Complexation of alkali metal cations by p-sulfonato calix(4)arene in aqueous solution

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Abstract

Introduction: Calixarenes are obtained from the condensation of phenols with formaldehyde and possess a hydrophobic cavity capable of including molecular guests in solution. p-sulfonato calix(n)arenes are able to complex with variety of organic compounds as well as inorganic ions in water. It is known that calixarene molecules exhibit a strong sterical flexibility by comparing with cyclodextrins, and therefore there is a possibility to use calixarenes in a wide field of applications. There are many studies dedicated to calixarenes and their derivatives, most of them directed toward the selective complexation of biological substrates.

Aim: The present study investigated the formation constant for complexation of alkali metal cations by the water- soluble p-sulfonatocalix(4)arene and discussed about their interactions.

Materials and Methods: All the measurements were carried out at $25°$ C and pH=2 using a spectrophotometer. Absorbance, A, was measured by successive addition of an alkali metal cation solution(Li^+, Na^+, K^+, Rb^+, Cs^+) to p-sulfonatocalix(4)arene solution. Treatment of the spectrophotometric data obtained during the titrations was conducted with the computer program Squad.

Results: The complexation of alkali metal cations by p-sulfonato calix(4)arene are consistent with the formation of a 1:1 complex resulting from electrostatic interactions between the sulfonato groups and alkali metal cations. In this study, we determined formation constants (log K) of the complexes at pH 2 and $25°C$, that were log K_{Li^+}=4.5130± 0.06, log K_{Na^+}=4.0898± 0.08 , log K_{K^+}=3.9556± 0.04, log K_{Rb^+}=3.4489± 0.07 and log K_{Cs^+}=3.1601± 0.09, respectively.

Conclusion: It is concluded that Li^+ forms strongest binding with p-sulfonato calix(4)arene by cation-π interactions with benzene rings and electrostatic interactions with the SO_3^- groups because of suitable size-fit on cavity, whereas for Rb^+ and Cs^+ those are week because they have not significant cation-π interaction

Key words: formation constant, spectrophotometeric titration, alkali metal cation, p-sulfonato calix(4)arene .

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Introduction

Calixarenes [1] are the third class of supramolecular host systems along with crown ethers [2] and cyclodextrins [3]. They are obtained from the condensation of phenols with formaldehyde and possess a hydrophobic cavity capable of including molecular guests in solution. p-sulfonato calix(n)arenes are able to complex with variety of organic compounds as well as inorganic ions in water [4]. Many complexation studies have already been performed with water- soluble calixarenes and its analogues. Schneider et al. [5] have studied the electrostatic attraction between a water soluble anionic host molecule with a single positively charged organic cation by ^1H and ^{13}C NMR. Shinkai and co-workers [6-10] studied the association of water soluble p-sulfonato calix(n)arenes with neutral and charged guests by spectrophotometric, ^1H NMR or induced circular dichroism methods. As it was reported, calixarenes and their derivatives are attractive hosts for certain neutral and charged inorganic and organic species in solution, solid state [11], and in the gas phase as well [12]. It is known that calixarene molecules exhibit a strong sterical flexibility by comparing with cyclodextrins, and therefore there is a possibility to use calixarenes in a wide field of applications [13]. There are many studies dedicated to calixarenes and their derivatives, most of them directed toward the selective complexation of biological substrates [14-21].

It has been found that water- soluble calix(n)arene derivatives are able to catalyze aldol-type condensation and Michael addition reactions of activated methyl and methylene compounds smoothly in aqueous NaOH solution [22]. The complexation properties of water-soluble calixarenes towards organic ions [23], amino acids [24], small neutral organic molecules such as alcohols, ketones and nitriles [25], lanthanid cations and alkylammonium cations [26] in aqueous solution have extensively been investigated by ^1H NMR spectroscopy, calorimetric and microcalorimeteric titration [27,28]. Bonal et al.[26] had studied the electrostatic attraction between host *1* (Scheme 1) and several rare-earth metal cations representative of the whole lanthanide series (La^{3+}, Nd^{3+}, Sm^{3+} Eu^{3+}, Gd^{3+}, Dy^{3+} and Yb^{3+}) in an acidic solution (pH 2)(see Table 3) that we have discussed about them and compared to complexation of alkali metal cations in result section. In this article, we investigated complexation of alkali metal cations by p-sulfonato calix(4)arene by spectrophotometeric titration method and the formation constants of complexes were determined at 25°C and pH =2 .

Experimental
Chemicals

p-sulfonic acid calix(4)arene (25, 26, 27, 28- tetrahydroxy–5, 11, 17, 23- tetrasulfonic acid-calix(4)arene) purchased from ACROS, was used without further purification. LiCl, NaCl, KCl, RbCl and CsCl were obtained from Merck (pro analysi grade); after drying in vaccum, they were stored in a desiccator and used without further purification. All the solutions were prepared from double distilled water. The Electro conductivity of this water was 0.5 $\mu s/cm$. The pH of the calixarene and the salt solutions were set at 2.0 using 0.1 mol L^{-1} HCl solution(Merck). According to the pK_a values [29], all the sulfonic acid groups of calixarene at pH 2.0 are dissociated whereas all the phenolic hydroxyl groups are protonated. This situation remains unchanged upon titration of the calixarene by the cations.

Table 1- pK_a values of p-sulfonato calix(4)arene

calixarene	$pKa_{1,2}$	$pKa_{3,4}$	pKa_5	pKa_6	pKa_7	pKa_8
p-sulfonato calix(4)arene	$0.6<pK_a<1$	$1<pK_a<1.85$	3.26 ± 0.02	11.3 ± 0.3	12.8 ± 0.3	> 13.6

Procedure

2.5 ml of the ligand solution (2×10^{-4} mol L^{-1}) was titrated with stepwise addition of an alkali metal cation solution (1.0×10^{-3} mol L^{-1}), all in water solvent. The UV-Vis spectra of the mixtures undergo small changes at 250-350 nm, but the measured absorbances were sufficient to allow the treatment of the data with the computer program.

Measurements

All the measurements were carried out at 25° C using a spectrophotometer (UV-Vis 2101 Shimadzu) 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 deviations from the average are shown in the text and Table. The pH of the solutions was regulated by Metrohm pH-meter(Metrohm 6.0228.000 , pH (0-14/ ±0.01) Pt 1000/B/2 3M KCl).

Results and Discussion

The complex M$^{+}_{p}$SC$_{4\,q}$ formed is characterized by its stoichiometry, p and q, where M^{+} and SC$_4$ represent each metal ion and p-sulfonato calix(4)arene , respectively. To determine the formation constant of complexation, K, Eq. 1 is defined,

$$p\text{M}^{+} + q\text{SC}_4 \rightleftharpoons \text{M}^{+}_{p}\text{SC}_{4\,q} \qquad K = [\text{M}^{+}_{p}\text{SC}_{4\,q}] / [\text{M}^{+}]^{p}[\text{SC}_4]^{q} \qquad (1)$$

Absorbance, A, was measured by successive addition of an alkali metal cation solution to *1* solution,Scheme 1, see experimental section. The absorption bands of the *1* decrease upon addition the metal ion solution in all cases. Treatment of the spectrophotometric data (250-350 nm with an interval of 1 nm) obtained during the titrations was conducted with the computer program Squad [30-31].
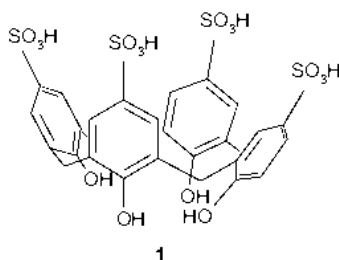
Scheme 1. Structure of p-sulfonic acid calix(4)arene (25, 26, 27, 28- tetrahydroxy–5, 11, 17, 23- tetrasulfonic acid-calix(4)arene)

All proposed species(M$_1$L$_1$, M$_2$L$_1$, M$_2$L$_2$, M$_1$L$_2$) 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 M^{+}SC$_4$, resulted in a satisfactory numerical and graphical fitting for all systems.

The values of the formation constants for complexation of the alkali metal cations by p-sulfonato calix(4)arene in aqueous solution and their calculated standard deviations by program are given in Table 3. Depending on the guest, different types of interactions are involved (ionic, hydrophobic, van derwaals, $\pi - \pi$, cation-π, hydrogen bonding, etc) each of these interactions imply a partial desolvation of the host and guest and also some modification of the degrees of freedom of the species.

The recent investigation [26] has showed that the monovalent metal cations are included to the calixarene cavity, in contrast to the trivalent metal cations which remain outside the cavity

cavity and bind to *1* by ionic interactions with the SO_3^- groups of the upper rim. Therefore monovalent metal cations have cation-π interactions in addition of electrostatic interactions with the SO_3^- groups. According to Bonal et al. [26] SC_4 forms 1:1 binding stoichiometry with lanthanide cations. Their formation constants are listed in Table 3. The results show weak binding abilities for monovalent cations and moderate strong binding abilities for trivalent cations. The monovalent metal ions are included into the cavity of ligand due to the cation-π interactions. The trivalent metal ions are hydrated to more extent than the monovalent ones, and then are not included in to the cavity of SC_4. In fact, the relatively stable association of SC_4 with multivalent metal ions occurs out side the cavity and it is a typically outer-sphere progress involving strong electrostatic interactions, in results are essentially originated from the partial desolvation of M^{n+} and SO_3^- upon interaction and from the consequent release of water molecules. Moreover, the affinities for alkali metal ions are almost one order of magnitude lower than those for lanthanid(III) ions, mainly owing to the less important desolvation of the monovalent cations.

Recent theoretical studies on cation- benzene complexes showed indeed that for Rb^+ and Cs^+ the induction contributions to the binding energies are of the same order of magnitude as the electrostatic contributions, whereas for Li^+, Mg^{2+} and Ca^{2+} they are much more important, which indicates that the cation-π interaction largely depends on the distance between the species [32,33].

Table 2: The values of Absorption for the complexation of alkali metal cations by p-sulfonato calix(4)arene in different volume of cations solution at pH 2.0, $\lambda = 278.2 nm$ and 25° C

| V_{Metal}	Li^+	Na^+	K^+	Rb^+	Cs^+
0	0.7117	0.7098	0.7113	0.7098	0.7104
0.1	0.6857	0.6811	0.6854	0.6772	0.6801
0.2	0.658	0.6558	0.6605	0.6588	0.6487
0.3	0.6384	0.6342	0.6348	0.6286	0.6368
0.4	0.6143	0.6129	0.6123	0.6133	0.6104
0.5	0.5971	0.5877	0.5954	0.589	0.5929
0.6	0.5776	0.5677	0.5742	0.5717	0.5647
0.7	0.5572	0.5533	0.5539	0.5492	0.5536
0.8	0.5426	0.5364	0.5412	0.5378	0.5363
0.9	0.526	0.5229	0.5247	0.5223	0.5232
1	0.5114	0.5058	0.5103	0.5067	0.5069
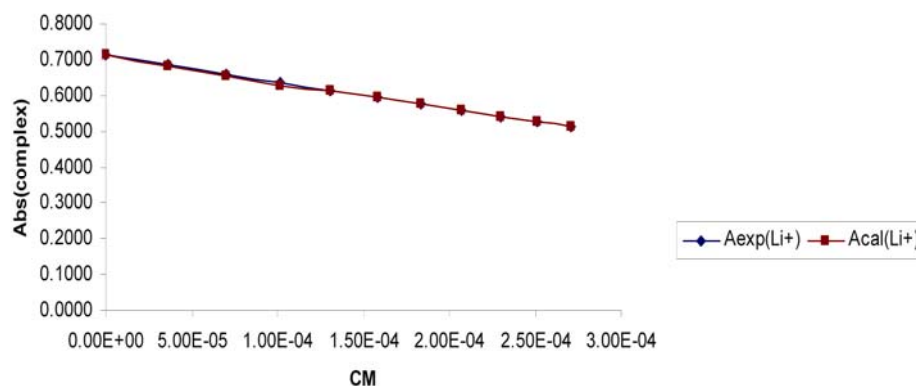
Figure 1- Comparison of Abs_{exp} and Abs_{calc} values for complexation of Li^+ by p-sulfonato calix(4)arene at different concentration of Li^+ at pH 2.0, $\lambda = 278.2 nm$ and 25 °C

Table 3- The values of the formation constants for the complexation of alkali metal and lanthanide cations by p-sulfonato calix(4)arene in water at pH 2.0 and 25° C

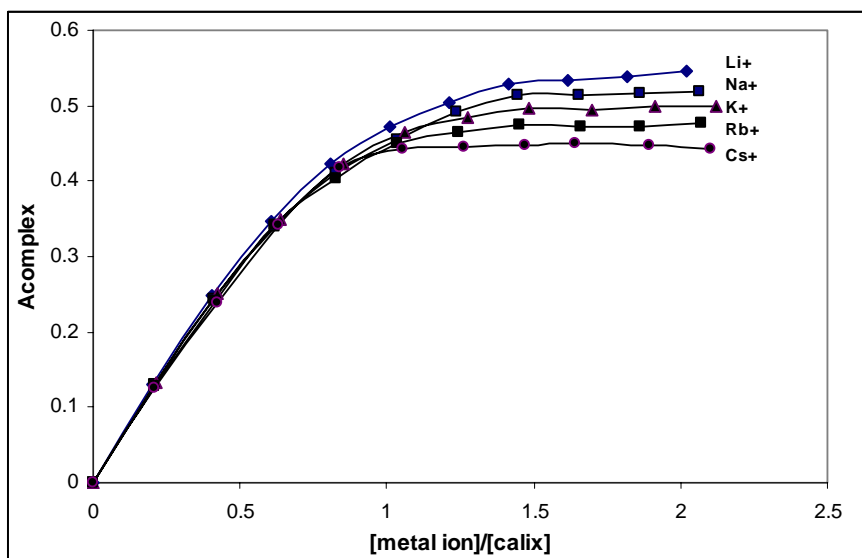| cation	logK	Ref
Li^+	4.51 ± 0.06	This work
Na^+	4.09 ± 0.08	This work
K^+	3.96 ± 0.04	This work
Rb^+	3.45 ± 0.07	This work
Cs^+	3.16 ± 0.09	This work
La^{3+}	4.23	[26]
Nd^{3+}	4.08	[26]
Sm^{3+}	3.82	[26]
Eu^{3+}	3.83	[26]
Gd^{3+}	3.94	[26]
Dy^{3+}	3.88	[26]
Yb^{3+}	3.81	[26]

Figure 2- Spectrophotometric titration plots of the ligand p-sulfonato calix(4)arene by the metal ions, Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ at pH 2.0 ,25 °C and 275 nm.

Figure 2 shows a sharp break point when the concentration of alkali metal cations to the ligand ratios reaches unity, indicating the formation of stable 1:1 complexes for Li$^+$, Na$^+$ and K$^+$ with *1*. The same titration for Cs$^+$-*1* system shows the absorbance increase within a very small and no significant break point in complexation curve, indicating low stability constant of formation. This behavior indicates a typical of less stable complexes than those found for Li$^+$, Na$^+$ and K$^+$.
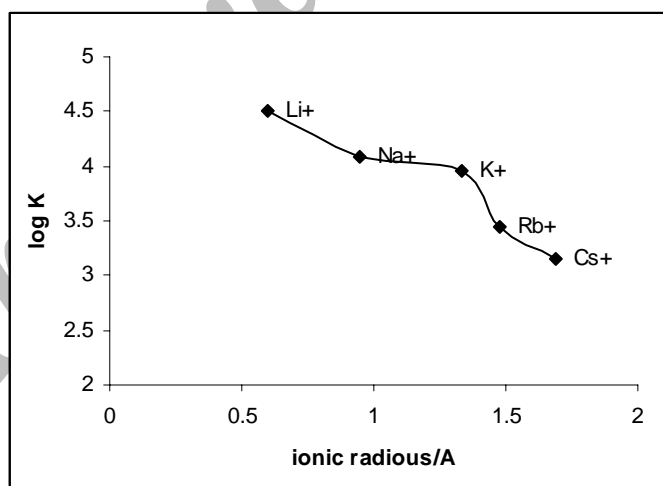

Figure 3- The plots of log *K* versus the ionic radious of the alkali metal cations at pH 2.0 and 25 °C.

Figure 3 gives the formation of alkali metal cation complexes with p-sulfonato calix(4)arene as a function of the radius of the cations. It appears that the formation constant values of the complexes increase with decreasing the ionic radius of the cations. The binding selectivity of *1* towards the alkali metal cations based on the formation constant values of the complexes, is in the order of Li$^+$> Na$^+$ ≅ K$^+$> Rb$^+$ >Cs$^+$.

According to the Table 1, Li$^+$ forms strong binding with *1* by cation-π interactions with benzene rings and electrostatic interactions with the SO$_3^-$ groups because of suitable size-fit

on cavity, whereas for Rb^+ and Cs^+ those are week because they have not significant cation-π interaction.

Conclusion

The formation constant of the alkali metal cations and p-sulfonato calix(4)arene (SC_4) systems have been performed by spectrophotometeric titration in water. It has been shown that these cations are included within the ligand cavity due to the favourable formation constant of cation-π interactions. In aqueous solution, thus the cation dehydration governs the selectivity of SC_4 for the alkali-metal cations. The complexation of monovalent cations is totally different from these were observed previously with multivalent lanthanide cations. In fact, trivalent monoatomic cations, are more hydrated than the monovalent ones. So, the trivalent cations are not included within the SC_4 cavity and they strongly associate with the ligand, but outside the cavity through ionic interactions with the SO_3^- groups. It can be noticed that, although weak, the association of SC_4 with Cs^+ in water is not negligible and could possibly be enhanced by changing the solvent. Finally we have shown that Li^+ forms strongest binding with the ligand by cation-π interactions with benzene rings and electrostatic interactions with the SO_3^- groups because of suitable size-fit on cavity.

Acknowledgements

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