

Studies on the Inclusion Behavior of Amphiphilic *p*-Sulfonatocalix[4]arene with Ascorbic Acid by Spectrofluorometric Titrations

Yunyou Zhou, Xueping Ding, Xiaoli Fang, Tao Li, Dongbao Tang, Qin Lu

Key Laboratory of Chemo-Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, China

E-mail: zy161299@mail.ahnu.edu.cn.

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Abstract

The aqueous solution of tetrabutyl ether derivatives of *p*-sulfonatocalix[4]arene (SC4Bu) and ascorbic acid (AA) complex has been studied based on fluorescence and ¹H NMR spectroscopic results. It was found that the fluorescence intensity of SC4Bu quenched regularly upon the addition of AA. A 1:1 stoichiometry for the complexation was established and was verified by Job's plot. The temperature-dependent inclusion constants were calculated, from which ΔH and ΔS values were calculated. Meanwhile the proposed interaction mechanism of the inclusion complex was discussed based on ¹H NMR results. The various factors (ionic strength, and surfactants) effecting the inclusion process were examined in detail.

Keywords: *P*-Sulfonatocalix[4]arene, Ascorbic Acid, Fluorescence Spectrometry, Inclusion Interaction

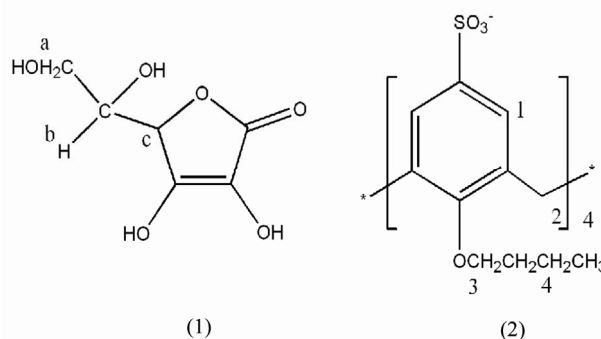
1. Introduction

Calixarenes and their derivatives have attracted considerable attention in host-guest chemistry due to their excellent recognition ability [1,2]. The water-soluble *p*-sulphonated calyx[*n*]arenes (SC*n*A, *n* = 4, 6, 8) derivatives display wider applications in supramolecular chemistry science because they allow the study of host-guest interactions in a solvent where most biological processes take place [3-9]. *P*-sulphonated calix[*n*]arenes (SC*n*A, *n* = 4, 6, 8) have been reported to interact with specific drugs or their intermediates [10-12]. However, SC4A and SC6A have very weak fluorescence and absorption signals in an aqueous solution [10]. They are difficult to be used for the investigation of inclusion behavior of non-fluorescent or weakly fluorescent guest molecules [13]. Therefore, it is of great importance to synthesize fluorescent water-soluble calixarene derivatives for studying the inclusion behavior of these non-fluorescent molecules.

Ascorbic acid (AA, **Scheme 1**), commonly known as Vitamin C, is one of the most important water-soluble vitamins in foods and drinks [14,15]. It is also widely used as a food additive and antioxidant [16], which can prevent scurvy and reduce the incidence and mortality

from cardiovascular disease and cancer [17].

Herein, we have synthesized the tetrabutyl ether derivative of *p*-sulfonatocalix[4]arene (SC4Bu, Scheme 1) with strong fluorescence in aqueous solution and also investigated the inclusion behavior of SC4Bu with AA in aqueous solution using fluorescence spectrometry. The results indicate that SC4Bu and AA form a complex (1:1 mole ratio), with a binding constant of $1.78 \times 10^3 \text{ L}\cdot\text{M}^{-1}$. The interaction mechanism of the inclusion process was discussed. This work may extend the application of SC4Bu in the biochemistry area.



Scheme 1 chemical structure of ascorbic acid (1) and SC4Bu (2)

2. Experimental

2.1. Apparatus

Fluorescence spectra and relative fluorescence intensities were performed on a model F-4600 fluorescence spectrophotometer (Hitachi, Japan) using a 1 cm × 1 cm quartz cell. The slit widths for excitation and emission were both set to 5.0 nm. The fluorescence lifetimes were measured on a FLS920 combined steady-state lifetime fluorescence spectrometer (Edinburgh Instrument). All measurements were carried out at desired temperature adjusted by a thermostatic cell holder. ^1H NMR was performed on an Avance Bruker-300 MHz spectrometer. IR was obtained using a PE983 infrared spectrophotometer (Perkin Elmer).

2.2. Chemicals

SC4Bu was synthesized according to the literature [18, 19] and identified by IR and ^1H NMR. AA was purchased from Shanghai Chemical Reagent Co. All other reagents were of analytical reagent grade and used without any further purification. Doubly distilled water was used throughout.

2.3. Procedure

A 1.0 mL of 1.00×10^{-4} mol·L $^{-1}$ SC4Bu, and an appropriate amount of 1.00×10^{-3} mol·L $^{-1}$ AA were transferred into a 10 mL volumetric flask. The mixture was diluted to the final volume with water and mixed thoroughly. Fluorescence spectra were measured at 25.0°C.

3. Results and Discussion

3.1. Characteristics of Fluorescence Spectra

Figure 1 displays the fluorescence spectra of 1.00×10^{-5} mol·L $^{-1}$ SC4Bu in aqueous solution. It is clear that SC4Bu shows strong fluorescence in aqueous solution with excitation and emission wavelengths at 230 and 315 nm, respectively. When an appropriate amount of 1.00×10^{-3} mol·L $^{-1}$ AA was added to SC4Bu, the fluorescence quenching of SC4Bu was observed, as shown in **Figure 2**, indicating the formation of the inclusion complexes.

The formation of inclusion complex was also revealed by the fluorescence decay curves obtained at different concentrations of AA. The fluorescence lifetimes of the SC4Bu molecule in aqueous and in AA were determined from the decay curves and the results are shown in **Table 1**. The fluorescence decay of SC4Bu without AA obtained from monitoring the emission at 312 nm is a single-exponential decay with lifetime value of 0.72 ns (τ_1).

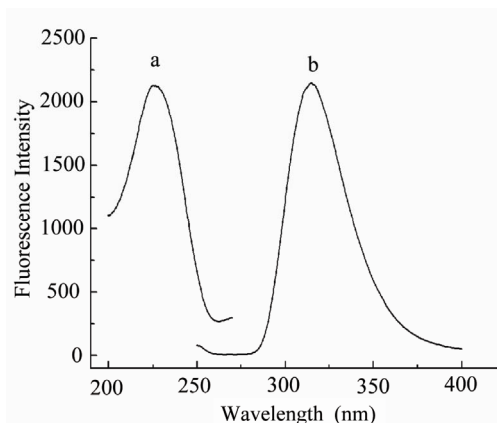


Figure 1. Fluorescence excitation (a) and emission (b) spectra of SC4Bu (1.00×10^{-5} mol·L $^{-1}$) in solution.

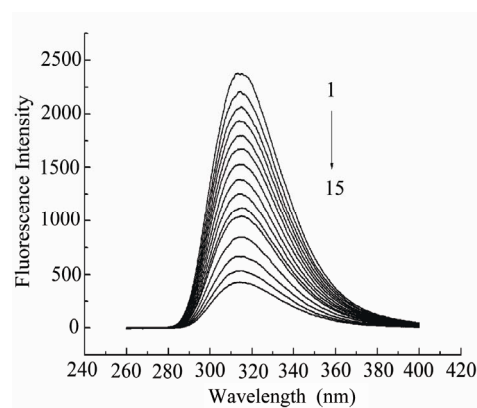


Figure 2. Fluorescence spectra of SC4Bu with different concentrations of AA. The concentrations from (1) to (15) of AA were: (1) 0.00, (2) 0.20, (3) 0.40, (4) 0.60, (5) 0.80, (6) 1.00, (7) 1.20, (8) 1.40, (9) 1.60, (10) 1.80, (11) 2.00, (12) 2.50, (13) 3.00, (14) 3.50 and (15) 4.00×10^{-4} mol·L $^{-1}$. SC4Bu = 1.00×10^{-5} mol·L $^{-1}$, 25.0°C.

Table 1. Time-resolved fluorescence spectral data of SC4Bu in the absence and presence of different concentrations of AA ($\lambda_{\text{ex}} = 250\text{nm}$, $\lambda_{\text{em}} = 310\text{ nm}$; [SC4Bu] = 1.0×10^{-5} M)

Concentration of AA (M)	Lifetime (ns)	Relative amplitudes (%)	χ^2	Standard deviation (ns)
0	0.72	100	1.018	0.02
0.2×10^{-5}	0.78	84.12	1.062	0.02
	2.52	15.88		
0.4×10^{-5}	0.77	82.53	1.002	0.02
	2.62	17.47		
0.8×10^{-5}	0.76	81.86	1.021	0.02
	2.50	18.14		

Upon the addition of AA, single exponential decay changes to biexponential decay with lifetime τ_1 and τ_2 , respectively, suggesting the presence of two species, SC4Bu and its complex. It is also evident from **Table 1** that the short-lived species (τ_1) is close to the measured lifetime of

SC4Bu in pure water, and that of the long-lived species τ_2 are correspond to the inclusion complex. The amplitude of the complex form also increases due to an increase in complex formation and the free species decreasing.

3.2. Stoichiometry and Inclusion Constant

The formation of 1:1 SC4Bu-AA complex was confirmed by the continuous variation method (Job's plot) using fluorescence spectrometry. Here, the solutions of SC4Bu and AA were mixed in different mole ratio keeping the total of the SC4Bu and AA concentration constant. The maximum relative fluorescence intensity was observed when $[\text{SC4Bu}]/([\text{SC4Bu}] + [\text{AA}]) = 0.5$ as shown in **Figure 3**, this is in agreement with the double reciprocal plot and confirmed the formation of a 1:1 inclusion complex in the system.

Assuming that SC4Bu and AA forms a 1:1 ratio complex, according to our earlier work [12, 20] the equation of host-guest inclusion complex can be expressed as:

$$\frac{1}{F - F_0} = \frac{1}{F_1 - F_0} + \frac{1}{K[G](F_1 - F_0)} \quad (1)$$

Here F_0 is the intensity of fluorescence of SC4Bu without AA, F is the observed fluorescence intensity at different AA concentration tested, F_1 is the intensity with the highest concentration of AA and K is the binding constant. The double reciprocal plots of $1/[F - F_0]$ versus $1/[\text{AA}]$ are depicted in **Figure 4**. The plot displays a linear relation with a relative correlation constant of 0.9993, indicating the formation of a 1:1 stoichiometry between SC4Bu and AA. The association constant (K) obtained from the ratio of the intercept to the slope is $1.78 \times 10^3 \text{ L}\cdot\text{M}^{-1}$.

3.3. Thermodynamic Parameter Value

The binding constants at various temperatures were investigated by measuring the fluorescence spectra of SC4Bu in the presence of AA, and the results were summarized in **Table 2**. By plotting $\ln K$ against $1/T$ (the Van't Hoff method) [19] (see **Figure 5**), the enthalpy (ΔH) and entropy (ΔS) were calculated to be $25.25 \text{ kJ}\cdot\text{mol}^{-1}$, $146.75 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$, respectively. These results suggested that the entropic driving force favored the formation of SC4Bu-AA complex. The relevant free energy change for this system is $\Delta G = -18.48 \text{ kJ}\cdot\text{mol}^{-1}$ at 298 K, indicating that this inclusion process is an energetically favored process.

3.4. ^1H NMR Studies

Chemical shift variations of specific host or guest nucleus could provide evidence for the formation of inclusion complexes in solution, since significant changes in

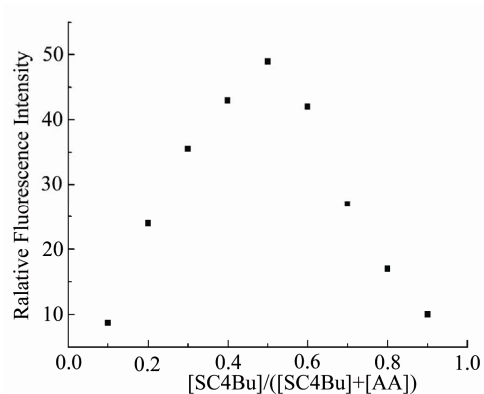


Figure 3. Job's plot of SC4Bu-AA system, $[\text{SC4Bu}] + [\text{AA}] = 1.00 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, 25.0°C .

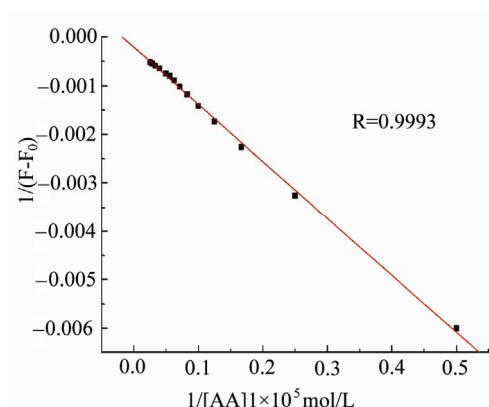


Figure 4. A plot of $1/(F - F_0)$ versus $1/[\text{SC4Bu}]$ for SC4Bu-AA complex.

Table 2. Inclusion constants of complexes at different temperatures.

Temperature (K)	288	298	208	318
Inclusion constant ($\times 10^3$)	1.26 ± 0.14	1.78 ± 0.09	2.32 ± 0.11	3.38 ± 0.05
R	0.9996	0.9993	0.9997	0.9969

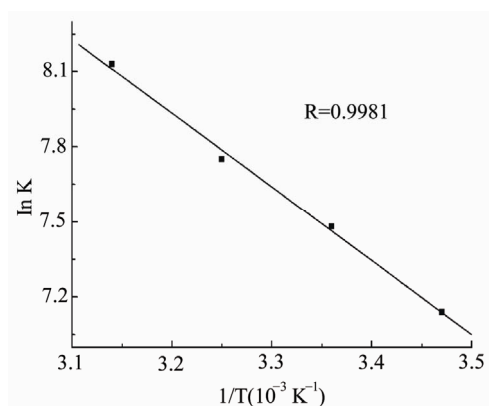


Figure 5. The plot of $\ln K$ versus $1/T$ for the SC4Bu-AA complex.

Table 3. Chemical shifts δ and $\Delta\delta$ of protons of AA in free guest and inclusion complex.

	H ₁	H ₂	H ₃	H ₄	H _a	H _b	H _c
(AA) δ					3.7185	4.0281	4.9374
(SC4Bu) δ	7.6359	4.1250/3.4247	3.9762	1.4676			
(SC4Bu-AA) δ	7.5850	4.0354/3.3976	3.9607	1.4657	3.7463	4.0354	4.9212
$\Delta\delta$	-0.0509	-0.0896/-0.0271	-0.0155	-0.0019	+0.0278	+0.0073	-0.0162

microenvironment are known to occur between the free and bound states [21]. The interaction between SC4Bu and AA were studied by ¹H NMR spectra. The significant distinction between the ¹H NMR spectra of SC4Bu and the inclusion complex of AA with SC4Bu in D₂O confirms that the inclusion complex was formed and the value of chemical shifts for different protons in SC4Bu, AA and SC4Bu-AA inclusion complex as shown in **Table 3**.

The ¹H NMR shifts are in agreement with those reported in the literatures [21-22], which mentioned that downfield shifts should be observed for guest protons and upfield shifts for host protons upon hydrophobic interactions between both partners. The complexation causes an upfield shift of SC4Bu protons: a great upfield was recorded for H₁ and H₂. Since both of them are located inside the cavity. The upfield shift observed for H₂ and H₁ confirms the inclusion inside the cavity. Further confirmation was obtained by observing the changes in the chemical shifts of AA.

The H-chemical shifts in both the free and the complexed state are reported in **Table 3**. We can see that H_c proton was shifted upfield, while H_a and H_b were deshielded upon complexation. In fact, the downfield shifts of the guest protons have been attributed to a variation of local polarity when these protons are inside the cavity [21]. The shielding of H_c proton has been attributed to it is close to the cavity of SC4Bu. As expected, the probable binding mode in the SC4Bu inclusion complexes involves the insertion of less part of the guest into the cavity and exposure of more groups to the bulk solvent outside.

3.5. Discussion of Interaction Mechanism

Calixarenes and their derivatives have been known to be able to form non-covalent inclusion complexes with various guest molecules through many interactions, such as the electrostatic interaction, cation- π interactions, hydrogen bonding, van der Waals and hydrophobic interactions [23]. In this context, considering the size/shape fitting, multiple recognition and ¹H NMR results, pattern inclusion manner between SC4Bu and AA was proposed as show in **Figure 6**. AA partially goes into the cavity of SC4Bu with the help of hydrogen bonding, which formed by the hydroxyl groups of AA bonding with sulphonyl groups of SC4Bu, respectively.

The main driving force for the inclusion of AA by SC4Bu was investigated. The electrostatic effect was studied by varying the ionic strength of NaCl and the results were shown in **Figure 7**. As can be see when the NaCl concentration is 0.01 mol·L⁻¹, the fluorescence intensity of the SC4Bu-AA system had no significant changes compared with the absence of NaCl in the system. Thus the main driving force for inclusion of AA by SC4Bu should not be electrostatic interaction. The hydrogen bonding and the hydrophobic interaction should play the main driving force for this inclusion process. This is different from what the literature suggests, in which electrostatic interaction was thought to play important part in the inclusion process [12].

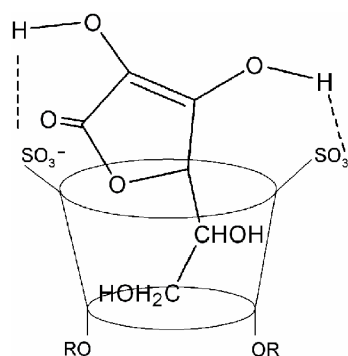


Figure 6. The proposed inclusion pattern of the SC4Bu-AA complex.

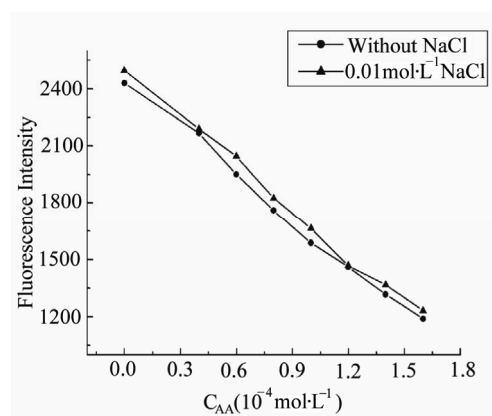


Figure 7. Influence ionic strength of NaCl on the fluorescence intensity of SC4Bu-AA system; [SC4Bu] = 1.00 × 10⁻⁵ mol·L⁻¹, C_{NaCl} = 0.01 mol·L⁻¹.

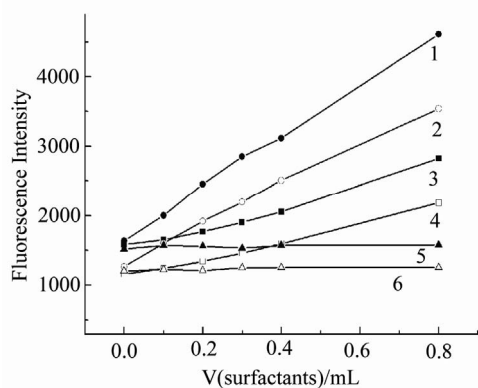


Figure 8. Influence of surfactants concentration on the fluorescence intensity of SC4Bu-AA system; (1) SC4Bu+TritonX-100; (2) SC4Bu+AA+TritonX-100; (3) SC4Bu+CTAB; (4) SC4Bu+AA+CTAB; (5) SC4Bu+SDS; (6) SC4Bu+AA+SDS; [SC4Bu] = $5.00 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$, [AA] = $6.00 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$.

3.6. Influence of Surfactants

The influence of surfactants on this inclusion process was also investigated. Three types of surfactants: the cationic surfactant cetyltrimethylammonium bromide (CTAB), the anionic surfactant sodium dodecyl sulfate (SDS) and the non-ionic surfactant octylphenylpolyoxyethylene ether (Triton X-100) were chosen to study their effect on SC4Bu and AA complex. Among those, SDS showed no influence on the fluorescence intensity of SC4Bu and the SC4Bu-AA complex as shown in **Figure 8**, while Triton X-100 and CTAB enhanced the fluorescence intensities of SC4Bu and the corresponding SC4Bu-AA complex. Triton-100 itself has been reported to be able to enhance the fluorescence intensity of certain types of sulfuric fluorophores [24]. Similarly, it may also lead to the increase of the fluorescence intensity of SC4Bu and the SC4Bu-AA complex. In our previous work, we have reported that SCnA can form a 1:1 complex with CTAB, which lead to the enhancement of the fluorescence intensity of SCnA [24]. Similarly, CTAB may lead to the increase of the fluorescence intensity of SC4Bu through the inclusion process. Upon addition of AA, the quench of the fluorescence intensity of the SC4Bu-CTAB complex was observed, indicating the partial replacement of CTAB with AA [25].

4. Conclusions

In this work, a water-soluble *p*-sulfonatocalix[4]arene derivative (SC4Bu) with strong fluorescence was synthesized and inclusion process between SC4Bu and AA in aqueous solution was also investigated by fluorescence

spectrometry. AA and SC4Bu were found to form a 1:1 host-guest inclusion complex. The possible interaction mechanism was discussed. Similar to cyclodextrins, SC4Bu and its inclusion complexes show potential for biological and medical applications.

5. Acknowledgements

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