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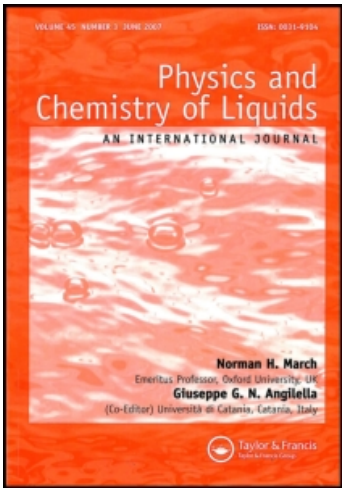

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Complexation behaviour of *p-t*-butyl-calix[4]arene propoxy derivatives toward alkali metal cations in chloroform

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Spectrophotometric technique is used to evaluate the alkali metal ion binding selectivity's of a series of calix[4]arenes in chloroform solution. On the basis of formation constant values calculated, complexation of K^+, Na^+, and Li^+ are favored toward di propoxy (L1), tri propoxy (L2), and bromopropoxy calix[4]arenes (L3), respectively, in agreement with the cavity sizes of the ligands. All ligands have been shown to form exclusively 1 : 1 (metal ion to ligand ratio) complexes with alkali cations in our experimental conditions. Chloroform stabilize endo complexes and the spectrophotometery results predict that in weakly polar solvents endo complexation is preferred.

Keywords: Spectrophotometry; Calixarenes; Molecular recognition

1. Introduction

Numerous attempts have been made to design new host systems which can selectively interact with the target guest and perform intriguing molecular recognition processes [1–3].

Calixarenes are synthetic macrocycles obtained by the condensation of *p*-substituted phenol and formaldehyde in alkaline medium [4]. Lower and upper rim fictionalizations of parent calixarenes had led to a large variety of derivatives. 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 [5]. Calixarenes are of interest in chromatography [5], slow release of drugs [6], transport across membranes [7], ion channels [8], and many other applications.

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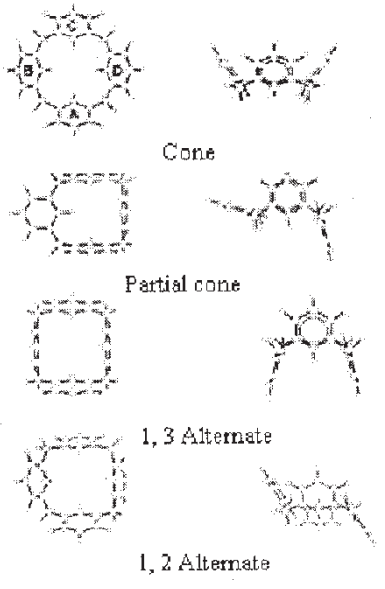

Figure 1. Two perspective of the conformers.

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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 [9,10]. Several experimental [11–21] and theoretical studies [22–26] on the complexation of calix[4] arenes with charged species have been reported.

Cation-π interaction play an important role in the complexation of alkali metal cations with benzene and with an extensive series of aromatic structures [27,28] and several studies suggest a strong correlation between the total binding energy and the electrostatic contribution to the interaction diameter for the bigger ones leading to a smaller electrostatic interaction with the molecular structure.

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 (figure 1).

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^+ [29].

We have chosen these ligands as the ligand framework due to their ready synthesis and existence of very few reports on their chelating abilities toward metal ions [30].

The four functional groups in the lower rim of the ligand can independently modify to increase its binding ability and make it more specific for chelating by alkali cations.

In this work, stability constants of alkali metal cations and three calix[4]arenes in chloroform were determined at 25°C using spectrophotometric technique. The structure of the studied calixarenes in shown in figure 2 and because of the esteric effects of propoxyl groups in lower rim the conformation locks in cone conformer. The calixarenes in this study all consist of four benzene rings which are arranged conically,

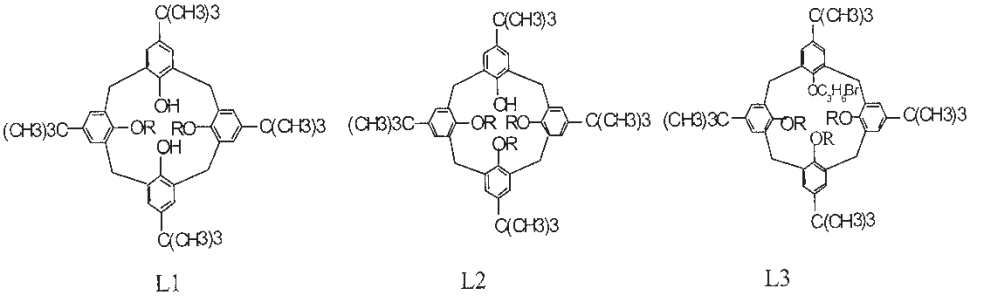

Figure 2. Structures of L1, L2, and L3, in their cone conformation R=C_3H_7.

so that hydroxyl, bromine, and the propoxy groups form a coordination sphere where metal cations can be bound. The different substituents in lower rim of the ligands change the ability of these molecules to tailor to the different cavity sizes and rigidities, prepare them by having various preferences toward alkali cations complexation.

One important aspect of the calix[*n*]arene structures is their π–rich cavity that favors the inclusion of charged guest compounds that are stabilized by noncovalent binding forces related to cation-π interactions [31,32]. The physical model behind cation-π interactions that describe the binding of a cation to the *p* face of an aromatic structure is based on different contributions, including the electrostatic attraction between the cation and the aromatic quadrupole moment, non-additive polarization effects, and dispersion interactions [31,32]. Cation-π interactions are usually an important contribution to binding energies.

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2. Material and methods

2.1. *Chemicals*

The different calix[4]arenes, figure 1, 25,27,dipropoxy-26,28, di hydroxy 5,11,17,23, tetra-tert-butyl calix[4]arene (L1), 25,26,27, tripropoxy-28 hydroxy 5,11,17,23, tetra-tert-butyl-calix[4]arene, (L2), and 25 (3-Bromo Propoxy) 5,11,17,23 tetra tertio butyl, 26,27,28 tris propoxy calix[4]arene (L3), were synthesized [33–35].

The solvent, chloroform (from Merck, p.a.), was used without further purification. 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 48 h before use.

2.2. *Measurements*

Absorption spectra were measured on an Uvikon 992 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 tables.

2.3. *Procedure*

2.5 cm^3 solution of each ligand (1.67×10^{-4}, 1.98×10^{-4} mol dm^{-3} for L1, L2, and L3, respectively) was titrated with stepwise addition of an alkali cation solution (1.61×10^{-3}, 1.75×10^{-3}, 1.61×10^{-3}, 1.59×10^{-3}, and 1.63×10^{-3} mol dm^{-3} for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively) both in chloroform solution. The UV-vis spectrum of the mixture undergoes small changes at 280–290 nm. However, the absorbance changes were sufficient to allow the treatment of the data by the computer program [36].

3. Results and discussion

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

$$pM + qL = M_pL_q \quad K_S = \frac{[M_pL_q]}{[M]^p[L]^q} \tag{1}$$

The method of determination of formation constant has been described before [37–40]. The absorbance, A, was measured for 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

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

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

$$[\text{metal ion}] = C_M - [\text{complex}] \tag{3}$$

$$[L] = C_L - [\text{complex}] \tag{4}$$

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

$$\begin{aligned} A = {} & (C_L\varepsilon_L - C_M\varepsilon_L - C_L\varepsilon_M + C_L\varepsilon_C + C_M\varepsilon_C - \varepsilon_L/K_S - \varepsilon_M/K_S \\ & + \varepsilon_C/K_S \pm \varepsilon_L B \pm \varepsilon_M B \pm \varepsilon_C B)1/2 \end{aligned} \tag{5}$$

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 [12] the data were fitted in to eq. 5 for estimating the formation constant of equation (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),

$$S = \Sigma(a_i - b_i)^2 \quad (i = 1, 2, 3, \ldots) \tag{6}$$

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where a_i is a quasi-experimental quantity and b_i is a calculated one. The computer program consisted of two different kinds of fittings – 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. Figure 3 is shown as a typical example of a graphical fitting for the observed and calculated absorbencies (from the computer program) of Cs^+ and dipropoxy against C_L at 280 nm.

It was checked for other proposed species existed in significant concentration over a reasonable range of data. As expected polynuclear complexes were systematically rejected by the computer program, as also M_2L and ML_2. 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 complexes of L1, L2, and L3 against each metal ion for various wavelengths are listed in table 1.

The interesting curve resulting from the spectrophotometric titrations of the ligand by K^+ and Na^+, figure 4, shows a sharp break point when the concentrations of metal ions to the ligand ratios reaches unity, indicating the formation of stable complexes for K^+ and Na^+. The same titration for Rb^+ shows titration for Rb^+ shows the absorbance increase within a very small range and no significant break in complexation curve,

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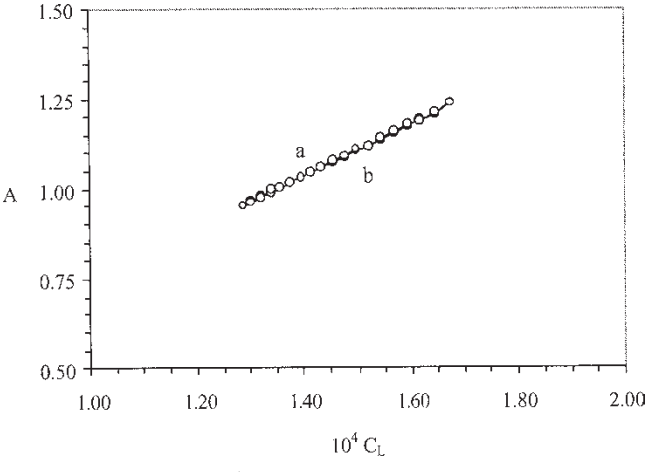

Figure 3. A typical graphical fitting for K^+ and di propoxy system at 25°C and 280 nm, (a) experimental corrected absorbance, (b) calculated absorbance from the computer program by the fitting method.

Table 1. Average values of log K_s in different wavelengths for various calixarenes and alkali metal ions at 25°C.

metal ion	log K_s (L1)	log K_s (L2)	log K_s (L3)
Li^+	2.26 ± 0.10	3.79 ± 0.15	4.42 ± 0.11
Na^+	4.85 ± 0.15	4.52 ± 0.05	4.34 ± 0.10
K^+	5.37 ± 0.16	3.37 ± 0.06	1.43 ± 0.12
Rb^+	0.96 ± 0.08	1.33 ± 0.06	1.46 ± 0.05
Cs^+	4.13 ± 0.11	4.27 ± 0.13	3.55 ± 0.12

indicating the formation of low stability constant. However, the spectrophotometric titration curve of the ligand by Li^+ displays a more continuous variation in the absorbance with concentration ratio. In this case the extrapolating of the slopes at high and low metal to ligand ratios corresponds to 1 : 1 complex stoichiometry at the points of intersection. This behaviour indicates a typically less-stable complex than the one found for K^+ and Na^+.

Although the ligands present two potential complexation sites, the complex stoichiometry was found to be 1 : 1 (each calixarene : each alkali cation). This behaviour may be explained by a negative allosteric effect, which has been found in complexing systems containing two conformationally related subunit [41–43]. These systems are able to form complex cations in only one of their two subunits at a time because when one complex is formed, the other subunit has an unsuitable conformation to bind any species [42].

The three calix[4]arenes form complexes with alkali metal cations, but show different affinities for small cations (Li^+ and Na^+) and large cations (Rb^+ and Cs^+). Between the three calixarenes L1 appears to be the most efficient ligand for chelating alkali metal ions, certainly because of its cavity size which is able to accommodate almost all the cations of the series except Rb^+. Rubidium cation is too large to form stable exo complexes and too small to have enough polarizability to form endo complexes [44]. The binding selectivity of L1 toward alkali cations on the stability constant values of the formed complexes, table 1, is in the order of $K^+ > Na^+ > Cs^+ > Li^+ > Rb^+$. The results suggest that the smallest cation, Li^+, could be located near the cavity of L1 part and hence be more shielded than the bigger ones, Na^+ and K^+, which better fit the cavity

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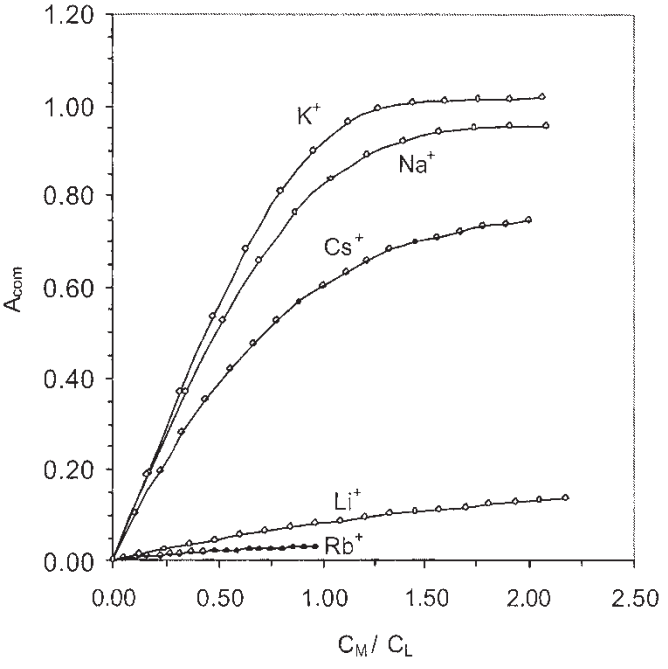

Figure 4. Spectrophotometric titration plots of di-*o*-propyl-*p*-tert-butyl-calix[4]arene by metal ions, Li^+, Na^+, K^+, Rb^+, and Cs^+ at 25°C and 285 nm.

size of the ligand. The fact that no break point was observed with Rb^+ and a more continuous variation of absorbance with concentration for Li^+, should be due to the very low complexation level of these cations, respectively. Similar discussion can be stated for L2 and L3 but with some changes in the cavity sizes. The binding selectivity of L2 and L3 towards alkali cations is Na^+ and Li^+, respectively, certainly because of smaller cavity sizes for L2 and L3. The stability constant values obtained in this work confirm that Na^+, K^+, and Li^+ should be well encaged and protected by the ligands L1, L2, and L3, respectively, and resulting in the formation of a higher constant and more stable complexes. However, in all cases Cs^+ appears to have a good tendency to chelate with the ligands. The results obtained in this work suggest Cs^+ possibly binds with the ligands and form endo complexes due to the participation of phenyl π electrons with soft dispersion and induction interaction a large soft cation. But in the case of L3 the little electron attractive tendency of bromine causes the observed differences.

In the complexation of cations with calix[4]arenes, two aspects are worth referring to: the interactions between a charged species and the calix[4]arene depends on the specific conformation of the host, and the cation-π interactions can be certainly enhanced by a cooperative effect due to the simultaneous presence of several aromatic structures. The first aspect characterizes conformational binding selectivity and the second one suggests that the role of cation-π interactions is more important for the present system than in the case of simple aromatic structures. Moreover, it is known that the calix[4] arene cone conformer is energetically stabilized due to the esteric effect of propoxyl groups in lower rim. We find that this feature is also present in the complexes of calix[4]arene with cationic species. Thus, we can anticipate that the complexation of calix[4]arene with alkali metal cations involves a competition between different factors, including the interactions of the cation with the alkoxy groups and with the π faces of phenol, hydrogen bonding interactions or esteric effects in the calix[4]arene lower rim, and size property.

Chloroform stabilizes endo complexes and the spectrophotometry results predict that in weakly polar solvents endo complexation is preferred while in more polar ones like acetonitryl, exo complexation is preferred. Thus, there has been much interest in cation interactions as a possible source of stabilization of endo complexes.

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