

## The pH effect on complexation of Alkali metal cation by p-sulfonatocalix (4) arene in aqueous solution

K.Zare<sup>1,\*</sup> and N. Osouleddini<sup>2</sup>

<sup>1</sup> Chemistry Department, Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>2</sup> Ph. D student, Science and Research Branch, Islamic Azad University, Tehran, Iran

### ABSTRACT

The complexation of Alkali metal cations by the water-soluble p-sulfonic acid calix(4)arene was thermodynamically characterized using spectrophotometric data which 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 the formation constants (log K) of the complexes and have compared in deferent pH (1.0 and 1.5) at 25°C .

**Keywords:** Formation constant; spectrophotometric titration; alkali metal cation; p-sulfonatocalix(4)arene.

### INTRODUCTION

The calixarenes constitute a class of macrocyclic receptors that is of great importance in supramolecular chemistry. There hosts , which are formed by phenolic units bridged by ortho-methylene group, are able to complex a variety of guests such as certain neutral and charged inorganic and organic species , in solution, the solid state [1] and in the gas phase [2]. Contrary to most of the calixarenes, the p-sulfonatocalix(4)arenes are soluble in water.

The water soluble p-sulfonatocalix(4)arenes (n =4, 6, 8 ) synthesized mainly by Shinkai et al.[3] and Ungaro et al. [4] are able to recognize compounds of biological interest in aqueous

Solution. The p-Sulfonatocalix(4) arene is able to complex a variety of metal and organic cations in water. The binding of cations in water is a complicated phenomenon in which electrostatic forces, Vander-Waals forces and hydrophobic effects play a major role but other factors also have to be considered. For instance, the weak cation- $\pi$  interactions between the positive charge of the cation and an electron rich aromatic ring could be of special portance , particularly in biological recognition [5].

The electrostatic attraction between host p-sulfonatocalix (4) arene and lanthanide cations, several alkaline earth metal cations and quaternary ammonium cations [6, 7] were studied by microcalorimetry study at pH 2.

\*.Corresponding author : Info@dr-karimzare.com

Also, complexation of p-sulfonatocalix (4) arene by alkylammonium ions  $H(CH_2)_n NH_3^+$ ,  $n = 3-7$  at pH 7.1 were studied by Stodeman et al. using microcalorimetry method[8].

In this article, the complexation of alkali metal cations by p-sulfonatocalix(4)arene have studied at different pH. Further, the effect of pH on the formation constant has been discussed.

## EXPERIMENTAL

### Chemicals

LiCl, NaCl, KCl, RbCl and CsCl were obtained from Merck (pro analysi grade); after drying them in vacuum, they were stored in a desiccator and used without further purification. All the solutions were prepared from double distilled water. The pH of the calixarene and salt solutions were set at 1.0 and 1.5 with  $0.1 \text{ mol L}^{-1}$  HCl (Merck). This situation remains unchanged upon titration of the calixarene by the cations.

### Procedure

2 ml of the ligand solution ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ) was titrated with stepwise addition of an alkali metal cation solution ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ), 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.

### Spectrophotometric Measurements

All measurements were carried out at  $25^\circ \text{C}$  using a spectrophotometer scanning (UV-Vis 2101 Shimadzu) with a Pentium IV computer using 10 mm quartz cells. The system was thermostated at  $25^\circ \text{C}$  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 Tables. The pH determination have been performed using a metrohm pH-meter.

## RESULTS AND DISCUSSION

The complex  $M^+_p SC_{4q}$  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,

$$pM^+ + qSC_4 \rightleftharpoons M^+_p SC_{4q}$$

$$K = \frac{[M^+_p SC_{4q}]}{[M^+]^p [SC_4]^q} \quad (1)$$

Absorbance,  $A$ , was measured by successive addition of an alkali metal cation solution to the 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 (250-350 nm with an interval of 1 nm) obtained during the titrations were conducted with the computer program Squad [9,10].

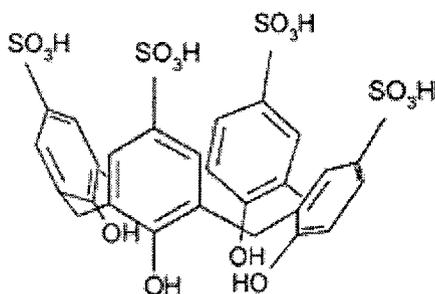


Fig.1. Structure of p-sulfonic acid calix(4)arene (25, 26, 27, 28- tetrahydroxy-5, 11, 17, 23-tetrasulfonic acid-calix(4)arene).

All proposed complex 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  $M^+SC_4$ , resulted in a satisfactory numerical and graphical fitting for all systems.

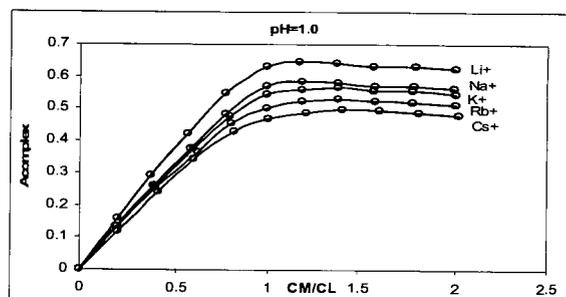
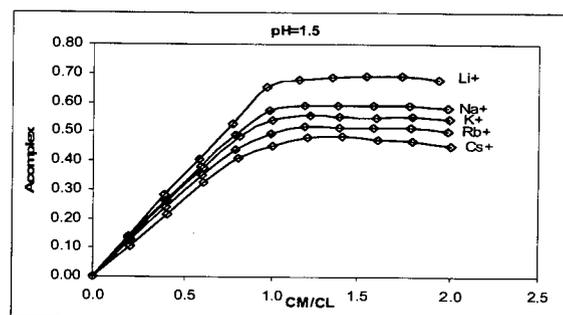
The formation constants values of complexation of alkali metal cations and p-sulfonic acid calix(4)arene in aqueous solution are given in Table 1. The study was carried out under different pH at 25° C. At pH 2.0 according to the pKa values [11-13], all sulfonic acid groups of the ligand are dissociated whereas all the phenolic hydroxyl groups are protonated. The recent investigations [6] have showed that the monovalent metal cations are included in to the calixarene cavity, in contrast to the divalent and trivalent metal cations which remain outside the cavity and bind to the ligand by ionic interactions with the  $SO_3^-$  groups of the upper rim. Therefore monovalent metal cations have  $\pi$ -cation interaction in addition of interactions with the  $SO_3^-$  groups.

**Table1.** Formation constant values for the binding of alkali metal cations by p-sulfonic acid calix(4)arene in water at different pH and 25° C.

cations	log K					
	pH= 1.0		pH= 1.5		pH= 2.0	
		ref		ref		ref
Na <sup>+</sup>	4.1344	this work	4.20	this work	4.5130	[14]
Li <sup>+</sup>	3.4922	this work	3.6571	this work	4.0898	[14]
K <sup>+</sup>	3.4847	this work	3.5163	this work	3.9556	[14]
Rb <sup>+</sup>	3.1986	this work	3.2004	this work	3.4489	[14]
Cs <sup>+</sup>	2.9591	this work	3.0084	this work	3.1601	[14]

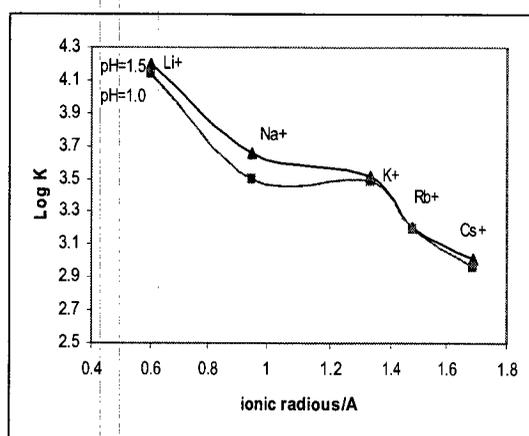
The cation position within the cavity depends on the cation size and on the conformation adopted by the calixarene.

Obviously, the ligand adopts cone conformations in water that are stabilized by intramolecular hydrogen-bonding between the OH groups of the lower rim[15,16]. According to the Table 1, at pH 2.0 [14] Li<sup>+</sup> form strongly binding to the ligand by cation- $\pi$  interactions with benzene rings and electrostatic interactions with  $SO_3^-$  groups whereas for Rb<sup>+</sup> and Cs<sup>+</sup> are weak because they have not significant cation- $\pi$  interactions. As it is shown in Table 1, at pH 1.5, the binding abilities of cations with to the ligand become weaker, when the pH value decrease, which is absolutely because of the competitive binding by the hydronium ion. The binding constants decrease again in more highly acidic solutions (pH =1.0) because of above reasons. That values indicate that electrostatic interaction between alkali metal cations and  $SO_3^-$  groups of the ligand become weaker.



**Fig.2.** Spectrophotometric titration plots of the ligand p-sulfonato calix(4)arene by the metal ions, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> at pH 1.0, 1.5, 25 °C and 280 nm in water .

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 complexes for  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  with the ligand for both pH. The same titration for  $\text{Cs}^+$ -ligand 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  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ .



**Fig.3.** The plots of  $\log K$  versus the ionic radii of the alkali metal cations at pH 1.0, 1.5 and 25 °C.

## REFERENCES

- [1] J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr, and R. L. Vincent: *Nature* 39, 1991, 683.
- [2] P. S. H. Worg, X. J. Yu, and D. V. Dearden: *Inorg. Chem. Acta* 246, 1996, 259.
- [3] K. Araki, S. Shinkai, and T. Matsuda: *Chem. Letters* 581, 1989.
- [4] A. Pochini and R. Ungaro: in F. Vogtle (ed.), *Comprehensive supramolecular chemistry*, Pergamon press, Vol. 2, 1996, 103.
- [5] (a) D. A. Dougherty and D. A. Stauffer, *Science*, 1990, 250, 1558. (b) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, 97, 1303.
- [6] C. Bonal, Y. Israeli, J. P. Morel and N. M. Desrosiers, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1075.
- [7] J. P. Morel and N. M. Desrosiers, *Org. Boimol. Chem.*, 2006, 4, 462.
- [8] M. Stodeman and N. Dhar, *J. Chem. Soc., Faraday Trans.*, 1998, 94(7), 899.
- [9] D. J. Leggett, *computation Methods for the Determination of Formation Constants*; Plenum Press: New York, 1985.
- [10] M. Meloun, M. Javurek, J. Havel, *Talanta*, 33, 513, 1986.

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 the ligand towards the alkali metal cations based on the formation constant values of the complexes given in Table 1 and are in the order of  $\text{Li}^+ > \text{Na}^+ \cong \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ .

According to the Table 1,  $\text{Li}^+$  forms strongly binding with the ligand by cation- $\pi$  interactions with benzene rings and electrostatic interactions with the  $\text{SO}_3^-$  groups because of suitable size-fit on cavity, whereas for  $\text{Rb}^+$  and  $\text{Cs}^+$  those are weak because they have not significant cation- $\pi$  interaction.

As a total result, p-sulfonatocalixarene afford weaker binding abilities towards alkali metal cation guests at pH 1.0 and 1.5 than towards them at pH 2.0.

- [11] J. P. Scharff, M. Mahjoubi and R. Perrin, *New J. Chem.*, 1991, 15, 883.
- [12] G. Arena, R. Cali, G. G. Lombardo, E. Rizzarelli, D. Sciotto, R. Ungaro and A. Casnati, *Supramol. Chem.*, 1992, 1, 19.
- [13] I. Yoshida, N. Yamamoto, F. Sagara, D. Ishii, D. Ueno and S. Shinkai, *Bull. Chem. Soc. Jpn.*, 1992, 65, 1012.
- [14] N. Osouledini, F. Gharib, K. Zare; *J. Sci. I. A. U (JSIAU)*, Spring 2009, in press.
- [15] S. Shinkai, K. Araki, M. Kubota, T. Arimura and T. Mastuda, *J. Org. Chem.*, 1991, 56, 295.
- [16] C. D. Gutsche and L. J. Bauer, *J. Am. Chem. Soc.*, 1985, 107, 6052.

