Complexation of alkali metal ions by tetrapropoxy-monoamine and tetrabutoxy-triamine calix[4]arenes

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ABSTRACT

The complexive abilities of 5,11,17-tri-tert-butyl-23 amino-25.26,27,28-tetrapropoxy-calix[4]arene and 5,11,17-tri-amino-23 acetyl-tert-butyl-amide-25,26,27,28-tetrabutoxy-calix[4]arene towards alkali metal ions Li^+, Na^+, K^+, Rb^+ and Cs^+ in methanol-chloroform mixture have been evaluated at 25 °C, using UV-Vis spectrophotometric techniques. The results showed that the ligands are capable to complex with all of the alkali cations by 1.1 metal to ligand ratios. The selectivity presented considering the calculated formation constants are in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ for the ligands.

Keywords: Calix[4]arene; Alkali metal cations; Complexation; Formation constant

INTRODUCTION

The cyclic oligomers of phenolic units linked through the ortho position, called calixarenes, associate their skeleton simplicity with versatile recognition properties both of ions and neutral molecules[1]. Calixarenes are basket-shaped compounds by potential interest for host-guest complexation. Functionalization at the lower and upper rim may lead to design and synthesis of the ligands suitable for various metal complexation[2-5]. The control of cation-binding ability of calixarenes has been the subject of more recent investigations[6-10]. A quantitative measure of the interaction strength between two chemical species (macrocycle and guest) in the given solvent is provided by stability constant and the conformation of both uncomplexed and complexed species appears to be a distorted cone. The focus has been on the introduction of donor groups onto the calixarene framework for controlling their complexation phenomena. The ability of calixarene systems to interact with alkali metal ions has been long recognized and has led to several ionophores increasingly selective for a specific cation. A variety of optical methods for the detection of cations in solution is well established

and has been extensively reviewed. One of the successful approach is using spectrophotometic properties of calixarenes. These compounds show UV absorption bands at around 250-330 nm due to the electronic transitions in the phenol groups. For photometric diagnosis of an ion or molecule by calix[n]arene, therefore, a spectroscopic active chromophore(s) should be introduced to the molecule, since calix[n]arenes themselves do not exhibit absorption and emission in the visible region. Calix[4]arene derivatives can adopt four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate which their selectivity of complexation towards metal ions have been proved to depend on the conformation of the calix[4]arene moiety.

In this work, the formation constants of alkali metal cations and two new synthesized calix[4]arenas, Fig.1, are determined in a methanol-chloroform mixture (30/70 by volume) at 25 °C using spectrophotometric technique.

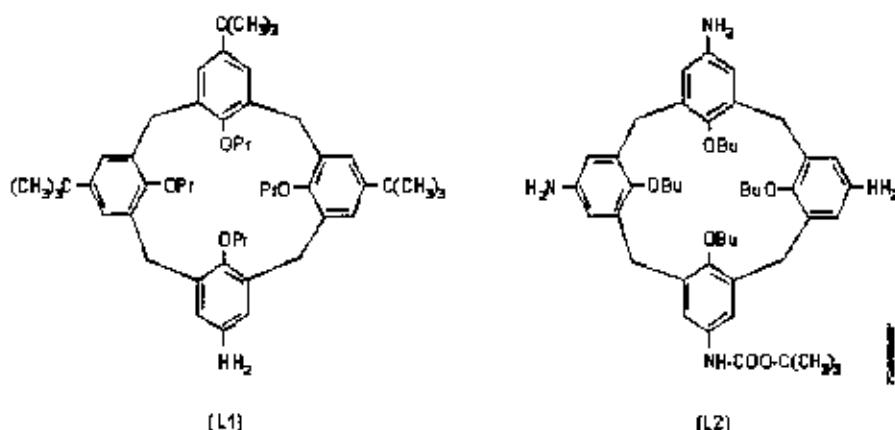+Corresponding author: osouleddini.n@gmail.com

Fig.1. Structure of 5,11,17-tri-tert-butyl-23 amino-25,26,27,28-tetrapropoxy-calix[4]arene, L1 and 5,11,17-tri-amino-23 acetyl-tert-butyl-amide-25,26,27,28-tetrabutoxy-calix[4]arene, L2.

EXPERIMENTAL
Chemicals
Parent calixarene was obtained from Aldrich and used without further purification. The ligands were synthesized following the procedure described in ref.11. The solvents, methanol and chloroform (from Merck, p.a.), were used without further purification. LiCi (Merck, p.a.), NaCl (Merck, p.a.), KCl (Merck, p.a.), RhCl (Fluka, Purum), and CsCl (Merck, p.a.) as the alkali cations sources were dried under vacuum at room temperature for at least 72 hours before use.

Measurements
Absorption spectra, 250 -330 nm, were measured on Shimadzu 2101 UV-Vis scanning spectrophotometer with a Pentium IV computer using 10 mm quartz cells. The system was thermostated at 25 °C by circulating water from an isothermal bath. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Table 1.

Procedure
2 mL solution of the ligands (1.98×10^{-4} and 9.13×10^{-5} mol dm^{-3} for L1 and L2, respectively) were titrated with stepwise addition of an alkali cation solution (1.99×10^{-4}, 2.04×10^{-4}, 2.00×10^{-4}, 1.95×10^{-4}, and 2.01×10^{-4} mol dm^{-3} for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, respectively) all in the same solvent (methanol-chloroform 30:70 by volume).

The UV-Vix spectra of the mixtures undergo small changes at 250-330 nm, but the measured absorbances were sufficient to allow the treatment of the data by the computer program Squad[12,13]. (fig.2 -3)
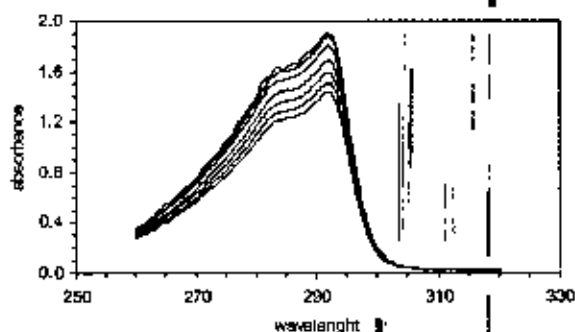

Fig.2. The variation of UV absorption spectrum of L1 upon successive addition of Li$^+$.
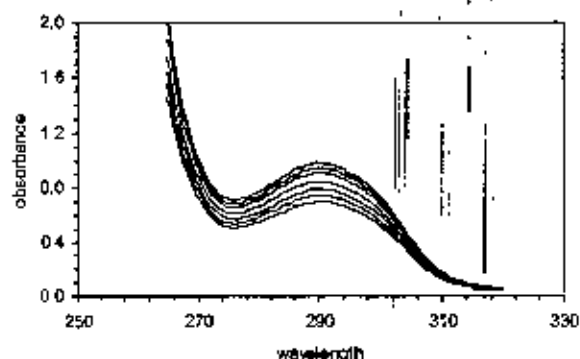

Fig.3. The variation of UV absorption spectrum of L2 upon successive addition of Li$^+$.

RESULTS AND DISCUSSION

Assuming that the absorbance of the ligand would change upon complexation with an alkali cation, we performed spectrophotometric measurements. The complex M_pL_q formed is characterized by its stoichiometry p and q, where M and L represent each metal ion and each ligand, respectively. To determine the formation constant of complexation, K, Eq. (1) is defined,

$$pM + qL \rightleftharpoons M_pL_q \quad K_S = [M_pL_q] / [M]^p[L]^q \quad (1)$$

Determination of the formation constant was employed using the method mentioned before [6-10]. Absorbance, A, was measured by successive addition of an alkali metal ion solution to each ligand solution, see experimental section. The absorption bands of the ligand decrease upon addition the metal ion solution in all cases. Treatment of the spectrophotometric data (250-330 nm with an interval of 0.3 nm) obtained during the titrations was conducted with the computer program Squad [12-13].

All proposed species existed in significant concentration were checked over a reasonable range of data. As expected, polynuclear complexes were systematically rejected by the computer program. Taking into account a binuclear complex alone or together with the mononuclear one does not improve the goodness of the fit and even leads to the rejection of the model. The model finally chosen, formed by ML, resulted in a satisfactory numerical and graphical fitting for all of the systems. The average values of the formation constants of the 1:1 complex species for L1 and L2 with alkali cations in various wavelengths are listed in Table 1.

The interesting curves resulting from the spectrophotometric titration of L1 and L2 with alkali cations are shown in Fig. 4. The Fig. shows a sharp break point when the concentration of metal ion to the ligand ratios reaches unity, indicating the formation of stable complexes for Li^+ and Na^+ with L2 (Fig 4b). The same titration for Cs^+-L2 system shows the absorbance increases within a very small and no significant break point in complexation curve (Fig. 4b), indicating low stability constant of formation. However, the spectrophotometric titration curves for the other complexes display more continuous variation in the absorbance with

concentration ratios. In this case the extrapolating of the slopes at high and low metal to ligand ratios correspond to 1:1 complex stoichiometry in the point of intersections. This behavior indicates a typical of less stable complexes than those found for Li^+.

Table 1. Average values of log$K$ at different wavelengths for the alkali cations and the ligands at 25°C

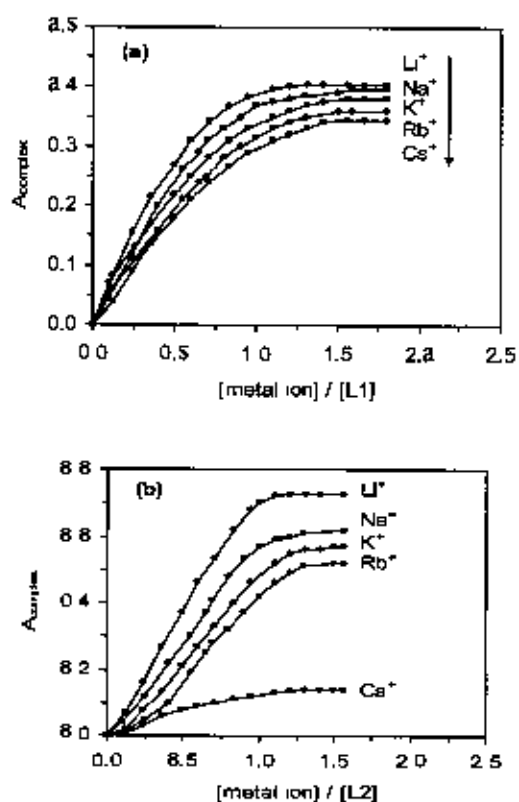| metal ion	log$K$ (L1)	log$K$ (L2)
Li^+	3.95 ± 0.02	6.96 ± 0.06
Na^+	3.54 ± 0.04	4.95 ± 0.07
K^+	3.53 ± 0.06	4.61 ± 0.04
Rb^+	3.41 ± 0.03	4.03 ± 0.05
Cs^+	3.43 ± 0.04	2.44 ± 0.03

Fig.4. Spectrophotometric titration plots of the ligands L1, (a) and L2,(b), by the metal ions, Li^+, Na^+, K^+, Rb^+, and Cs^+ at 25 °C and 280 and 270 nm, respectively.

The two calix[4]arenes, L1 and L2, form complexes with alkali metal ions, but show different affinities for the small and the large

cations. Figure 5 shows the formation constant values of the species formed by the ligands and the alkali cations versus the ionic radius of each cation. L1 appears to be more efficient for chelating with small cations, Li^+ and Na^+. The binding selectivity of L1 towards alkali cations, based on the formation constant values of the formed species, is in the order of $Li^+ > Na^+ > K^+ > Rb^+ \cong Cs^+$. investigation and optimization of energy for L1 and L2 in the computer program "hyperchem 7"[14] are shown that alkali metal ions interact with L1 by four functionality groups in the lower rim and with L2 by the amine groups in the upper rim of ligands as well as other conditions of interaction are independently modified to increase their binding abilities and make them more specific for chelating by alkali metal ions.

The electron donating tendency of the amine groups located in the upper rim of L2 is possibly effective especially towards small cations. The results suggest that Cs^+ is possibly located near the cavity of L2 and hence, is more shielded than the other ions, which better fit the cavity size of the ligand. The fact that a more continuous

variation of the absorbance with the concentration of Cs^+ was obtained (Fig. 4b), should be due to the very low complexation ability of this cation.
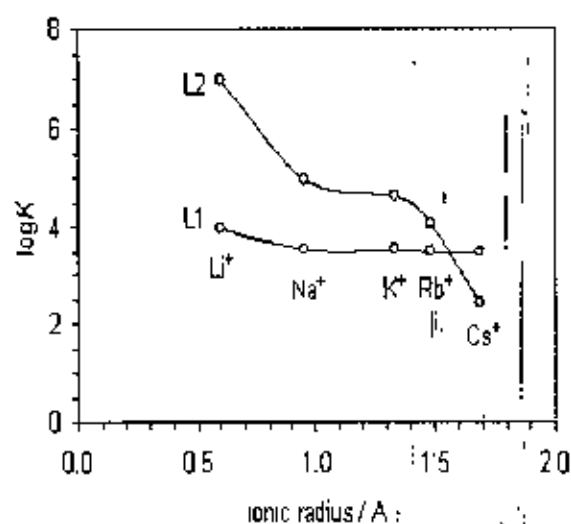

Fig.5. The plots of log$K$ versus the ionic radii of the alkali cations at 25 °C.

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