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Determination of alkali metal ion binding selectivities of calixarenes by matrix-assisted laser desorption ionization and electrospray ionization in a quadrupole ion trap

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Abstract

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) and electrospray ionization mass spectrometry (ESI-MS) are used to evaluate the alkali metal ion binding selectivities of a series of calixarenes. Each calixarene of interest is mixed with one or more alkali metal salts (1:100 ratio of calixarene to metal), either in the ESI solution or on the MALDI probe surface, and the relative binding selectivities are directly determined from the intensities of the calixarene/metal complexes in the mass spectra. For *t*-butylcalix[4]arene-tetraacetic acid tetraethyl ester (calixarene **1**), complexation of Na^+ is favored over complexation of K^+, in agreement with prior solution results obtained by conventional methods. For the three calixarenes that do not have *t*-butyl groups on the upper rims, the calixarenes preferentially bind K^+ over Na^+, thus demonstrating that size selective complexation can be probed with both the ESI and MALDI methods. Collision-activated dissociation results indicate that the phenyl oxygens, but not necessarily the ethoxy ethyl oxygens of the lower rims, are the primary binding sites for the alkali metal ions. (Int J Mass Spectrom 193 (1999) 197–204) © 1999 Elsevier Science B.V.

Keywords: MALDI; Electrospray ionization; Calixarene; Quadrupole ion trap; Binding selectivity

1. Introduction

Some of the most varied and complex macrocycles belong to the class of compounds known as calixarenes. The representative calixarene structure depicted in Fig. 1 (calixarene **1**) is notable for its polar "lower rim" and hydrophobic, alkyl "upper rim," and the possibilities for derivatization of these structures to further modify their physical and chemical properties are enormous. The solution-phase conformations that stem from the properties of the upper versus lower rims give calixarenes their unusual binding and solubility characteristics. For example, it has been shown that, for molecules such as crown ethers, the inclusion of a guest atom or molecule is dependent on the size and flexibility of the cavity relative to the guest [1–17]. Furthermore, the solubility of some calixarenes in apolar solvents has been utilized for the extraction of ions from picrate salts out of polar solvents [2]. Thus, the ability to tailor these molecules to the desired cavity size, hydrophobicity, and rigidity makes them appealing in numerous applications of host–guest chemistry.

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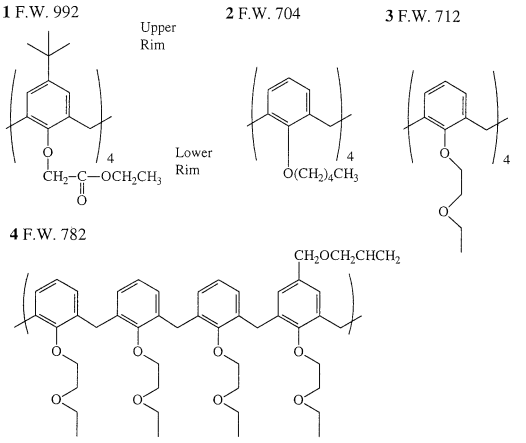

Fig. 1. Calixarene structures.

Mass spectrometric study of host–guest complexes has been advanced by the development of electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) techniques which have allowed more detailed characterization of nonvolatile, thermally nonlabile compounds such as the calixarenes in the past few years. The initial studies of calixarenes involved use of desorption chemical ionization or secondary ion mass spectrometric methods [18,19]. Gas-phase relative complexation constants were measured for calixarenes binding to neutral esters, ketones, and acetonitrile based on mass spectral intensities. By using ESI, Mann and co-workers evaluated the alkylammonium ion complexation of resorcinol-based calix[4]arenes [20]. The complexation of calixarenes with alkali metal ions created by laser desorption was investigated by Dearden et al. in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer and size-selective effects were noted [21]. Most recently, MALDI-mass spectrometry was used to study calixarenes, and alkali metal adducts were detected [22]. Numerous other ESI-MS and occasional MALDI-MS studies have focused on the generation and analysis of host–guest complexes containing other types of hosts, including crown ethers, lariat ethers, carcerands, and cyclodextrins in the gas phase [23–32].

There has been increasing interest in the capabilities of ESI-MS and MALDI-MS methods for quantitative measurements related to host–guest chemistry, such as the evaluation of binding selectivities or binding constants [33–39]. For example, we have undertaken a series of studies aimed at validation of ESI-MS measurements for the determination of metal ion and ammonium binding selectivities of model hosts, mainly crown ethers and related analogs [33,34,39]. In many cases, good correlation was found between selectivity values predicted from known stability constants of host–guest complexes in solution and from ESI mass spectral ratios for host–guest complexes generated by spraying solutions containing mixtures of hosts and guests. The use of MALDI-MS for estimating selectivities is less well-studied, and there remain questions about the feasibility of MALDI-MS for quantitative measurements in general. Accurate quantitative analysis by MALDI-MS typically relies on the use of internal standards due to shot-to-shot variations in signal intensities [40–45], but relative intensities of different ions within a spectrum generally remain consistent despite the shot-to-shot changes in total intensity.

In the present article, the use of MALDI-MS for estimation of alkali metal binding selectivities of a series of calix[4]arenes is undertaken in a quadrupole ion trap mass spectrometer. A comparison of MALDI-MS to ESI-MS for measurement of binding selectivities is presented, and initial evidence indicates that the results are comparable for analogous experiments. CAD experiments are undertaken to further probe the nature of the calix[4]arene/alkali metal complexes, and the high binding energies of the calixarene hosts to the alkali metal ions are reflected in the fragmentation patterns of the complexes where the complexes undergo elimination of the side chains on the rims rather than simple disassembly of the complexes.

2. Experimental

The MALDI and electrospray mass spectrometers were built in-house using Finnigan trap electrodes and Finnigan ITD electronics. ITMS software allowing TTL triggers for laser firing and SWIFT operation

was used for experiment control and data collection. The spectrometers were operated in the positive ion mode. Mass-range extension during resonant ejection was accomplished by application of the appropriate waveform to the endcap electrodes using a SWIFT program and arbitrary waveform generator, described in detail previously [46]. SWIFT waveforms were also used for isolation and collision activated dissociation.

2.1. MALDI

A Laser Science Model 337 nitrogen laser was focused on a fiber optic external to the vacuum chamber. The fiber entered the chamber through a Swagelok fitting and was routed through a series of three electrostatic lenses, whereupon the light exited and illuminated a portion of the 4 mm diameter probe surface. The probe was introduced axially and was kept approximately 1 mm from the fiber. Manual rotation of the probe was required to introduce a new sample area to the light beam. The probe was kept at −5 V, whereas −20, −50, and −165 V were applied to lenses 1–3, respectively. Helium was used as a background gas at nominally 2–3 $\times$ 10^{-5} Torr and was necessary for damping the kinetic energy of the laser desorbed ions.

Matrix (2,5-dihydroxybenzoic acid in every case) and analyte solutions were made up in chloroform as required for the calixarenes. The matrix to analyte ratio was 1000:1 and typically 2–4 μL of solution were applied to the probe tip, representing about 100 pmol of sample. Alkali metal chloride salts were dissolved in methanol to millimolar concentrations, and appropriate volumes were added to the calixarene solutions to achieve a hundredfold excess of metal ion. One laser shot per scan provided ample amounts of signal, and 10 scans were averaged per spectrum.

2.2. ESI

The electrospray instrument consists of two differentially pumped regions with an interface and ion optics fashioned after the Oak Ridge National Laboratory design [47]. Solutions were prepared similarly to those used for MALDI, with calixarene concentrations of 5 $\times$ 10^{-5} M in chloroform with equal volumes of 5 $\times$ 10^{-3} M alkali metal solutions added for each metal. The flow rate was set at 3–4 μL/min. The needle was held at approximately 4.5 kV, and electrostatic lens voltages were optimized for maximum throughput. Helium buffer gas was not used in these experiments due to the high pressure of solvent admitted via the ESI interface.

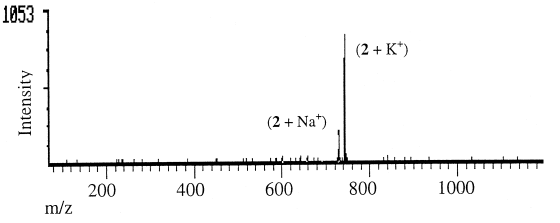

Fig. 2. MALDI spectrum of calixarene **2** with equal concentrations of Na^+ and K^+ present in the analyte mixture (1:100:100).

Calixarene compounds **2–4** were synthesized in the laboratory of Professor Michael Blanda and co-worker [48]. Calixarene **1** was purchased from Aldrich Chemical Co. (Milwaukee, WI) as were the matrix compound, chloroform, methanol, and metal salts. All chemicals were used without further purification.

3. Results and discussion

3.1. MALDI-MS measurements

The main objective of the study was to estimate alkali metal binding selectivities based on signal intensities of complexes formed from well-defined mixtures of calixarenes and metal salts. The calixarenes in this study (see Fig. 1) all consist of four aromatic rings with different lower rim substituents. Only calixarene **1** possesses the bulky *t*-butyl groups on the upper rim. Each of the calixarenes display excellent detectability by MALDI, and complexes containing a single sodium or potassium cation dominate the spectra. An example of a typical MALDI mass spectrum for calixarene **2** with sodium and potassium salts at a 1:100:100 ratio is shown in Fig. 2. The (calixarene **2** + K^+) complex is the most intense ion in the spectrum, and the (calixarene **2** + Na^+)

Table 1
Ion abundance (percent of total) from MALDI experiments with alkali metals 100 times more concentrated than the calixarenes[a]

Compound	$(M + Na)^+$	$(M + K)^+$
1	75	25
2	25	75
3	40	60
4	40	60

[a]All values rounded to nearest 5%.

complex has substantially lower intensity. Table 1 summarizes the MALDI results for the other calixarenes in terms of the percentages of the alkali metal complexes observed.

Calixarene **1** shows a preference for Na^+ complexation over K^+ complexation. For calixarenes **2–4**, the (calixarene + K^+) complex is the dominant ion, suggesting that this series of calixarenes has a strong preference for binding the larger K^+ ion over the smaller Na^+ ion. If the binding selectivity was dictated solely by the gas-phase stabilities of the K^+ versus Na^+ adducts, then a preference for Na^+ would be observed consistently due to the greater charge density of Na^+ over K^+. Therefore, size selectivity is reflected by the MALDI results.

To provide further validation of the MALDI method for determination of binding selectivities, the complexation of dibenzo-18-crown-6 with K^+ and Na^+ was studied as a model system. The binding constants of dibenzo-18-crown-6 have been reported previously in methanolic solution [49]. The log *K* for the complexation of dibenzo-18-crown-6 and K^+ is 5.0, whereas it is 4.37 for dibenzo-18-crown-6 and Na^+, indicating a preference for K^+ complexation. For the MALDI experiments, solutions containing dibenzo-18-crown-6 with one of the alkali metal salts were prepared at 1:100 molar ratios (4.7×10^{-4} M alkali metals and 4.7×10^{-6} M dibenzo-18-crown-6) and applied to the probe tip. MALDI spectra were acquired for each of the 1:100 mixtures, followed by analysis of a 1:100:100 mixture of dibenzo-18-crown-6 with both metals. Alkali metal contamination is an unavoidable problem, but this factor can be corrected upon examination of the 1:100 mixtures. MALDI analysis of the two 1:100 metal-containing mixtures indicates that the intensity of the (dibenzo-18-crown-6 + Na^+) complex requires a correction factor of about 1.4 to normalize it to the intensity of the (dibenzo-18-crown-6 + K^+) complex, stemming from the differences in MALDI efficiencies. For the MALDI analysis of the 1:100:100 mixture, the intensity of the K^+ complex is about 4.7 times greater than that of the Na^+ complex, indicating greater selectivity for K^+. The factor of 4.7 is the preference for K^+ over Na^+ and is designated the "selectivity." Upon incorporation of the correction factor of 1.4, the selectivity for K^+ over Na^+ is reduced to 3.4. The calculated selectivity of dibenzo-18-crown-6 for complexation of K^+ over Na^+ is 4.2, assuming equilibrium in solution and by using the log *K* values and concentrations listed above. The agreement between the calculated selectivity and the experimental MALDI selectivity is quite good considering the vastly different environments of the MALDI versus solution equilibrium experiments. At the very least, the qualitative agreement in the preference for K^+ over Na^+ by dibenzo-18-crown-6 indicates that the MALDI method offers promise as a means to rapidly screen binding selectivities.

It was found that despite fluctuations in the absolute signal intensities of as much as 35%, the relative standard deviation of the peak ratios was calculated to be 13%. This relative standard deviation was calculated based on sampling nine different locations on the MALDI target, with eight spectra averaged from each location.

Previous studies have shown that calixarenes possessing upper rim functional groups transport and bind Na^+ preferentially [50,51]. For example, the alkali metal complexation of calixarene **1** has been studied in detail by conventional extraction and UV spectrophotometric methods [52], and it was found that the extraction percentage (from water to CH_2Cl_2) for Na^+ was approximately twice that of K^+, and the stability constant of (calixarene **1** + Na^+) was 5.0 and that of (calixarene **1** + K^+) 2.4 in methanol. The difference in stability constants was less dramatic in acetonitrile (5.8 versus 4.5) [52]. One possible explanation for this reported preference for Na^+ complexation by calixarene **1** relative to the K^+ selectivity

observed for calixarenes **2–4** is that the presence of bulky, branched alkyl groups on the upper rim of **1** forces the molecular subunits to pinch together at the lower rim, consequently constricting the opening which is then unable to accommodate a larger guest ion. In fact, the ability of the calixarenes to extract K^+ over Na^+ has been shown to be enhanced when the host can intraconvert from the cone conformation to partial cone [51]. Second, calixarene **1** possesses ester functional groups on its lower rim, in contrast to the ether groups on the lower rims of calixarenes **2–4**. The dipoles associated with the carbonyl oxygens of calixarene **1** may have more favorable orbital overlap with the smaller Na^+ ion than the larger K^+ ion. Furthermore, a series of compounds with 1–3 connectivity bridged by diethyl ether groups, termed calix-crowns, have demonstrated high selectivity for K^+ over Na^+ [51]. Compounds **3** and **4** are structurally similar to these calix-crowns in that they feature additional ether oxygens, although not fully bridged as in the former compounds. Thus, the K^+ selectivity observed from the MALDI measurements can be logically rationalized based on the structures of the calixarenes.

3.2. ESI measurements

For the comparative ESI measurements of selectivity, solutions containing each calixarene with sodium and potassium salts were analyzed. An example is shown in Fig. 3. Fig. 3 clearly shows that when NaCl and KCl salts are added separately to solutions of calixarene **2**, complexation is efficient for either of the alkali metals. The spectrum that results from spraying a mixture of the two alkali metal salts with the calixarene (100:100:1) indicates a large preference for K^+ complexation. The results of the other ESI measurements are summarized in Table 2. As was noted for the MALDI measurements, each of the calixarenes **2–4** shows binding selectivity for K^+ over Na^+ whereas calixarene **1** still favors Na^+ in the ESI experiments.

"Correction factors," as described by our group previously [33] and briefly mentioned in the MALDI section, were not applied for the ESI measurements.

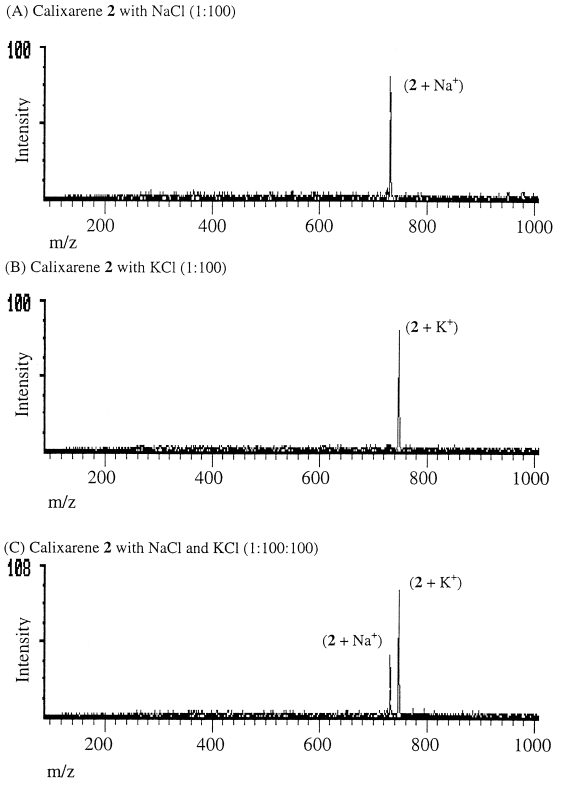

Fig. 3. ESI spectra of calixarene **2** with Na^+ and K^+. (A) Calixarene **2** with NaCl (1:100), (B) calixarene **2** with KCl (1:100); (C) calixarene **2** with NaCl and KCl (1:100:100).

Dibenzo-18-crown-6, a model used in the MALDI validation studies, has been examined extensively by ESI-MS [53]. Complexation studies involving Na^+ and K^+ with dibenzo-18-crown-6 revealed that spray efficiencies and response factors were virtually identical [53], thus alleviating the need for any data correction. Furthermore, due to the lack of published log *K* values for the novel calixarenes in the present

Table 2
Ion abundance (percent of total) from ESI experiments with alkali metals 100 times more concentrated than the calixarenes[a]

Compound	$(M + Na)^+$	$(M + K)^+$
1	85	15
2	30	70
3	15	85
4	20	80

[a]All values rounded to nearest 5%.

study, the implementation of correction factors was not pursued further.

There are some moderate differences in the specific ratio of K^+ complexes to Na^+ complexes reflected in the MALDI versus ESI spectra for each calixarene, but the preference towards K^+ or Na^+ for the various calixarenes is consistent. The precisions of the spectral K^+/Na^+ ratio measurements vary by up to 20%, so the variations between the ESI and MALDI selectivity ratios may stem in part from the variabilities of the experimental errors in the ESI and MALDI methods in addition to reflecting differences in the mechanisms of complex formation. For example, it has been shown that solvent effects have a large effect on complexation of the calixarenes [51]. Likewise, a complete lack of solvent that is inherent to the MALDI process may promote a change in complex formation. While some x-ray studies of calixarene complexes have implied that the crystalline state mimics that of the solvent state from which the crystal formed [51], it seems likely that the evaporation of solvent to dryness may exert some influence on the observed selectivity. For example, the concentration of free ions will increase dramatically, and the difference in ion solubility and association with the counterion will be amplified.

The added ether functionality on the upper rim of compound **4** versus compound **3** allows scrutiny of this flexible arm as a factor in complexation. The K^+/Na^+ selectivity ratios for these two calixarenes differ by only five percent in both the MALDI and ESI experiments. It is generally accepted that cation complexation is the role of the lower rim functional groups [40]. Unlike a lariat ether compound, the extra "arm" on the upper rim in calixarene **4** is unable to assist in the complexation of the tightly enveloped cation. Moreover, the extra ether oxygens in calixarene **3** that are absent in calixarene **2** should be able to contribute to complex stability, especially in the case of binding larger cations. However, complexation of K^+ is clearly favored for all three calixarenes **2**–**4**, suggesting that the sizes of K^+ and Na^+ are not sufficiently different to cause the change in selectivity observed for calixarene **2** relative to calixarene **3**. Likewise, the preference for K^+ complexation indicates that the extra arm on the upper rim of calixarene **4** does not play a significant role in defining the binding selectivity. In fact, CAD data for all of the calixarene/alkali metal complexes indicates that the oxygen atoms adjacent to the aromatic rings are primarily responsible for cation binding, as discussed in Sec. 3.3.

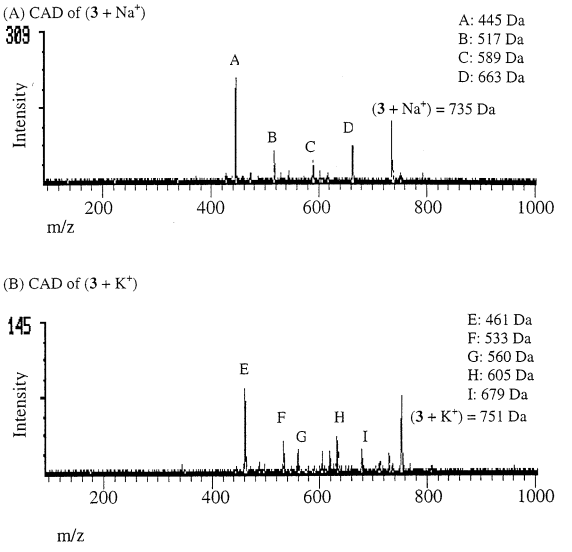

Fig. 4. CAD Spectra of calixarene **3**. (A) CAD of (**3** + Na^+); (B) CAD of (**3** + K^+).

3.3. CAD results

Collisionally activated dissociation was used to probe the structures of the calixarene/alkali metal complexes. In several previous studies of gas-phase host–guest complexes, it was found that collisional activation results in disassembly of the complex via disruption of the electrostatic bonds between the donor atoms of the host and the metal ion, thus resulting in release of the metal ion [54,55]. In the case of the calixarene/alkali metal complexes in the present study, the metal ion is not released. Examples of this behavior are shown in Fig. 4 for collisional activated dissociation of the calixarene **3**/alkali metal complexes. A series of losses corresponding to elimination of neutral diethyl ether units is observed, and in all cases the alkali metal ion is retained by the

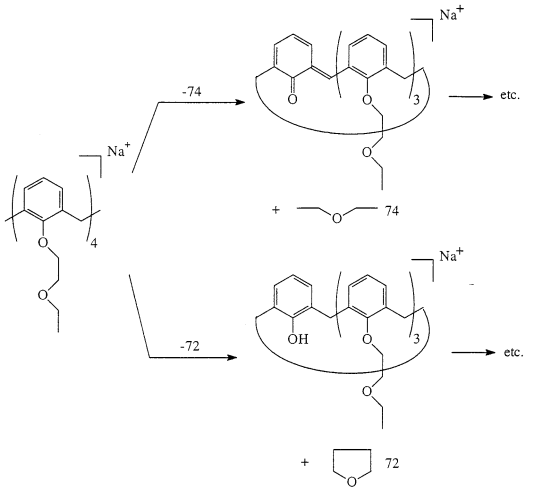

Fig. 5. Possible mechanism of losses for CAD of (calixarene **3** + Na^+).

remaining portion of the calixarene. Fig. 5 illustrates the pathways proposed to account for these neutral losses. The diethyl ether units stem from the lower rim functional groups, leaving the alkali metal ion bound to the phenyl oxygens of the lower rim. Similar types of fragmentation processes are observed for calixarene **4**/alkali metal complexes, suggesting similar binding interactions that do not involve the upper rim or ethyl ether oxygens.

4. Conclusions

MALDI-MS offers a new alternative method for evaluation of binding selectivity of hosts. The mass spectra resulting from MALDI of mixtures of calixarenes and alkali metal salts indicate that binding selectivity is reflected in the intensities of the complexes. In fact, the K^+/Na^+ selectivity ratio obtained from the MALDI measurements agrees with the ratios obtained from comparable ESI experiments. For the calixarenes that do not possess *t*-butyl groups on the upper rims, all show a preference for complexation with the larger K^+ ion. CAD experiments indicate that the phenyl oxygens are the primary binding sites rather than the ethyoxy ethyl oxygens present on the lower rim.

Acknowledgements

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