# Study of Complexion of p-sulfonatothiacalix [4]arene with Fluorescein and $Zn^{2+}$ by spectroscopic methods

**Sharadchandra Gawhale, Dipalee Malkhede, Gajanan Chaudhari**

*Abstract*— The inclusion behavior between a water soluble p-sulfonatothiacalix[4]arene with fluorescein and $Zn^{2+}$ has been studied by using spectrofluorometric titration method. The binding constant has been determined for p-sulfonatothiacalix[4]arene with fluoroscein as binary system and p-sulfonatothiacalix[4]arene with fluorescein and $Zn^{2+}$ as ternary system by using spectrofluorometric and spectrometric titration method. The cooperative interaction of $Zn^{2+}$ with p-sulfonatothiacalix[4]arene and fluorescein may have potential biological applications although further research need to be carried out.

*Index Terms*— cooperative binding, fluorescein, para-sulfonatothiacalix[4]arene, ternary system.

## I. INTRODUCTION

Third generation supramolecule i.e. Calix(n)arenes are cyclic oligomers consisting of n phenol units bridged by methylene groups in ortho-position to the phenolic hydroxyl group [1] Calixarenes are in the form of a cyclical oligomer having a basket shape, where the cavity can serve as a binding site for numerous guest species [2]. Calixarenes can form inclusion complexes with a wide range of ions and molecules. The phenomenon of molecular recognition is very important in analytical determinations of various inorganic and organic species. Therefore the application of supramolecules for creation of chemical and biochemical systems is of especial interest [3]. Therefore among different types of calixarenes, the water soluble calixarenes are of special interest because of their possible applications in biochemical research. Among water soluble calixarenes, thiacalix[4]arenes have attracted the attention of the supramolecular community since their first report in 1997 [4]. The chemistry of thiacalix[4]arenes is similar to that of classical calix[4]arenes but has different reactivity patterns and results in products with different conformations. This is due to the presence of four sulfur atoms in thiacalix[4]arenes which lead to many novel features in thiacalix[4]arenes chemistry [5]. The bridging sulfur possesses lone pairs of electrons and vacant 3d orbital which imparts many interesting features to thiacalixarenes scaffolds particularly with regard to soft transition metal ion recognition compared to conventional calixarenes which itself has poor binding ability towards transition metal ions [6]. Thiacalix[4]arenes also possess remarkably higher complexation ability for the transition-metal cations due to

sulfur-metal interactions and /or unusual conformational preferences or dynamic behavior in solution [7].

There are many reports of recognition of metal with calixarenes like: The isomorphous complexes of p-sulfonathiacalix[4]arene with cobalt and zinc and methyl viologen dihexafluorophosphate form a dimer through the coordination of the sulfonate groups [8]. The two rhodamine B lactams as fluorophores that are 1,3-altenately linked to thia[4]arene behaves as fluorescent sensor for $Fe^{3+}$ and $Cr^{3+}$ [9]. Chawla and group synthesized novel chromogenic functionalized thiacalix[4]arene for mercury and palladium [10]. The complexation of thiacalizarenes with various metal ions was studied [11]. Lots of work is carried out for Sensing of metal ions using calixarenes with covalently attached fluorophore. However this requires synthetic efforts for covalently attached fluorophore with calixarene for sensing metal ion. To avoid complicated job of synthesis, instead of covalently attachment, an optical probe may be assembled with an ion-selective receptor by means of intermolecular forces including $\pi$-$\pi$ and hydrophobic interactions[12].

Herein, we present the systematic study on the inclusion complexation of p-sulfonatothiacalix[4]arene fluorescein as binary system and fluorescein-p-sulfonatothiacalix[4]arene-$Zn^{2+}$ as ternary system using absorption and emission titrations for these complexation.

## II. EXPERIMENTAL SECTION

The p-sulfonatothiacalix[4]arene is purchased from TCI chemicals and used as it is whereas Fluorescein was procured from Sigma-Aldrich ( Fig. 1). Metal salt of $Zn^{2+}$ nitrate was of analytical grade and used without further purification. All aqueous solutions were prepared with ultrapure water obtained from a Millipore Milli-Q. For all experiments pH was adjusted to 2.0 using dilute HCl.
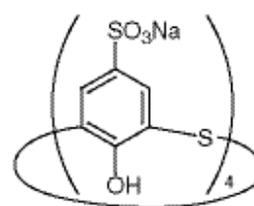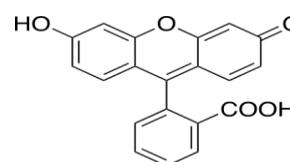


Fig. 1 (a) p-sulfonatothia calix[4]arene



(b) Fluorescein

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## 2.1 Instruments:

pH-was measured by digital pH meter of Elico LI 120 make with combined glass and calomel electrode. Absorbance spectra were performed on Shimadzu UV-1800 spectrophotometer. The variation in fluorescence intensity for the determination of stability constants were monitored on a JascoFP-8300 spectrofluorometer using 1 cm x 1 cm quartz cell. The excitation wavelength was set at 460nm. Emission spectra were collected in the range 460 -700nm. The slits for the excitation and emission monochromator were fixed at 2.5nm.

## 2.2 Procedure:

An appropriate volume of 1x10$^{-6}$M Fluorescein was taken in cuvette. To this solution 1x10$^{-4}$M solution of p-sulfonatothiacalix[4]arene was added in different volumes. To the same solution 1x10$^{-3}$M of Zn$^{2+}$ was added in different volumes till saturation obtained.

## III.   RESULTS AND DISCUSSION

It was observed that pK$_1$ of p-sulfonatothiacalix[4]arene is 2.10 [13]. Therefore all readings were taken at pH 2.0.

### 3.1 UV-Visible absorption spectral titration:

To study interaction in binary and ternary system first concentration of   Fluorescein is kept fixed at 1x10$^{-6}$M and varying the concentration of the host p-sulfonatothiacalix(4)arene at pH 2.0 (Fig.2). Here it was observed that fluorescein absorbed at 486nm. With addition of p-sulfonatothiacalix[4]arene, the wavelength of absorbance showed blue shift  from 486 to 480 nm.  Excess of p-sulfonatothiacalix[4]arene is absorbed at 301nm.  At this wavelength, the absorbance goes on increasing with addition of p-sulfonatothiacalix[4]arene. When to the same solution, Zn$^{2+}$ was added with varying concentration, then it was observed that wavelength of absorbance is shifted to 476 nm. This indicates binding between Fluorescein and Zn$^{2+}$. However, the overall spectral response is relatively small. Also absorbance at wavelength 301nm showed red shift as 308nm with increasing optical density with addition of Zn$^{2+}$. This indicates binding between p-sulfonaticalix[4]arene and Zn$^{2+}$(Fig.3). Therefore we can propose that there is a strong binding between fluorescein and p-sulfonatothiacalix[4]arene when we consider binary system. Whereas when we study ternary system we observed cooperative binding of Zn$^{2+}$ with fluorescein and p-sulfonatothiacalix[4]arene.
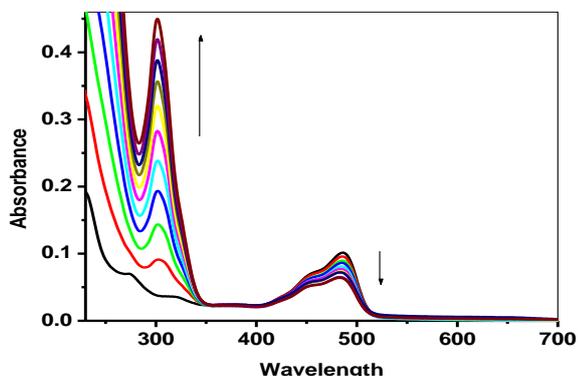


Fig. 2: Absorption spectra of binary system: Fluorescein [1x10$^{-6}$M] in the presence of increasing amounts of p-sulfonatothiacalix[4]arene (1x10$^{-4}$M) ( 0.00 to 1.00 ml)
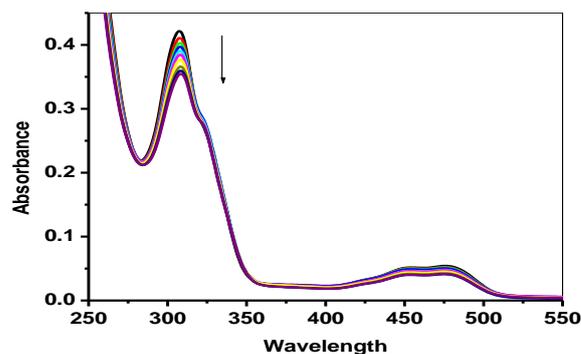


Fig.3: Absorption spectra of ternary system: Fluorescein [1x10$^{-6}$M] + p-sulfonatothiacalix[4] arene (1x10$^{-4}$M)+Zn$^{2+}$(1x10$^{-4}$M) ( 0.00 to 1.00 ml).

The binding constant/ sability constant Ka of fluorescein with p-sulfonatothiacalix[4]arene  as binary system was evaluated with the aid of Valuer's method [14] from the plot of (Ao/Ao-A) versus [p-sulfonatothiacalix[4]arene]$^{-1}$(Fig. 4). Where Ao is initial absorbance of fluorescein, A is change in absorbance with addition of p-sulfonatothiacalix[4]arene. The plot gives a good straight line. From the intercept and slop of the line, the binding constant is calculated (Table 1). In the similar way binding constant was determined by plotting Ao/Ao-A versus [Zn$^{2+}$]$^{-1}$ for ternary system. Here Ao is absorbance of fluorescein and last addition of p-sulfonatothiacalix[4]arene and A is change in absorbance with addition of Zn$^{2+}$( Fig 5).
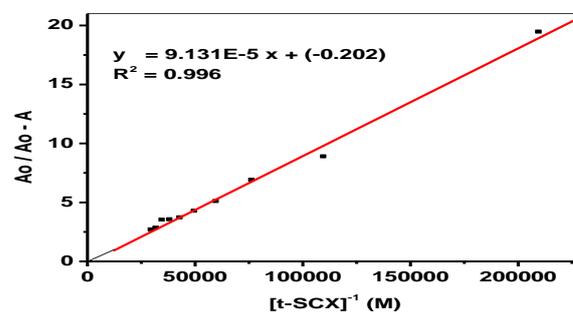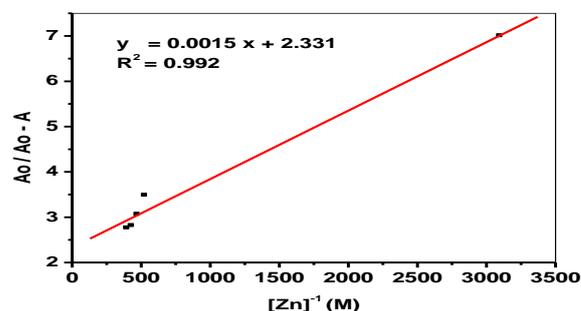


Fig. 4: Stability constant of binary system



Fig. 5: Stability constant of ternary system

### 3.2 Fluorescence spectral titrations:

*Stern–Volmer kinetics:*

The experimental quenching rate constant Ksv can be calculated as,

Io/I = Ksv  [G] + 1

where Io and I are the steady-state fluorescence intensities in the absence and in the presence of quencher, respectively. Ksv s the Stern–Volmer constant [15]. Generally, the ratio

I0/I is plotted against the quencher concentration (Stern–Volmer plot). If the variation is found to be linear, the slope gives the Stern–Volmer constant. Io and I are the initial and final fluorescence intensities respectively Fig. 6 for binary and fig. 7 for ternary system. From the Stern–Volmer constants we can propose that quenching effect is more in binary than in ternary system.
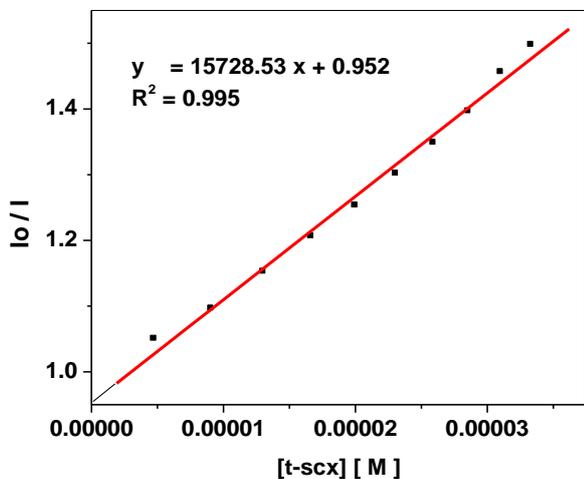


Fig.6 :Stern-Volmer plot of fluorescence quenching for Fluorescein Vs p-sulfonatothiacalix[4]arene; Ksv = 1.57 x $10^4$
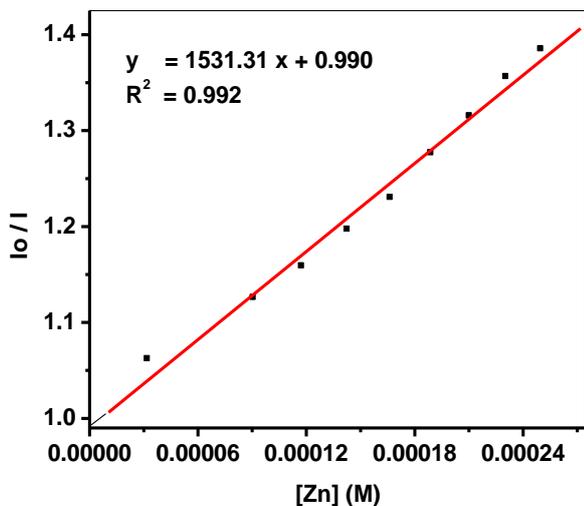


Fig.7 :Stern-Volmer plot of fluorescence quenching for p-sulfonatothiacalix[4]arene Vs $Zn^{2+}$; Ksv = 1.53 x$10^3$

For this titration, by fixing the concentration of the guest, at $1x10^{-6}$M, the concentration of the host p-sulfonatothiacalix[4]arene is varied from $1x10^{-4}$M to $1x10^{-5}$M at pH 2.0. It is observed that intensity at wavelength 510nm decreased from 700 to 450 with no change in wavelength (Fig. 8). This indicates stronger interaction between fluorescein and p-sulfonatothiacalix[4]arene. When to the same solution $Zn^{2+}$ was added, then it was observed that the intensity at wavelength 510nm decreased from 450 to 350. The decreased in intensity is lesser for ternary system i.e. for (fluorescein + p-sulfonatocalix[4]arene + $Zn^{2+}$) than for binary system i.e. (fluorescein and p-sulfonatothiacalix[4]arene) (Fig.9).



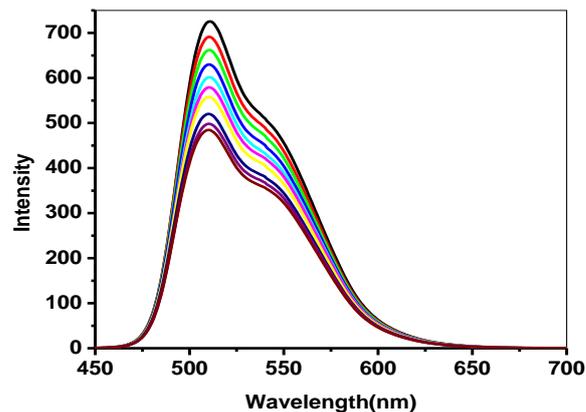Fig. 8: Fluorescence spectra of fluorescein $(1x10^{-6}$M) with varying p-sulfonatothiacalix[4]arene $(1x10^{-4}$M) ( 0.00 to 1.00 ml)



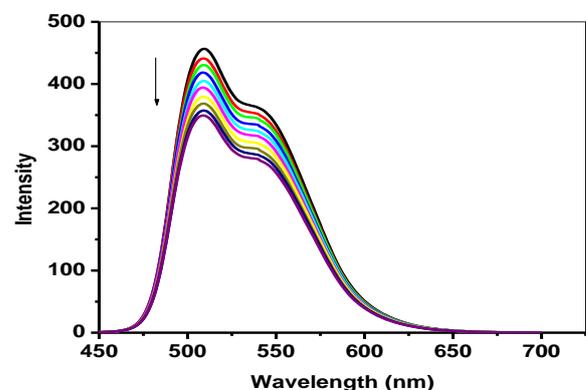Fig. 9: Fluorescence spectra of p-sulfonatothiacalix[4]arene $(1x10^{-4}$M) and fluorescein $(1x10^{-6}$M) with varying $Zn^{2+}(1x10^{-4}$M)( 0.00 to 1.00 ml)

The complex stability constant was calculated using Valuer's method [22]. The quantity Io/Io-I is plotted against [p-sulfonatothiacalixarene]$^{-1}$ with the stability constant given by the ratio of intercept/slop (Fig. 10). Stability constants for complexation of (fluorescein and p-sulfonatothiacalix[4]arene) as binary system and (fluorescein + p-sulfonatothiacalix[4]arene + $Zn^{2+}$) as ternary system are approximately the same calculated by two methods, spectrophotometric and spectrofluorometric (Table 1).
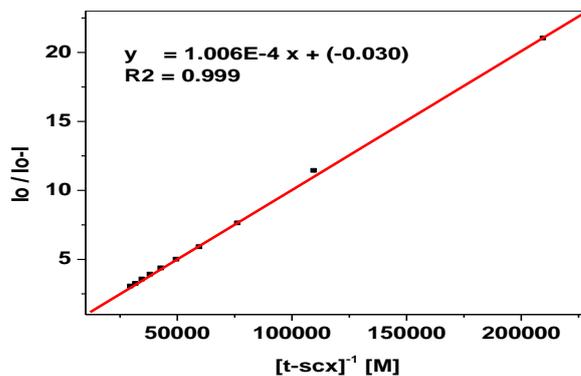


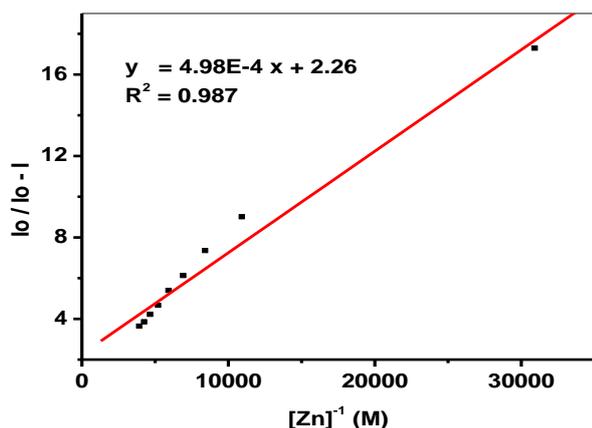Fig. 10: Stability constant for binary system

Fig.11: Stability constant for ternary system

Table 1: Stability constant of binary and ternary complex:

| Stabiity constant | p-sulfonatothiacalix[4]arene + Fluorescein | p-sulfonatothiacalix[4]arene+Zn$^{2+}$ |
|---|---|---|
| UV-measurement | $2.21 \times 10^3 M^{-1}$ | $1.554 \times 10^3 M^{-1}$ |
| Fluorescence measurement | $2.982 \times 10^3 M^{-1}$ | $4.538 \times 10^3 M^{-1}$ |

## IV. ACKNOWLEDGMENT:

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