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Alkali metal ion select ability of di-propoxy- p-tert-butyl-Calix[4]arene, synthesized in acetonitrile

Afsaneh Amiri [*], Mahshid Nikpour Nezhati

Department of Chemistry, Islamic Azad University, Central Tehran Branch, Tehran, Iran

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Abstract

Synthesis and cation selectivity of 25, 27, dipropoxy-26, 28, Di-propoxy 5, 11, 17, 23, p-tert-butyl Calix[4]arene are studied in acetonitrile solution. The stability constants of different complexes of Calixarene (as a ligand) with alkali metal cations are determined at 25 °C by using spectrophotometric technique.On the basis of calculations, complexation of Calixarene with Cs^+ and Li^+ are more favored than others. In all cases, it has been shown to form exclusively 1:1 (metal ion to ligand) complex with alkali cations in experimental condition.

Keywords: Di-propoxy- p-Tert-butyl-Calix[4]arene; Alkali Metal; Synthesis; Acetonitrile.

1. Introduction

Calixarenes are synthetic macrocycles obtained by the condensation of p-substituted phenol and formaldehyde in alkaline medium. Lower and upper rim functionalisation of parent Calixarenes had led to a large variety of derivatives. Their bowl-like structure allows them to form complexes with a variety of species [1]. Fine control of the size of Calix[n]arenes, by changing the value of n and the introduction of various functional groups makes it possible to prepare a variety of molecules with various applications. Calixarenes are of interest to chromatography, slow release of drugs, transport across membranes, ion channels, and many other applications [2-5].

It has been shown recently, using rigidified Calix[4]arenes, that the complexation properties depend not only on the nature of the donor groups but also on their stereo-chemical arrangement, which is determined by the conformation of the Calixarenes [6, 7]. Depending upon the relative orientation of the para and phenolic sites, the tetramer can adopt four different conformations: cone, partial cone, 1, 2-alternate, and 1, 3-alternate. These conformers display selective properties of complexation of alkali metal cations. The cone conformer of Calix[4]arenes shows usually the highest affinity for Na^+, whereas the partial cone and 1,3-alternate conformers show the best selectivity for K^+ and Cs^+ [8]. While several Calixarene-metal cation complexes have been reported, in most of cases, the conversion of hydroxyl groups in Calixarene to esters or ethers [9] are required due to the poor solubility of the p-tertbutyl-Calixarenes. The Cs^+-p-tertbutyl-Calixarene complex is used for the recovery of cesium from nuclear waste solutions [10], and as a lanthanide complexing agent under basic conditions [11].

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[*] Corresponding author. Tel.: +98 919 2155094, fax: +98 21 8856140.
E-mail address: afsaamiri@gmail.com (A. Amiri)

Calixcrowns show a high Na^+/Cs^+ selectivity, and are used as carriers through supported liquid membranes [10]. The conformation of the Calixarene in these complexes is normally a cone, except when derivatization forces other conformations, as in the case of 1,3-Calix[4]bis-crown, which shows an alternate 1,3 conformation [10]. There is evidence of some conformational freedom for the metal complexes in solution [12]. Alkyl ketone residues have been introduced in the lower rim of Calix[5]arene and Calix[6]arene [13], which show affinity for complexation of alkali metal cations. Phosphoryl and amide ligands, both at the lower and upper rim, facilitate extraction of lanthanides and actinides [14-15].

In this work, we have chosen 25, 27, dipropoxy-26, 28, Di-propoxy 5, 11, 17, 23, p-tert-butyl Calix[4]arene (Di-propoxy Calix[4]arene), for the ligand framework studying due to its readily synthesis and existing a very few report on its chelating abilities towards metal ions [16]. The four functionality ligating groups in the lower rim of the ligand can independently modified to increase its binding ability and make it more specific for chelating by alkali cations.

The stability constants of alkali metal cations in complex with Calix[4]arene is determined in acetonitrile at 25 °C using spectrophotometric technique. The structure of the studied Calixarene, which is shown in Fig. 1, consist of four benzene rings which are arranged conically, so that hydroxyl and the propoxy groups form a coordination sphere where metal cations can be bound.

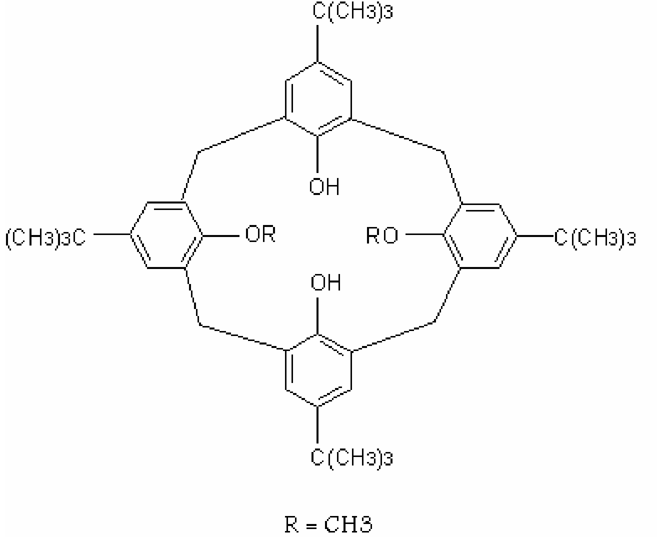

Fig. 1. Structure of 25, 27, dipropoxy-26, 28, di hydroxy 5, 11, 17, 23, p-tert-butyl Calix[4]arene in its cone conformation.

2. Experimental

2.1. Chemicals

Parent Calixarene was obtained from Aldrich and used without further purification. The solvent, acetonitrile (from Merck, p.a.), was used without further purification. Di-propoxy derivative of Calix[4]arene was synthesized in acetonitrile [16]. HCl (Merck, p.a.), K_2CO_3 (Merck, p.a.), Pr-I (Merck, p.a.), LiCl (Merck, p.a.), NaCl (Merck, p.a.), KCl (Merck, p.a.), RbCl (Fluka, purum), and CsCl (Merck, p.a.) as the alkali cations sources were dried under vacuum at room temperature for at least 48 hours before use.

2.2. Procedure

Di-propoxy derivative of Calix[4]arene was synthesized in acetonitrile [16]. 2.5 cm^3 solution of ligand (7.74×10^{-4} mol dm^{-3}) was titrated with stepwise addition of an alkali cation solution (1.51×10^{-3}, 1.37×10^{-3}, 9.92×10^{-4}, 1.82×10^{-4}, and 3.80×10^{-4} mol dm^{-3} for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively) in acetonitrile solution.

2.3. Measurements

Absorption spectra, 280 -290 nm, were measured on Uvikon 992 UV-vis scanning spectrophotometer with a Pentium computer using 10 mm quartz cells. The system was thermostated at 25 °C by circulating water from an isothermal bath. In all cases, the procedures were repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Tables.

3. 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_S, equation 1 is defined:

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

The method of determination of formation constant has been described before [17]. The absorbance, A, was measured for the solutions, as described in experimental section. For calculating the formation constants, the spectrophotometric titration data were analysed at a wavelength in UV range that is given by:

$$A = \varepsilon_M[\text{metal ion}] + \varepsilon_L[L] + \varepsilon_C[\text{complex}] \qquad (2)$$

where ε_M, ε_L, and ε_C are the molar absorptivities of each metal ion, each ligand, and the formed complex, respectively. For the mass balance

$$[\text{metal ion}] = C_M - [\text{complex}] \qquad (3)$$
$$[L] = C_L - [\text{complex}] \qquad (4)$$

where C_M and C_L are the total concentration of each metal ion and each ligand, respectively. Substituting eqs 1 and 3-4 into eq. 2 and rearranging and canceling like terms in a wavelength that the metal ion has actually no absorbance gives

$$A= C_L\varepsilon_L- C_M\varepsilon_L- C_L\varepsilon_M+ C_M\varepsilon_M+ C_L\varepsilon_C+ C_M\varepsilon_C- \varepsilon_L/K_S- \varepsilon_M/K_S+ \varepsilon_C/K_S\pm \varepsilon_LB\pm \varepsilon_MB\pm \varepsilon_CB)/2 \qquad (5)$$

where B is equal to $(1 + 2C_LK_S + 2C_MK_S + C_L^2K_S^2 - 2C_LC_MK_S^2 + C_M^2K_S^2) / K_S$. Using a suitable computer program [18], the data were fitted to eq. 5 for estimating the formation constant of eq.1. We used the Gauss-Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from equation 6:

$$S = \sum(a_i - b_i)^2 \qquad (i = 1, 2, 3, \ldots) \qquad (6)$$

where a_i is a quassi-experimental quantity and b_i is a calculated one. The computer program consisted of two different kinds of fitting, graphical and numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i.e. sums of squared residuals, differences of C_M (experimental) and C_L (experimental) from those of calculated one.

It was checked for other proposed species existed in significant concentration over a reasonable range of data. As expected polynuclear the computer program systematically rejected complexes. 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. The average values of the formation constants for the 1:1 complex of **1** and each metal ion for various Wavelengths are listed in Table 1.

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Table 1

Average Values of $\log K_S$ in Different Wavelengths for Alkali Metal ions at 25 °C

Metal ion	$\log K_S$ (**1**)
Li^+	5.08 ± 0.05
Na^+	4.41 ± 0.04
K^+	3.83 ± 0.02
Rb^+	4.07 ± 0.03
Cs^+	5.09 ± 0.04

The interesting curve resulting from the spectrophotometric titration of Calixarene by Cs^+ and Li^+, Fig. 2, shows a sharp break point when the concentrations of metal ions to the ligand ratios reaches unity, indicating the formation of stable complexes for Cs^+ and Li^+. However, the spectrophotometic titration curves of the ligand by other ions display a more continuous variation in the absorbances 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 behaviour indicates a typical of less stable complex than those found for Cs^+ and Li^+.

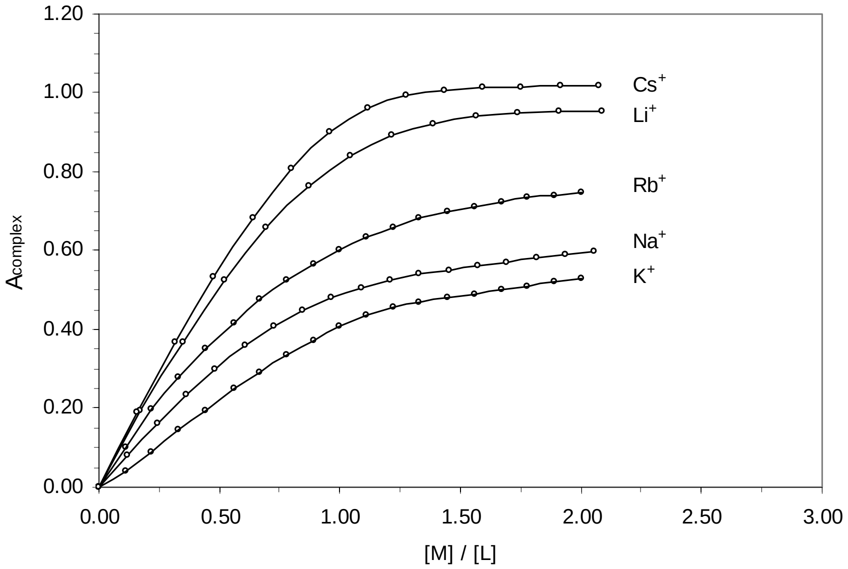

Fig. 2. Spectrophotometric titration plots of Di-propoxy Calix[4]arene by metal ions, Li^+, Na^+, K^+, Rb^+, and Cs^+ at 25 °C and 281 nm. The ionic radi are obtained from reference [19].

The Di-propoxy Calix[4]arene form complexes with alkali metal cations, but show different affinities for small cations (Li^+ and Na^+) and large cations (Rb^+ and Cs^+). The stability constants of Calixarene with alkali metal cations versus their ionic radius are showed in Figure 3. The most stable complexes are formed with Cs^+. The results suggest the electron-donating tendency of the hydroxyl group is effective especially on the smaller cations. The binding selectivity of Di-propoxy Calix[4]arene towards alkali cations on the stability constant values of the formed complexes, Table 1, is in the order of $Cs^+ > Li^+ > Na^+ > Rb^+ > K^+$ $Na^+ > K$. The results suggest that K^+, could be possibly located near the cavity of Di-propoxy Calix[4]arene and hence be more shielded than the other ions, which better fit the cavity size of the ligand. The fact that a more continuous variation of absorbance with concentration of K^+, Fig. 2, should be due to the low complexation level of this cation.

The binding selectivity of to Di-propoxy Calix[4]arene wards Li^+, could be possibly due to the cavity sizes of the ligands and the stability constant values obtained in this work confirm that Li^+ should well encaged and protected by the Di-propoxy Calix[4]arene and resulting a higher formation constant and more stable complexes. However, Cs^+ appears to have a good tendency to chelate with the ligand. The results obtained in this work suggest Cs^+ possibly binds with Calixarene and form endo complexes due to the participation of phenyl π electrons with soft dispersion and induction interaction a large soft cation.

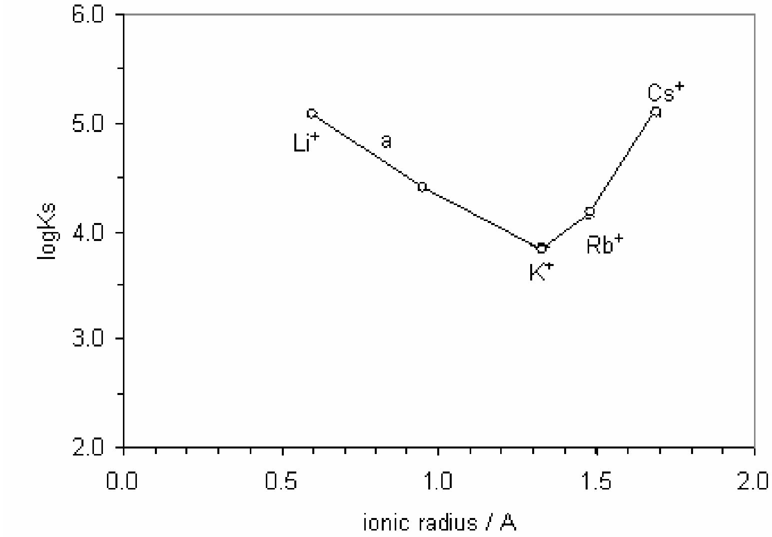

Fig. 3. The plots of $\log K_S$ versus the ionic radii of the cations at 25 °C.

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