and $\underline{2}$, we can reasonably assume that all calixcrown compounds have little sodium affinity in solution. These results, taken as a whole, confirm the interpretation of the MD simulations in aqueous phase, which lead us to conclude that cesium/sodium selectivity in solution is modulated by hydration of the sodium cation in the complex, benzo-crown derivatives having a greater selectivity as a result of the greater hydrophobicity of the complexation site. This shows the complementarity of the experimental and theoretical approaches.

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