



Study of complexation between two 1,3-alternate calix[4]crown derivatives and alkali metal ions by electrospray ionization mass spectrometry and density functional theory calculations

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ARTICLE INFO

Article history:

Received 7 August 2015

Received in revised form

12 November 2015

Accepted 20 November 2015

Available online 26 November 2015

Keywords:

1,3-Alternate calix[4]crowns

Alkali metal ions

Host–guest complexation

Electrospray ionization mass spectrometry

Theoretical calculations

ABSTRACT

Complexation of two 1,3-alternate calix[4]crown ligands with alkali metals (K^+ , Rb^+ and Cs^+) has been investigated by electrospray ionization mass spectrometry (ESI-MS) and density functional theory calculations. The binding selectivities of the ligands and the binding constants of their complexes in solution have been determined using the obtained mass spectra. Also the percentage of each formed complex species in the mixture of each ligand and alkali metal has been experimentally evaluated. For both calix[4]crown-5 and calix[4]crown-6 ligands the experimental and theoretical selectivity of their alkali metal complexes found to follow the trend $K^+ > Rb^+ > Cs^+$. The structures of ligands were optimized by DFT-B3LYP/6-31G method and the structures of complexes were obtained by QM-SCF-MO/PM6 method and discussed in the text.

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1. Introduction

Metal ion–ligand complexation in solution plays an important role in various areas [1], such as ion transfer through membranes of ion selective electrodes [2], enzyme interactions [3], antibodies activity [4], etc. For the understanding of the solution equilibria in a metal ion–ligand system, information on the number, stoichiometry and stability constant of the complexes formed is of critical importance [5]. These types of information are traditionally obtained by different electrochemical, spectroscopic and calorimetry methods [6]. All of these techniques have several drawbacks, for instance, limitation in solvent usage, time-consuming analysis, large amounts of required sample and etc.

During the last decades, the electrospray ionization mass spectrometry (ESI-MS) [7] has provided a successful and straightforward alternative for studying a wide variety of non-covalent

complexes such as host–guest systems [8]. ESI-MS allows direct analysis of complexes formed in solution, thus enabling study of the equilibria dynamics, the quantitative analysis of binding constants and the evaluation of binding selectivities [1]. Also the number and type of the complex species formed in solution can be evidently observed on the spectrum, in a single run, and the percentage of each species can be easily measured by dividing of its intensity to total intensity. ESI is a soft ionization process which minimizing the molecular fragmentation and leaving the species existing in the solution mostly unaltered, so that yielding a simple, clean and easy to interpret mass spectra, in which the protonated or cationic molecules are typically correspond to the base peaks observed [9]. The stoichiometry of the species can also be determined directly from their mass to charge ratio (m/z) values. Also every charged species in solution will result in a peak equivalent to its m/z in the recorded MS spectrum. ESI-MS also possesses a low detection level convenient to investigation of concentration values down to 10^{-6} M, which allows the analysis of solutions at concentrations which are more close to those usually encountered in environmental or biological samples [5]. Moreover, the analysis become

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more fast and variety of solvents from aqueous to organic can be used [8]. The ESI-MS can also be utilized for samples with very high molecular masses such as polymers, nucleic acids, peptides and proteins [9].

ESI mass spectra have already been used for determining binding constants and selectivities of different host–guest complex systems. Wang and Gokel used ESI-MS to examine complexation of two- and three-ring macrocycles with multiple alkali metal ions [10]. Liu and coworkers reported the use of ESI-MS to determine stability constants of the lariat ether-alkali metal ion complexes based on the use of an internal standard in the solutions that provided a reference peak to compare the spectral intensities [11]. Also, many researchers have studied the determination of binding constants and selectivities of some organic hosts with alkali, alkaline earth, and transition metal ions [12–15].

Calix crown compounds and, specially, calix[4]arene-crowns, are a type of mixed ligands composed of two different moieties, calix[4]arenes and a single or bis-oxa or aza crown ether units. The calixcrowns have been prepared from all four conformational isomers of the calix[4]arenes (i.e., cone, partial cone, 1,2-, and 1,3-alternates) and the structure-property correlations have been developed so that the application of these molecules has become assessable. These compounds specially 1,3-alternate calix-bis-crowns have shown high selectivity to alkali, alkaline-earth and Tl^+ metal ions in complexation interactions [16–20]. Mono-bridged calix crowns which contain a single crown ether moiety, all form 1:1 ligand: metal ion complexes, whereas calix-bis-crowns which contain two oxa or azacrown units may form 1:2 ones [21]. In the past decade, we have been involved in the synthesis and applications of different calix [4]arene derivatives [22–28].

In the present study, ESI-MS was used to examine selectivity of the crowns 1,3-alternate calix[4]crown-5 (L1) and calix[4]crown-6 (L2) (see Fig. 1) for alkali metal ions K^+ , Rb^+ and Cs^+ . The percentage of each complex species in their mixture and the binding constants of some formed host–guest complexes were determined. It is well known that the intensity of the ESI-MS signals [29] and stability of the complexes of macrocyclic ligands [6] are strongly solvent dependent. Thus, in this work, all experimental and theoretical data were obtained from methanol as a very suitable solvent. Also the calculations on the structures of the calixcrown ligands and their complexes with these metal ions were performed by the appropriate quantum mechanical methods. The computational methods employed cover both density functional theory (DFT) and semi-empirical approaches. The structure of the ligands was optimized by DFT-B3LYP/6-31G method [6,30].

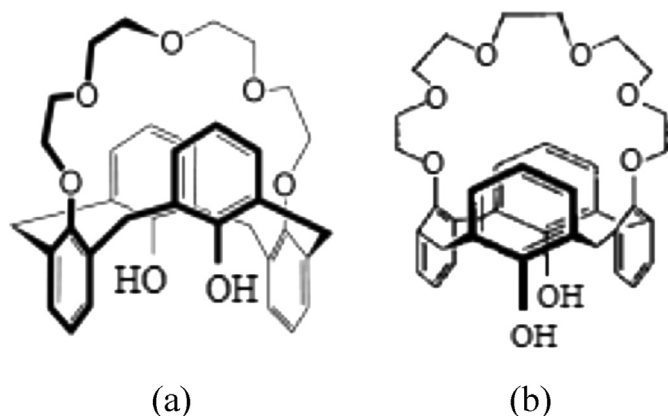


Fig. 1. The structure of 1,3-calix[4]arene-crown-5, L1 (a) and 1,3-calix[4]arene-crown-6, L2 (b).

2. Experimental

All mass spectrometry experiments were carried out with an Agilent1100 series LC/MSD trap mass spectrometer operating in positive ion current mode. The electrospray interface was based on the design developed by Oak Ridge National Labs involving differentially pumped regions containing ion focusing lenses [31]. A Kd scientific model 100 syringe pump system delivered the solution to the stainless steel needle at a rate of $7.3 \mu\text{L min}^{-1}$. Neither a heated desolvation capillary nor a sheath gas was used. The capillary voltage for the ESI interface was 3.5 kV. The pressure of nebulizer, flow rate of dry gas and dry temperature were 10 psi, 4 L min^{-1} and $325 \text{ }^\circ\text{C}$, respectively.

The reference crown ether (dibenzo-18-crown-6, DB18C6) and the alkali metal guests (K^+ , Rb^+ and Cs^+ as their chloride salts) were obtained from Merck. Mass spectrometric grade methanol and chloroform solvents were purchased from Sigma–Aldrich. The calix crown ethers were synthesized and purified as reported before [32–34].

All experimental solutions were prepared in methanol. Several types of solutions were prepared for injection into the ESI-MS system. The first set of solutions consisted of one host (L1 or L2) and three guests (K^+ , Rb^+ and Cs^+) at 1:1:1:1 concentration ratio, employed to determine the selectivity of macrocyclic ligands; the second set contained the reference crown ether (DB18C6) and one guest metal ion, at 1:1 concentration ratio and the third set composed of the reference crown ether, one guest metal ion (K^+ , Rb^+ or Cs^+) and one host (L1 or L2) with 1:1:1 concentration ratio, employed for obtaining the calibration curves and estimating the complex binding constants, respectively. The concentration of each component in first and third set was $2.0 \times 10^{-4} \text{ M}$ and in second was in a pre-determined concentration range.

3. Results and discussions

3.1. ESI-MS studies

3.1.1. Validation of the ESI-MS method for determining selectivities

Validation of ESI-MS for host–guest selectivity determining by ESI-MS has been performed for macrocycles with alkali and various transition metal cations in numerous earlier studies [8,35–40]. Here, similar experiments were performed to validate this method for investigation of relative stability and selectivity of the alkali metal ion complexes with calix crowns 1,3-calix [4]arene crown-5 (L1) and 1,3-calix[4]arene crown-6 (L2). Since extensive host–guest binding constant data is available in the literature for DB18C6 [41], this macrocyclic polyether was used as the reference host molecule in validation experiments. Then mixtures containing fixed amounts of the reference host and alkali metals DB18C6 in methanol were sprayed, and the intensities of the resulting host–metal complexes were evaluate from the recorded spectra. The calibration graphs of ESI-MS signal intensity vs. [DB18C6 + M^+] ($M^+ = K^+$, Rb^+ and Cs^+) concentration in methanol solution is shown in Fig. 2, from which the percentage of each complex species can be estimated using the equilibrium equations of solution. As can be seen, the estimated theoretical data confirmed the experimentally evaluated data, and the stability order of reference host for the guest alkali metal ions.

3.1.2. Estimations of binding constants

An experimental method to calculate the binding constant of complexes by ESI-MS has been reported previously [40]. Here, similar experiments were performed for measuring binding constants of new complexes obtained from interaction of alkali metal ions with calix[4]crowns L1 and L2, in conjunction with a reference

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