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Estimation of the Noncovalent Bond Dissociation Energies of the Gas-Phase Complexes of Macrocyclic Polyethers with Alkali Metal Cations Using an Electrospray Ionization/Triple Quadrupole Mass Spectrometer*

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An attempt to use the commercial triple quadrupole mass spectrometer, equipped with an electrospray ion source, to estimate the noncovalent bond dissociation energies of gas-phase complexes of macrocyclic polyethers with metal cations has been made. It was found that, after standardization of the experimental conditions, the collision cell voltage required for decomposition of 50% of the selected complex ions ($CE_{50\%}$) is proportional to the binding energies with reasonable accuracy. Even better correlation was obtained after recalculation of the $CE_{50\%}$ values to the center-of-mass frame ($ECM_{50\%}$). Measurements were made for 12-crown-4, 15-crown-5, 18-crown-6, and dibenzo-18-crown-6 complexes with alkali metal cations from Li^+ to Cs^+. These results indicate, that it is possible to estimate values of the binding energies after correct setting of the experimental conditions and using model compounds as the reference.

Key words: macrocyclic polyethers, complex ions, electrospray mass spectrometry, noncovalent bond energy

Macrocyclic polyethers, especially crown ethers, have many practical applications as cation-selective multidentate ligands [1,2]. They are used for selective extraction of the given cations and as the catalysts in many reactions used in organic synthesis. Crown ethers and their derivatives and analogs containing other heteroatoms (*e.g*. N and S) are broadly used also as the model systems for studying noncovalent interactions, molecular recognition and related phenomena both in a liquid [3] and gas phase [4].

Complexes of alkali metal cations with crown ethers were studied using various physicochemical methods and a large amount of data has been collected. The most important are the stability constants in different solvents and solvent mixtures. These data allow to calculate the complexation selectivity factors, which are essential for practical uses of crown ethers as selective complexation agents. During the last few years mass spectrometry became an important tool for such studies, mainly due to the

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development of the electrospray ionization (ESI) technique [5]. This ionization method allows transferring ions from the liquid to gaseous phase at very low energy level, providing that even very weakly bonded ion-molecule aggregates will be transferred without decomposition. The first systematic studies on application of ESI MS to investigate macrocyclic ethers complexes with metal cations were published in 1996 by Wang and Gokel [6] and Leize *et al.* [7]. These authors claimed, that the intensities of the peaks related to $[L + M]^+$ complex cations (L – ligand, M – alkali metal cation) in ESI mass spectrum reproduce roughly liquid phase concentrations of these ions. This statement would be true only in the case that the response factors, describing the relation between ion concentration in the liquid phase and intensity of the relative peak in a mass spectrum, are equal for all studied ion. Providing that the mass spectrometer used in the experiment shows constant peak intensity/ion abundance ratio in the studied *m/z* range, *i.e.* there is no discrimination of ions detection depending on their masses, the main phenomenon controlling the response factor is the solvation energy. It has been proved that for the complexes of one macrocyclic ligand with a series of alkali metal cations, solvation energies are similar, so for the semiquantitative estimations it is possible to draw conclusions directly from the relative peak intensities in the spectrum of a mixture of a ligand with several cations [7]. For comparing the selectivity of two different ligands with one cation, such a simple method is not applicable. In such case response factors have to be measured. Methods applicable for these measurements were described by Liu [8] and Brodbelt [9].

Mass spectrometry, by its nature, is very well suited for studying isolated ions and their reactions in a gas phase. Using various MS techniques it is possible to measure the properties and reactions of ions free from solvation [10,11]. This helps to understand better, between others, the intrinsic ion-ligand interactions without disturbances caused by a solvent. On the other hand, comparison of the gas phase and liquid phase properties of ions sheds light on the solvation phenomena. Properties of the isolated ions are also easier to calculate, using modern quantum chemistry methods, so it is important to have high quality experimental data for comparison purposes to determine the level of theory, necessary to achieve accurate results.

During the last few years, several attemps were made to apply mass spectrometry techniques for measuring relative and absolute binding energies of the complex ions. One of the first attempts to estimate the gas-phase selectivities of the crown ethers for alkali metal cations complexation was made by Maleknia and Brodbelt in 1992 [12]. Their results, obtained by Cooks' kinetic method [13], using LSIMS-generated ions, were not confirmed, however, by later measurements and seem to be incorrect. In the work of Dearden *et al.* [14] the authors concentrate on comparing the different ligands rather than cations. Their results show that in a gas phase alkali metal cations affinity of the crown ethers grows always with the size of the ring, in contrast to the liquid phase observations.

The most accurate absolute values of binding energies of the complex ions were obtained by a threshold collision-induced dissociation method, developed by the group of Armentrout and described in a series of papers. Their results up to beginning of the year 2000 are summarized in the review by Rodgers and Armentrout [15]. In this review, there are also references to the other methods of measuring of the binding energies in a gas phase, so they will not be discussed here. Even more recent results were described by Armentrout in a chapter of the „Modern Mass Spectrometry” series [16]. Another comprehensive review, dealing with the quantitative determination of noncovalent binding interactions in a gas phase, has been published recently by Daniel *et al.* [17]. In this work, the authors focus their attention mainly on the complexes of biomolecules, but a lot of information concerning metal ions complexes with macrocycles can also be found. Already during the course of this work a paper by Anderson, Paulsen and Dearden appeared [18], in which measurements of the binding energies of alkali metal cations with dibenzo-18-crown-6 were described, which promped us to include this ligand to our work also. These measurements were made using a bracketing method on the FT-ICR mass spectrometer. Other crown ethers were taken as the reference compounds. Unfortunately, the accuracy of this method was quite low (up to 25% uncertainty).

Many high level calculations of the properties of the isolated ligand – metal cation complex ions were made by Feller and coworkers [19–23]. Advanced calculations for dibenzo-18-crown-6 complexes were performed also by Dearden *et al*. [18]. Calculated binding energies of the crown ethers – alkali metal cations complexes are in fair agreement with the experimental data, however especially for heavy cations (Rb^+, Cs^+) discrepancies are significant [24]. One of the possible explanations is based on the assumption that the complex ions undergoing CID fragmentation are excited, so their internal energy is higher than the energy calculated for the ground state of the best conformation. Consequently, measured binding energies are significantly lower than calculated ones and the difference is growing with the size of the cation.

Threshold collision-induced dissociation method gives quite accurate absolute values of the ligand – cation binding energies but it has one significant drawback: it requires a sophisticated, custom-built instrument, *i.e.* guided ion beam mass spectrometer [25,26]. For the chemist working in the analytical or synthetic organic chemistry, it will be very important to have access to a rapid and simple, though less accurate method for estimation of the relative gas-phase binding energies. Such a method have to fulfill two main requirements: i) it should be possible to make the appropriate measurements using routine mass spectrometer available in the majority of MS labs, ii) it should give at least relative values of the binding energies accurate enough to make the comparisons between different ligands and cations.

In our laboratory we have tested the possibility of using a commercial triple quadrupole mass spectrometer, equipped with an electrospray ion source, as a tool for estimating the relative binding energies of noncovalent complexes. As the model compounds we selected four crown ethers: 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6), and dibenzo-18-crown-6 (DB18C6). Complexes of these ligands with alkali metal cations from Li^+ to Cs^+ have been studied. The obvious reason for selection of the first four model compounds was the availability of experimental and calculated data of ligand – cation binding energies.

EXPERIMENTAL

Alkali metal chlorides (purity above 99.8%) and crown ethers were purchased from Aldrich and used without further purification. Methanol (Merck, HPLC grade) and redistilled water were used as the solvents. Each reagent has been dissolved in MeOH–H_2O system (7:3 v/v) to obtain $1 \cdot 10^{-3}$ M stock solution. Solutions of complexes for infusion were prepared by mixing 100 μl of crown ether solution with 100 μl of the appropriate alkali metal chloride solution and diluting with methanol-water (7:3 v/v) to 1 ml. In some experiments the solutions of a single alkali metal chloride with all five crown ethers were used. The concentrations of the crown ethers were adjusted to even out the relative intensities of the corresponding peaks in the spectrum. Measurements were performed 30 min after preparation of the solutions. Samples were infused to the ion source using syringe Harvard Apparatus Pump 11.

All MS measurements were performed using API 365 triple quadrupole mass spectrometer (Applied Biosystems) equipped with a TurboIon Spray source. This source was operated as a standard electrospray ion source, *i.e.* without additional drying gas. Source parameters were as follows: flow rate 10 μl/min, capillary voltage 4000 V, nebulizer gas 12 and curtain gas 8 (arbitrary units). The position of the spray capillary relative to the entrance orifice was the same in all experiments. The entrance ion optics voltages were optimized for maximum transmission of the crown–metal complex ions and kept constant for all experiments: declustering potential (DP) 20 V, focusing potential (FP) 250 V. Nitrogen and argon were used as the collision gases. The plumbing for the collision gas inlet has been modified to allow introduction of the selected collision gas independently on the curtain gas. Pressure of the collision gas was set to 3 (arbitrary units) which, according to the manufacturers specification, corresponds to the pressure of approx. $3 \cdot 10^{-3}$ mbar. Collision cell parameters were set as follows: entrance potential (CEP) –10 V, exit potential (CXP) 15 V. Collision energy was ramped from 5 to 120 V with 1 V step. Spectra were acquired in Multiple Reaction Monitoring (MRM) mode with the first (Q1) and the third (Q3) quadrupoles set to the mass of the complex ion. Low resolution mode for both Q1 and Q3 was used to obtain the best signal-to-noise ratio. Recorded data were processed using Microsoft Excel 2000 software package.

RESULTS AND DISCUSSION

Using an electrospray ion source for the quantitative measurements is often quite difficult, due to the large number of parameters that can be varied. These parameters are not independent and changing one of them often causes the changes of some others. To standardize our measurements, we have fixed the position of the inlet capillary against the entrance orifice. We have used also the same concentrations of the solutions and the same flow rates, both for the liquids and gases, in all experiments. Voltages in the ESI ion source have been optimized for the maximum intensity of the complex ions beam for each ligand-cation system. In the next step average values, which give reasonable results for all studied complex ions, have been established and used for all experiments to assure possibly constant energy of the ions, entering mass analyzer region of the spectrometer.

We have also tested the influence of the flow rate and temperature of the additional drying gas, which can be used in the TurboIon Spray source. It has been found, that this gas causes some changes in the ions energy which are difficult to standardize. Therefore, in our experiments we decided not to use this gas. The flow rate of the solution has no significant influence on the results, providing it is kept high enough to assure the stable spray.

Another question concerns the possible fragmentation channels of the metal cation – crown ether complex ions. Our experiments, as well as the results described in the literature, show that within the entire range of collision energies (5–120 eV, laboratory frame) the only observed fragmentation process is the loss of the metal cation. No other charged species were recorded.

The crucial problem we had to solve was the correct selection of the spectral parameters to be acquired which could serve as a measure of the cation–ligand bond energy. Two main options could be considered: i) intensity of a peak corresponding to unchanged complex ion leaving collision cell (Fig. 1a) and ii) intensity of a peak corresponding to the metal cation liberated during fragmentation (Fig. 1b). From the presented plots it is obvious that on our instrument only measurements of the intesities of the peaks corresponding to unchanged complex ions can give meaningful results. The discrimination of the low masses on API 365 mass spectrometer is very strong, so the intensities of the signals corresponding to Li^+ and Na^+ ions are drastically reduced making them useless. Even for the cations with larger masses, the transmission characteristics of the collision cell are changing significantly with the mass, so even semiquantitative results are difficult to obtain.

As a measure of the relative stability of the crown–cation complex ions we selected a value of the collision energy required for 50% reduction of the parent ions

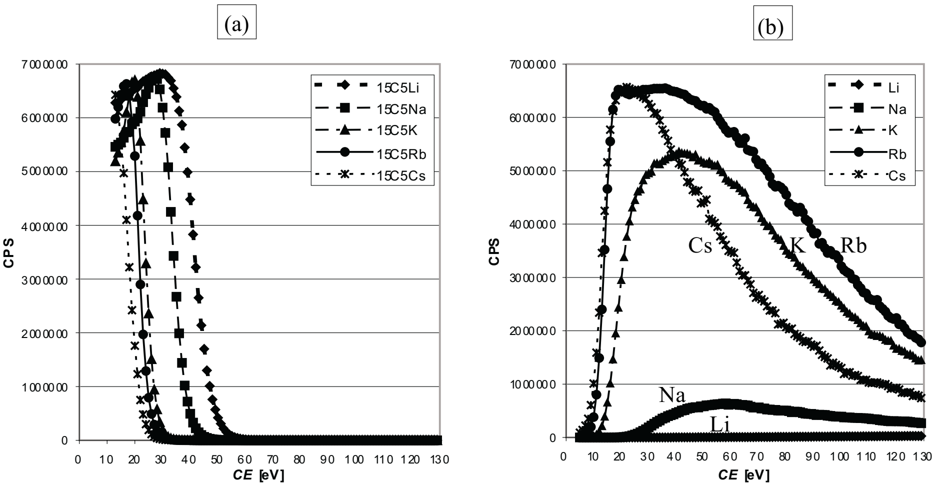

Figure 1. Abundances of: a) unchanged 15C5 – alkaline metal cations complex ions, b) alkaline metal cations liberated during fragmentation as a function of the collision energy *CE*.

beam intensity ($CE_{50\%}$). This method has been used recently for estimation of the relative binding energies of the oligodeoxynucleotides complexes with selected DNA-binding drugs [27]. Already during the course of our work, much more advanced study made by Nesatyy has been published [28]. In his work, describing semiquantitative determination of the gas-phase binding energy between selected proteins and enzymes, Nesatyy used quite sophisticated experimental procedure, followed by the complex calculations to establish the amount of energy transferred to the ions in the RF-only quadrupole after multiple collisions. In the second contribution from the same laboratory, the authors described Monte Carlo simulation of the dissociation of noncovalent protein complexes by triple quadrupole tandem mass spectrometry and compared their results with the experiment [29].

Selection of the $CE_{50\%}$ value as a measure of the complex ion stability has some important advantages. In this region breakdown curves are rather smooth and well reproducible. Our measurements have shown that for the single crown–cation complex ion $CE_{50\%}$ value can change in the range of several eV, depending on the ion source parameters which affect the ions energy. The size of these changes can be seen by comparing the results which can be read from the plots shown in Figures 1a and 2 with the data from Table 1, which were recorded in the other set of experiments. Comparing the results for complexes of the different cations we observed, however, that all $CE_{50\%}$ values are shifted proportionally in the same direction, preserving the correct order and relative ratios. These results imply also that for obtaining the meaningful results it is necessary to perform the entire series of measurements during one session to minimize the effects of the instrument setup.

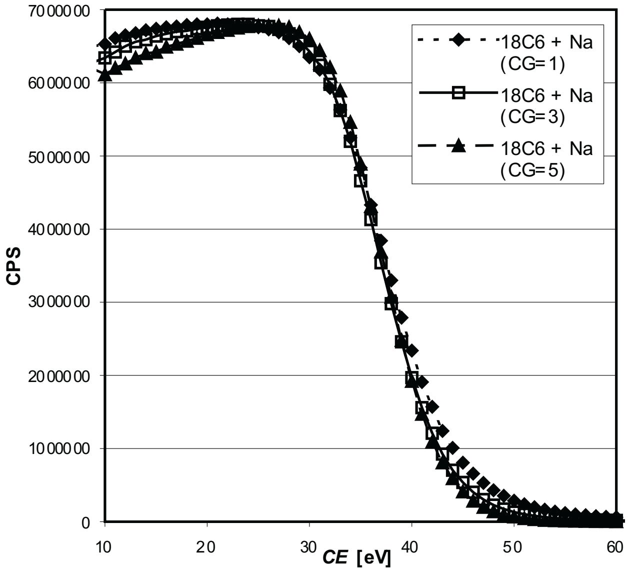

Figure 2. [18C6 + Na]$^+$ ions abundance as a function of the collision energy for three collision gas pressures.

The last important parameter was the pressure in the collision cell. On API 365 spectrometer the RF-only quadrupole pressure can be set in the range between 2 and 3.5 mbar. Under these conditions ions entering the collision cell at a given energy undergo several collisions and finally their energy is practically equilibrated with the collision gas. This results in a slow drift of the ions to the exit of the collision cell and consequently quite long residence time up to several hundred milliseconds. It is very difficult, if possible, to estimate theoretically the amount of energy transferred to the ion in a collision cell under such conditions. An attempt to do that has been done by Nesatyy [27] but his approach was quite complex. In our work we decided to keep our approach purely empirical and make only comparative measurements using the complexes with known binding energies as the references. We found also that the collision cell pressure, in the range we could set, shows practically no influence on the results of our experiments. Typical example is presented in Figure 2.

Table 1. $CE_{50\%}$ [eV] values for crown ether – alkali cation complex ions.

Collision gas N$_2$

Cation	12C4 + Cat.	15C5 + Cat.	18C6 + Cat.	DB18C6 + Cat.
Li$^+$	28.3	31.4	33.4	30.6
Na$^+$	19.1	25.6	30.5	31.2
K$^+$	13.9	18.2	23.1	25.2
Rb$^+$	13.0	16.4	20.6	21.9
Cs$^+$	11.8	14.0	17.6	18.6

Collision gas Ar

Cation	12C4 + Cat.	15C5 + Cat.	18C6 + Cat.	DB18C6 + Cat.
Li$^+$	27.7	31.4	33.0	-
Na$^+$	18.0	24.3	28.6	-
K$^+$	11.7	16.8	20.0	-
Rb$^+$	11.7	15.6	18.9	-
Cs$^+$	10.3	14.2	18.3	-

Correlation between $CE_{50\%}$ and binding enthalpy (ΔH_{298}) of the crown ether – alkali cations complexes. To check the validity of our method we have measured relative intensity – collision energy relationships for 12C4, 15C5, 18C6, and DB18C6 complexes with Li$^+$, Na$^+$, K$^+$, Rb$^+$ and Cs$^+$ cations. The breakdown curves, obtained using nitrogen as a collision gas, were in all instances very similar to those presented in Fig. 1a. From these curves $CE_{50\%}$ values for each complex ion have been determined. These values are collected in Table 1. The results from Table 1 show that for all five ligands studied in our work most stable complex ions are formed with the lithium cation. Stability of the complex ions decreased along the first group of a periodic table. This stability order is in agreement with the data published in the literature [15,18]. Therefore, the first positive result of our study is the correct reproduction of the stability order of crown ether – alkaline cation complex ions in a gas phase.

To tell more about the relative stabilities of the studied complex ions, we have plotted $CE_{50\%}$ values against binding enthalpies (ΔH_{298}) known from the literature [15,18]. These plots are presented in Figure 3. It has to be noted that there are no measured ΔH_{298} values for 15C5, 18C6, and DB18C6 complex ions with the lithium cation. For our comparison we have taken values calculated theoretically, using *ab initio* methods [15,18]. As can be seen in Figure 3a quite satisfactory correlation between $CE_{50\%}$ and ΔH_{298} values has been obtained. This result indicates, that under experimental conditions selected by us it is possible to reproduce not only the order but also the relative ratio of the binding energies of the crown ether – alkaline cation complex ions.

To test the influence of the collision gas on the results of the $CE_{50\%}$ measurements, a series of experiments with argon have been made. The results (Figure 3b) were very similar to those obtained with nitrogen (Figure 3a), however, a slightly worse correlation between $CE_{50\%}$ and ΔH_{298} values has been obtained. Because the measurements for DB18C6 were made much later than for three other crowns (see introduction) we decided not to perform the experiment with argon for this compound.

The results obtained by us can be interpreted also in a different way. In Figure 3 correlations were made within the series of complexes of the given ligand with the different cations. One can think also about the correlation within the series of complex ions of the given cation with different ligands. Positive results of such approach should give an opportunity to predict the relative binding energies of the ligands other than those studied in this work. Unfortunately, such correlation does not exist.

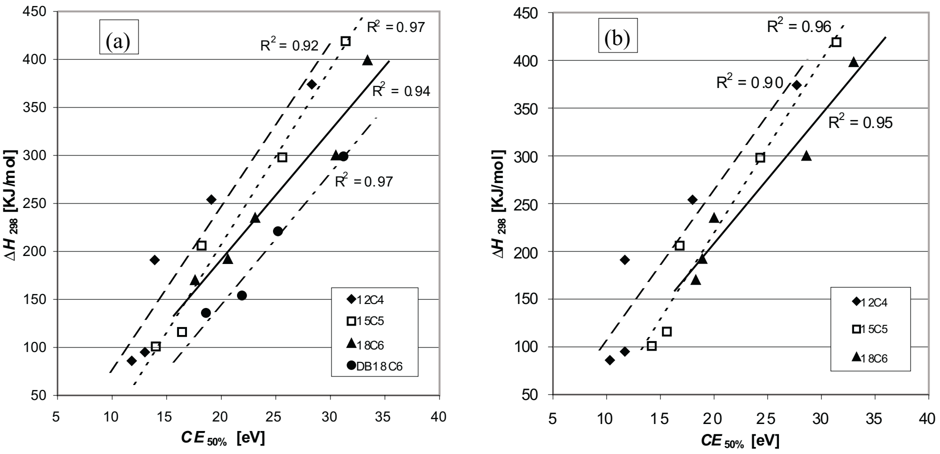

Figure 3. Correlation between collision energy $CE_{50\%}$ and binding enthalpy ΔH_{298} of the crown ether – alkali cations complex ions: a) collision gas N_2, b) collision gas Ar.

Fairly good correlation within the ligands series and lack of corelation within the cations series can be rationalized by taking the assumption, that the collisional crossection values, which are responsible for the amount of energy acquired by an ion during collisions, are similar (or at least are changing monotonically) for the complex ions of the given ligand with different alkali metal cations. On the other hand, collisional crossection values for the complex ions of the different ligands with the same cation can differ very significantly, due to the different sizes of the ligand molecules.

Correlation between $ECM_{50\%}$ and binding enthalpy (ΔH_{298}) of the crown ether – alkali cations complexes. Encouraged by the described above results concerning the relative binding energies of the alkali metal cations by crown ethers in a gas phase we made an attempt to process our data in a way to obtain better correlation between these data and the binding energies published in the literature. Due to the very complex behavior of the ions in a quadrupole collision cell of API 365 spectrometer it was not possible to use any reasonable physical model (*vide supra*). Therefore we decided only to take into account masses of the ions and collision gas molecules (or atoms) and recalculate collision energies to the center-of-mass frame according to the formula: $ECM_{50\%} = CE_{50\%} \cdot m/(M + m)$, where M and m are the ion and neutral reactant masses, respectively [23].

Plots of the calculated $ECM_{50\%}$ values against experimental binding enthalpies published in the literature [15,18] are presented in Figures 4a and 4b (N_2 and Ar were used as collision gases, respectively). These plots show surprisingly good correlation between $ECM_{50\%}$ values from our experiments and ΔH_{298} values published in the

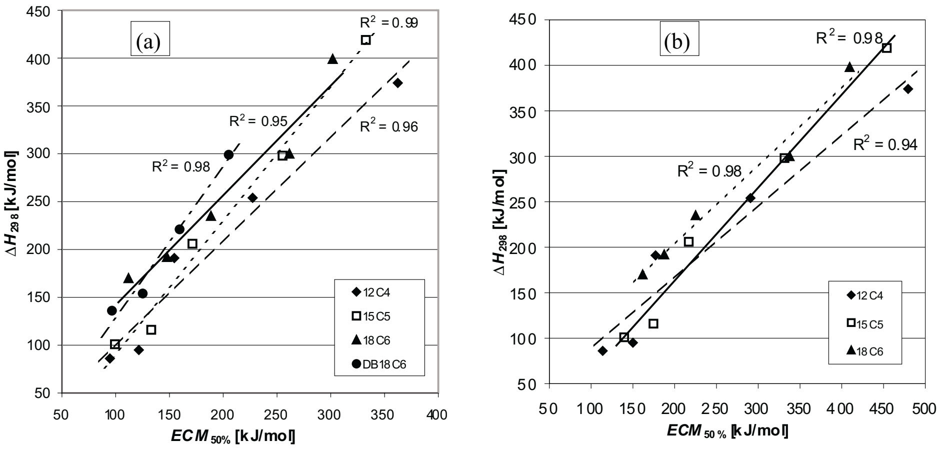

Figure 4. Correlation between the center-of-mass frame collision energy $ECM_{50\%}$ and literature binding enthalpy ΔH_{298} of the crown ether – alkali cations complex ions: a) collision gas N_2, b) collision gas Ar.

literature. It can be noticed also that the absolute values of $ECM_{50\%}$ are in most instances quite close to the absolute values of the binding energies but it is obvious that this result is accidental and is just a favourable coincidence of many factors, both instrumental and experimental.

To prove the general validity of our approach experiments on the other types of the triple quadrupole mass spectrometers have to be performed. As it has been stated above, in API 365 the energy of ions entering the collision cell is practically equilibrated with the collision gas because of the relatively long residence time resulting in a large number of collisions. Other designs of a quadrupole collision cell can shorten the ion residence time to a few milliseconds. It would be interesting to see how it affects the results described in this paper.

CONCLUSIONS

The results presented in this paper show, that at least for four studied crown ethers: 12C4, 15C5, 18C6, and DB18C6 it is possible to measure, with a reasonable accuracy, the order of the gas-phase binding energies of the alkali metal cations using a standard triple quadrupole mass spectrometer equipped with an electrospray ion source. It was found also, that the collision energies required for decomposition of 50% of the complex ions population ($CE_{50\%}$) are a fair measure of the relative binding energies of the ions studied. Better correlation was obtained after recalculation of the $CE_{50\%}$ values to the center-of-mass of the reactants system ($ECM_{50\%}$). More experiments on the other types of ESI/triple quadrupole mass spectrometers have to be performed to test the validity of our approach. Unfortunately, the presented metod is not suitable for comparing the relative binding energies of the complex ions of the different ligands with the same cation, unless a method for estimating the collisional crossection values will be available.

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