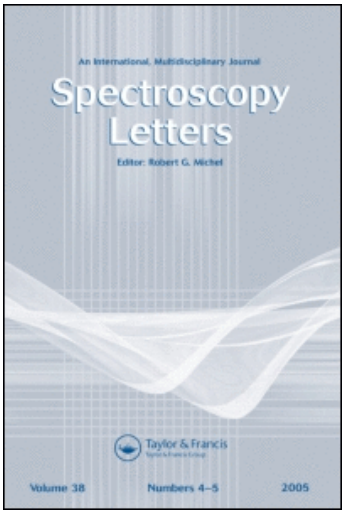

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A Preliminary Investigation of the Complexation of Dopamine by *p*-Sulfonated Calix[4, 6] Arene and β-Cyclodextrin Using Fluorescence Spectrometry

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Abstract: The inclusion complexes of *p*-sulfonated calix[4, 6] arene and *β*-cyclodextrin with dopamine were studied by fluorescence spectrometry in aqueous media. It was found that the fluorescence intensity of dopamine regularly decreased upon the addition of *p*-sulfonated calix[4, 6] arene, on the contrary, it increased upon the addition of *β*-cyclodextrin. ^{1}H NMR spectra were applied to verify the formation of the complexes. According to the experimental results, 1:1 stoichiometry for the complexes was established and their association constants at 25°C were calculated by applying a deduced equation. Judging from the magnitude of their inclusion constants, the *p*-sulfonated calix[4, 6] arene showed better inclusion capability than *β*-cyclodextrin. The probable interaction mechanisms are proposed.

Keywords: *β*-Cyclodextrin, dopamine, fluorescence spectrometry, inclusion interaction, *p*-sulfonated calix[4, 6] arene

INTRODUCTION

It is well-known that cyclodextrins (CDs) can form stable inclusion complexes with a variety of guest molecules, in which the guest molecules are included within the hydrophobic cavities of CDs.[1,2] Particularly, they have been

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widely used to enhance solubility, chemical stability, and bioavailability of poorly soluble drugs. Those complexes with drugs turned out to be very convenient to reduce the local concentration of free drug, thus reducing side effects.[3,4] Following CDs, in recent years, *p*-sulfonated calix[n] arenes (SCnA), which have flexible and often poorly defined cavities that tend to bind positively charged species and even have been often viewed as promising water-soluble hosts, have attracted the keen interest of researchers studying different area, such as conformational flexibility,[5,6] electrochemical behaviors,[7–9] molecular recognitions,[10,11] and biological activities.[12–14] However, there is less literature on the possible use of *p*-sulfonated calix[n] arenes in biological and pharmaceutical applications compared with the widespread use of CDs in counterpart fields.[15,16] In our previous papers, we have studied the spectral characteristics of host-guest complexes of *p*-sulfonated calix[4] arenes with one of the synthetic antibacterial fluoroquinolone reagents (lomefloxacin) and 9-amino-acridine, one of the important intermediates of drugs,[17,18] respectively.

Dopamine, a neurotransmitter, is one of the naturally occurring catecholamines, and its hydrochloride salt is being used in the treatment of acute congestive failure and renal failure.[19] There are several reports about the interaction between dopamine and CDs or their derivatives that have been modified on the electrodes.[20,21] The results indicate dopamine can form guest-host complexes with CDs. Besides, Tankshi has reported detection of the neurotransmitter acetylcholine in water using a dansylcholine complex with *p*-sulfonated calix[8]arenes,[22] in which is a suggestion that dopamine can also form complexes with *p*-sulfonated calix[n]arenes. However, to the best of our knowledge, there are no reports about the interaction between dopamine and CDs and *p*-sulfonated calix[n]arenes using spectral methods.

In this paper, the complexes of dopamine (DA) with *p*-sulfonated calix[4, 6] arenes (SCnA, n = 4, 6) and β-cyclodextrin (β-CD) (their structures are shown in Fig. 1) were investigated by using fluorescence spectrometry in aqueous media. When SCnA were added to the aqueous solution of DA, an obvious decrease in fluorescence intensity and a slight and slow red shift were observed. Conversely, the fluorescence intensity of DA increased upon

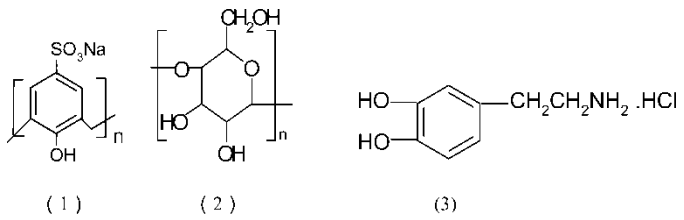

Figure 1. Structures of *p*-sulfonated calix[4, 6] arene (1), β-cyclodextrin (2, n = 7), and dopamine hydrochloride (3).

the addition of β-CD. The results indicate DA form 1:1 stoichiometry complexes with SCnA and β-CD, respectively. The stability constants of inclusion complexes were determined by a deduced equation and the interaction mechanisms of the inclusion complexes were discussed. This work may extend the application range of water-soluble calix arenes in biochemistry and pharmaceutical analysis.

MATERIALS AND METHODS

Apparatus

Fluorescence spectra and relative fluorescence intensities were measured on a model F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) using a conventional 1×1 cm quartz cell. Both excitation and emission bandwidths were set at 5 nm. Absorption measurements were performed with a Hitachi U-3010 spectrophotometer using a 1.0-cm path-length cell. All measurements were carried out at desired temperature adjusted by use of a thermostatic cell holder. A model pHS-3C (Da Zhong Analytical Instruments Factory, Shanghai, China) pH meter was used for accurate adjustment of pH. ^{1}H NMR spectra were measured using an Avance Bruker 300-MHz spectrometer (Bruker Co., Switzerland).

Reagents

All reagents used were of analytical reagent grade or the best grade commercially available. Doubly distilled water was used throughout. *p*-sulfonated calix[4, 6] arene (SCnA, n = 4, 6) was synthesized according to the literature[23] and identified by IR, ^{1}H NMR, and element analysis. Stock solutions of SCnA were prepared as 1.00×10^{-3} mol L^{-1}. β-Cyclodextrin (β-CD) was obtained from Shanghai Chemical Reagent Co. (China) and 1×10^{-2} mol L^{-1} stock solution was prepared in water. β-CD was recrystallized twice from doubly distilled water before used. Dopamine hydrochloride was purchased from ICN Biomedical Co. (Irvine, California) and 1.00×10^{-3} mol L^{-1} stock solution was prepared in water. Buffer solution (pH = 5.0) was prepared by mixing 0.1 mol L^{-1} potassium monohydrogen orthophosphate solution with 0.1 mol L^{-1} potassium dihydrogen orthophosphate solution. Deuterium oxide (99.9%) was purchased from Acros Co., USA.

Procedure

Different amounts of 1.00×10^{-3} mol L^{-1} SCnA solution or 0.01 mol L^{-1} β-CD solution were respectively added to 0.5 mL of

1.00×10^{-4} mol L^{-1} DA solution then diluted to 10.0 mL with phosphate buffer solution (0.1 mol L^{-1}). Fluorescence intensities (or absorption spectra) at 25.0°C were measured after incubation for 20 min.

RESULTS AND DISCUSSION

Fluorescence Spectra and Absorption Spectra Characteristics

Figure 2 shows the fluorescence excitation and emission of dopamine in phosphate buffer solution (pH = 5.0). As can be seen, it has strong fluorescence with maximum excitation and emission wavelengths of 285 nm and 324 nm. When appropriate amount of 1.00×10^{-3} mol L^{-1} SC4A or SC6A was added into it, the fluorescence intensities decreased obviously, accompanying with a slow red shift (SC4A 324.0 nm → 329.0 nm; SC6A: 324.0 nm → 334.0 nm) (see Figs. 3a and 3b). However, when a proper amount of 1.00×10^{-2} mol L^{-1} β-CD was added into it, the reverse fluorescence behavior and a slight blue shift (324.0 nm → 322.4 nm) were observed (see Fig. 4a). This "*opposite fluorescent behavior*" has been reported by Liu and his co-workers in acridine red dye and SCnA systems previously.[24]

The absorption spectra of DA in phosphate buffer solution at various concentrations of β-CD are shown in Fig. 4b. The absorption peak of DA is at 278 nm. The addition of β-CD leads to the increase of absorbance of this drug accompanied with a quite slight red shift (278.0 nm → 280.1 nm). However, due to the strong absorption of SCnA in the 200–300 nm region, the absorption intensity of DA also increased with the addition of SCnA.

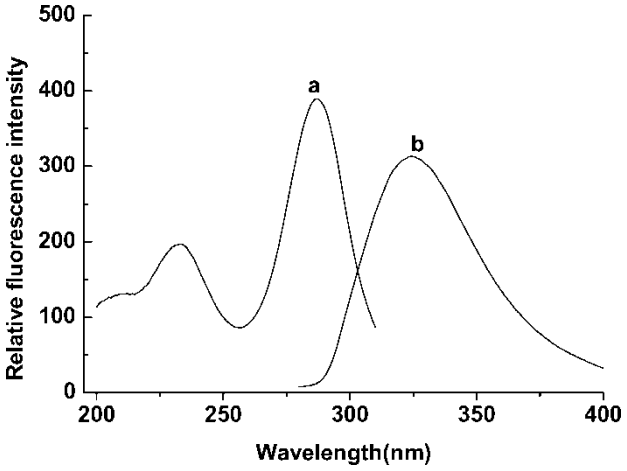

Figure 2. Fluorescence excitation (a) and emission (b) spectra of DA (5.00×10^{-6} mol L^{-1}) in phosphate buffer solution (pH = 5.00).

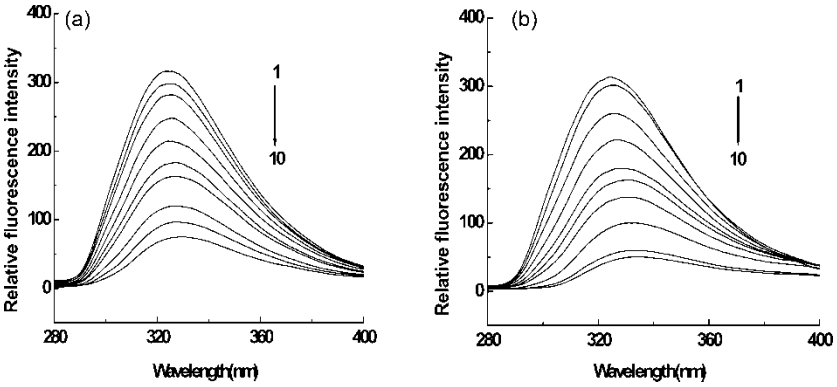

Figure 3. Fluorescence spectra of DA with different concentrations of SC4A (a) or SC6A (b): from 1 to 10: (1) 0.0; (2) 0.1; (3) 0.2; (4) 0.4; (5) 0.6; (6) 0.8; (7) 1.0; (8) 1.5; (9) 2.0; (10) 2.5×10^{-4} mol L^{-1} in phosphate buffer solution (pH = 5.00), $C_{DA} = 5.00 \times 10^{-6}$ mol L^{-1}, 25.0°C.

The Stern-Volmer plots of DA quenched by SC4A at different temperature are shown in Fig. 5. The Stern-Volmer constants that were obtained from the slopes of plots decreased with the rise of temperature ($K_1 < K_2 < K_3$), which indicated the quenching of DA by SC4A was a static quenching process. Similar phenomena were found for DA-SC6A system.

According to our earlier results[17,18] and further study, we suppose that the fluorescence and absorption spectra changes described above are probably induced by the formation of inclusion complexes.

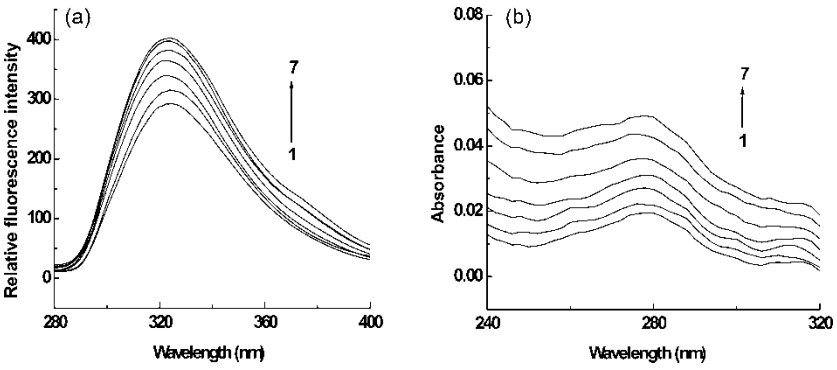

Figure 4. Fluorescence (a) and absorption (b) spectra of DA with different concentrations of β-CD: from 1 to 7: (1) 0.0; (2) 0.2; (3) 0.5; (4) 1.0; (5) 2.0; (6) 3.0; (7) 4.0×10^{-3}mol L^{-1} in phosphate buffer solution (pH = 5.00), $C_{DA} = 5.0 \times 10^{-6}$ mol L^{-1}, 25.0°C.

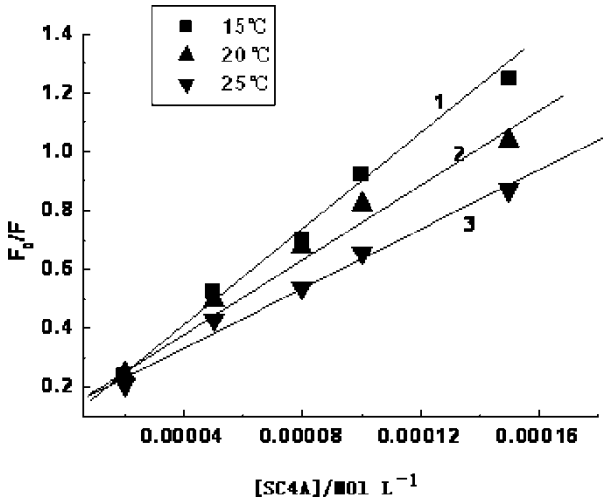

Figure 5. Stern-Volmer plots of DA quenched by SC4A at 15°C, 20°C, 25°C in phosphate buffer solution (pH = 5.00), $C_{DA} = 5.0 \times 10^{-6}$ mol L^{-1}.

The Stoichiometry and Formation Constants of Inclusion Complexes

The stoichiometry and association constant of the inclusion complex were studied under the established experimental conditions by the following method: assuming that the composition of the complex was 1:1, the following expression can be written as

$$H + G \rightleftharpoons H \cdot G \tag{1}$$

The formation constant of the complex (K) is given by

$$K = \frac{[H \cdot G]}{[H][G]} \tag{2}$$

where $[G]$, $[H]$, and $[H \cdot G]$ are equilibrium concentrations of guest molecule, host molecule, and the host-guest complex, respectively. By using $[H] \gg [H \cdot G]$, it can be assumed that $[H]_0 \approx [H]$ and the following equation can be derived:

$$\frac{1}{[H \cdot G]} = \frac{1 + K[H]_0}{K[G]_0[H]_0} \tag{3}$$

where $[G]_0 = [G] = [H \cdot G]$ and $[H]_0 = [H] + [HgG] \approx [H]$.

In this context, the guest molecule is DA and the host molecules are SCnA or β-CD. Because the fluorescence intensity of DA in the absence (F_0) and

presence (F_1) of SC4A is proportional to $[G]$ and $[H \cdot G]_\infty$, respectively, substitution of these values into Eq. (2) gives

$$\frac{1}{F - F_0} = \frac{1}{(F_1 - F_0)} + \frac{1}{K[H](F_1 - F_0)} \tag{4}$$

Here F is the observed fluorescence intensity at each host molecule concentration tested. (A similar equation was also deduced in cyclodextrin system by Mwalupindi et al.[25,26]) Herein the double reciprocal plots of $1/(F - F_0)$ versus $1/[\text{SCnA}]$ or $1/[\beta - \text{CD}]$ are shown in Figs. 6a, 6b and the inclusion constants of SC4A (K_a), SC6A (K_b), and β-CD (K_c) can be discovered by the ratio of the intercepts to the slopes (see Table 1). The excellent linear relationships verify the 1:1 complexes stoichiometry assumed above.

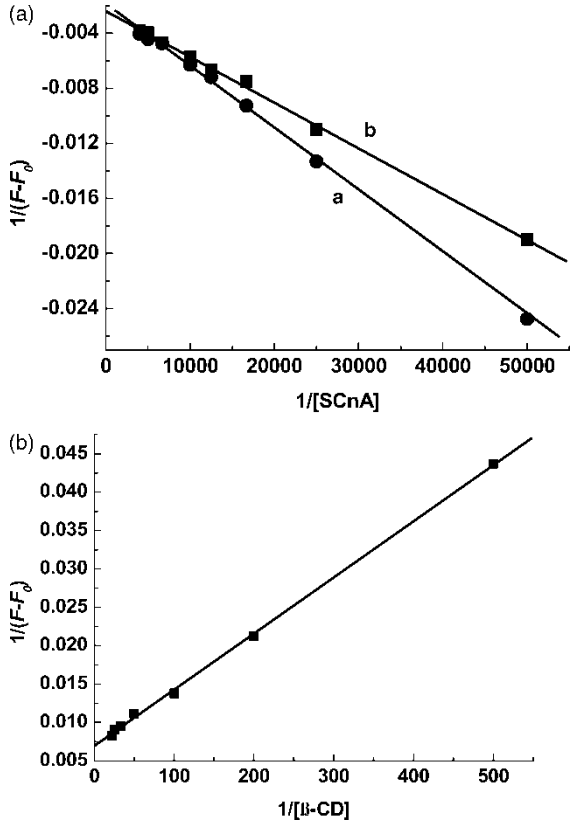

Figure 6. (a) Plots of $1/(F - F_0)$ versus $1/[\text{SC4A}]$ (*a*) and $1/[\text{SC6A}]$ (*b*) for DA-SCnA systems, $C_{DA} = 5.0 \times 10^{-6}$ mol L^{-1}, 25.0°C, pH = 5.0. (b) The plot of $1/(F - F_0)$ versus $1/[\beta\text{-CD}]$ of DA-β-CD system, $C_{DA} = 5.0 \times 10^{-6}$ mol L^{-1}, 25.0°C, pH = 5.0.

Table 1. Inclusion constants of complexes obtained from Fig. 6

Host-guest systems	Inclusion constants (K)	R
β-CD-DA	$K_c = 95.06$	R = 0.9995
SC4A-DA	$K_a = 4.06 \times 10^3$	R = 0.9991
SC6A-DA	$K_b = 7.19 \times 10^3$	R = 0.9993

The 1:1 complexes stoichiometry was also determined by Job's method. The solutions of DA and hosts were mixed in different mole ratio keeping the sum of the DA and hosts concentrations constant, and the maximal relative fluorescence intensity occurred at $[DA]/([host] + [DA]) = 0.5$. A typical plot for DA-SC6A complex is shown in Fig. 7 and similar plots can be obtained for DA-SC4A and DA-β-CD complexes.

DISCUSSION

Cyclodextrins have also been widely used to enhance the luminescence properties of different compounds.[27,28] The intensification of luminescent processes of lumiphors partial or totally encapsulated by the CD cavity is due to the better protection from quenching and other processes occurring in the bulk solvent. Apparently, the fluorescence and absorption intensities of DA increased upon the addition of β-CD for that the DA molecules insert into the hydrophobic cavity of β-CD.

On the other hand, *p*-sulfonated calix[4, 6] arene possesses hydrophobic cavity similar to the β-CD, however, when they were added into the solution of DA, the fluorescence of DA quenched regularly. It is well-known that calix

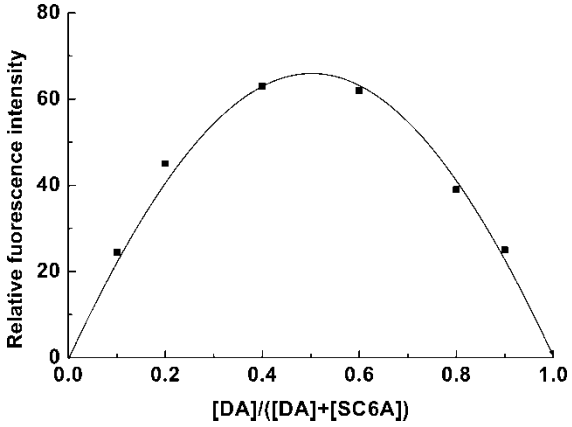

Figure 7. Job's plot of DA-SC6A system, 25.0°C, pH = 5.0.

arenes and their derivatives can form noncovalent inclusion complexes with various guest molecules of suitable size and characteristics with the aid of electrostatic interaction, cation-π interaction, hydrogen bonding, van de Waals, hydrophobic interaction, and so on.[29] Shinkai et al. have proposed that the main driving force of recognition of SC4A is electrostatic interaction.[30] In weak acidic media, there is strong electrostatic interaction between the protonated N atom of DA and one of the negatively charged sulfonyl groups of SC4A or SC6A to form salt, meanwhile the phenolic group of DA may enter the cavity of SCnA and be stabilized by the π-π interaction with the aromatic rings of SCnA.[5] Namely, *p*-sulfonated calix[4, 6] arene can form host-guest complexes with DA with the aid of electrostatic and hydrophobic interaction that may result in the changes of fluorescence spectra of DA.[17,24]

To confirm the formation of inclusion complexes, ^{1}H NMR spectra of DA in presence of SCnA were also examined. It can be seen from Fig. 8 that the proton signals of aromatic ring (**1**) and substituted carbon chain (**2**) are strongly shifted upfield by addition of SC6A or SC4A. These shifts reveal

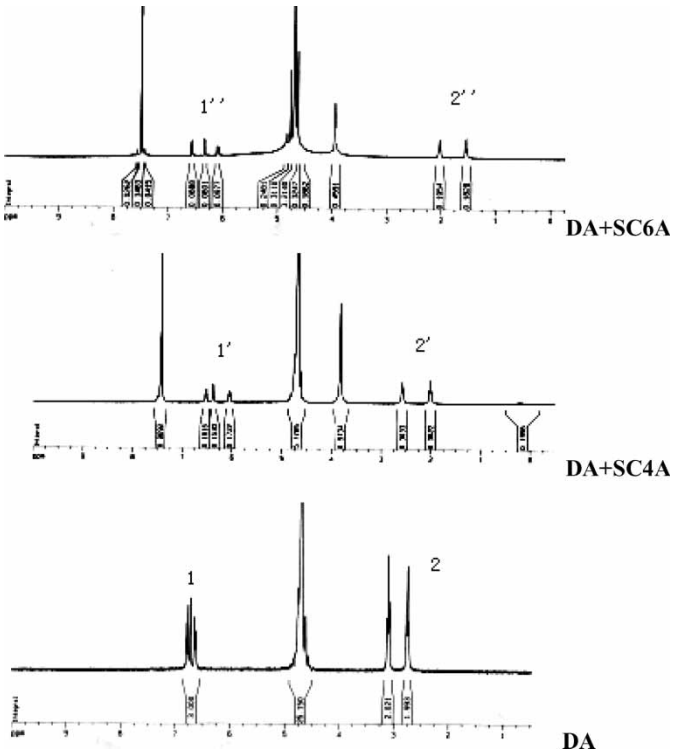

Figure 8. ^{1}H NMR spectra of DA in D_2O in the absence and presence of SC4A and SC6A. $C_{DA} = 1.0 \times 10^{-2}$ mol L^{-1}, $C_{SC4A} = 1.0 \times 10^{-2}$ mol L^{-1}, $C_{SC6A} = 1.0 \times 10^{-2}$ mol L^{-1}, 25.0°C, pH = 5.0.

that the molecule of DA is included within the cavity of SC6A or SC4A.[22] We also tried to study ^{1}H NMRspectra of DA in presence of β-CD under the same experimental conditions. However, it could not obtain counterpart ^{1}H NMR spectra due to solubility limitation of β-CD.

Besides, from Table 1, it is obviously seen that the inclusion constants of complexes follow the order $K_c < K_a < K_b$. Shinkai et al.[31] have estimated that the diameter of the upper rim of calix[4] arene is 0.38 nm, the calix[6] arene is 0.5 nm, whereas the diameter of β-CD is 0.78 nm. Therefore, SC6A gives a larger inclusion constant possibly because it has a better structural matching effect to dopamine molecule than SC4A and β-CD.

The results obtained above indicate that several noncovalent weak forces, including electrostatic, hydrophobic, π-π interaction, and van der Waals, cooperatively contribute to the formation of supramolecular complexes. Among these, electrostatic and hydrophobic interactions as well as structural matching effect were thought to play main roles to form the supramolecular systems.

CONCLUSIONS

Fluorescence spectrometry was applied to investigate the inclusion interaction of dopamine with *p*-sulfonated calix[4, 6] arene and β-CD in aqueous solution. The absorption and ^{1}H NMR spectra were accessorial to show the formation of complexes. Experimental results indicate they form 1:1 host-guest inclusion complexes. The stability constants of inclusion complexes were calculated by a deduced equation. Compared with the β-CD, the *p*-sulfonated calix[4, 6] arene showed better inclusion capability. The probable interaction mechanisms were also discussed. Water-soluble calix arenes and their inclusion compounds may have potential biological and medical applications like cyclodextrins, although further research still need to be carried out.

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