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Spectrofluorimetric study on the inclusion behavior of p-sulfonated calix [4, 6, 8] arene with cocaine hydrochloride

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ABSTRACT

The characteristics of host–guest complexations between p-sulfonated calix[*n*]arenes (*n* = 4, 6, 8) and Cocaine hydrochloride have been studied through fluorescence and ^{1}H NMR spectroscopic. It was found that the fluorescence intensity of Cocaine hydrochloride quenched regularly upon the addition of p-sulfonated calix[*n*]arenes (*n* = 4, 6, 8). A 1:1 stoichiometry for the complexation was established and was verified by Job's plot. The temperature-dependent inclusion constants were calculated. Meanwhile, the proposed interaction mechanism of the inclusion complex was discussed based on ^{1}H NMR and molecular modeling calculations. The various factors (pH, ionic strength, concentration, temperature, the addition order of reagents, reaction time, surfactants) effecting the inclusion process were examined in detail. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Cocaine hydrochloride;
P-sulfonated Calix[*n*]arenes;
Spectrofluorometry;
^{1}H NMR spectroscopy;
Inclusion interaction.

INTRODUCTION

As the third generation of host molecules[1], calixarenes have attracted much attention in recent years due to their ability to form host–guest complexation with a great variety of guests, from apolar compounds[2–6] to anions[7,8] and metallic cations[9-12]. However, these cyclic oligomers have some limitations for practical applications due to their poor solubility in water[13], Various functional groups have been introduced to either the upper or the lower rim of the 'cup' so far, which change the affinity of these cyclooligomers towards target molecules and increase the solubility of the calixarenes[14–16]. Among these calixarene derivatives, p-sulfonated calix[*n*]arenes have flexible and often poorly defined cavities that they can bind positively charged species. Especially recently, many research papers have been published on the inclusion of various guests, including inorganic cations[17,18], organic ammonium cations[19–22], neutral molecules[23–24], dyes[25–26], native amino acids[27], and even biological or pharmaceutical molecules[28,29]. Furthermore, p-sulfonated calix[*n*]arenes have been applied in the improvement of solubility and stability of drugs and enzyme mimics[30–33].

Cocaine, a kind of alkaloid ester, is extracted from plant leaves including coca. Cocaine hydrochloride (CH) is a local anesthetic and a vasoconstrictor used for clinical purposes, particularly for the eyes, ears, nose, and throat. Unfortunately, cocaine addiction is a serious public health problem that is difficult to treat because of high rates of relapse after abstinence. No effective pharmacothera-

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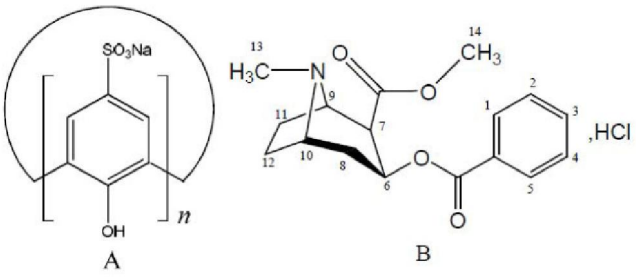

Figure 1 : Structures of p-sulfonated calix[*n*]arenes (A) and cocaine hydrochloride (B)

pies are currently available for treating this addiction in humans. Thus, the determination of cocaine is important. Studying the interaction of p-sulphonated calix[*n*]arenes (SC*n*A, *n* = 4, 6, 8) with cocaine to determine the latter may be an effective method; thus, research on this method has direct and practical significance. To the best of our knowledge, related research has never been reported.

In this paper, the supramolecular inclusion complex of p-sulfonated calix[*n*]arenes (SC*n*A, Figure 1B) with cocaine hydrochloride (CH, Figure 1A) were investigated by fluorescence spectroscopy and ^{1}H NMR in the pH 7.5 B-R buffer solution. The various factors affecting the inclusion interaction and the possible inclusion model were discussed. We wish this research will provide the useful information for the determination of cocaine.

EXPERIMENTAL

Apparatus

Fluorescence spectra were obtained using a Agilent Technologies Cary Eclipse with an excitation wavelength of 235 nm and an emission wavelength of 318 nm. Both excitation and emission band widths were set at 5 nm. ^{1}H NMR spectra were obtained with a Bruker DRX-600MHz spectrometer (Switzerland). The pH was measured using a pHS-3TC digital precision pH meter (Shanghai, China). Molecular modeling calculations were optimized at the B3LYP/6-31G (d) level of density functional theory with the Gaussian 03 program.

Reagents

All reagents used were of analytical-reagent grade or the best grade commercially. Doubly distilled water was used throughout. The cocaine hydrochloride used in the experiment were purchased from National Instisutes for Food and Drug Control. The stock solution of 1.0×10^{-4} mol L^{-1} cocaine hydrochloride were prepared by directly dissolving their powder in doubly distilled water. SC*n*A (*n* = 4, 6) (Product of Great Britain) and SC8A (TCI (Shanghai) Chemical Industry Co., Ltd.) were purchased for research and development use only. Stock solution of SC*n*A (*n* = 4, 6, 8) were prepared directly with distilled water as 1.0×10^{-4} mol L^{-1} Britton–Robinson buffer solution was prepared using a mixed acidic solution that contained 0.04 mol L^{-1} H_3PO_4, HAc and H_3BO_3, respectively, and then was adjusted to accurate values by using 0.2 mol L^{-1}NaOH.

Procedures

A 1.0 ml aliquot of the stock solution of cocaine hydrochloride was transferred into a 10 ml volumetric flask and an appropriate amount of 1.0×10^{14} mol L^{-1} SC*n*A (*n* = 4, 6, 8) was respectively added, followed by 1.0 mL of Britton – Robinson buffer solution of pH = 7.5. The mixed solution was diluted to final volume with double-distilled water and stirred thoroughly and equilibrated at room temperature, the fluorescence intensities were determined after 15 min. The fluorescence intensity values of the solution and the blank solution were measured at 318 nm using an excitation wavelength of 235 nm.

RESULTS AND DISCUSSION

Fluorescence spectra of systems

Figure 2 displays the fluorescence spectra of 1.0×10^{-5} mol L^{-1} cocaine hydrochloride in aqueous solution. It is clear that cocaine hydrochloride shows strong fluorescence in aqueous solution with emission wavelengths at 318 nm. When an appropriate amount of 1.0×10^{-4} mol L^{-1} SC*n*A (*n* = 4, 6, 8) was added to cocaine hydrochloride, the marked fluorescence quenching of cocaine hydrochloride was observed, as shown in Figure 2, indicating the formation of the inclusion complexes. Moreover, the order of the fluorescence quenching was consistent with the size of the calixarene ring, and SC*8*A experience the most obvious decline. The results showed that structural matching effect was thought to play an important role in the formation of the host–guest complex.

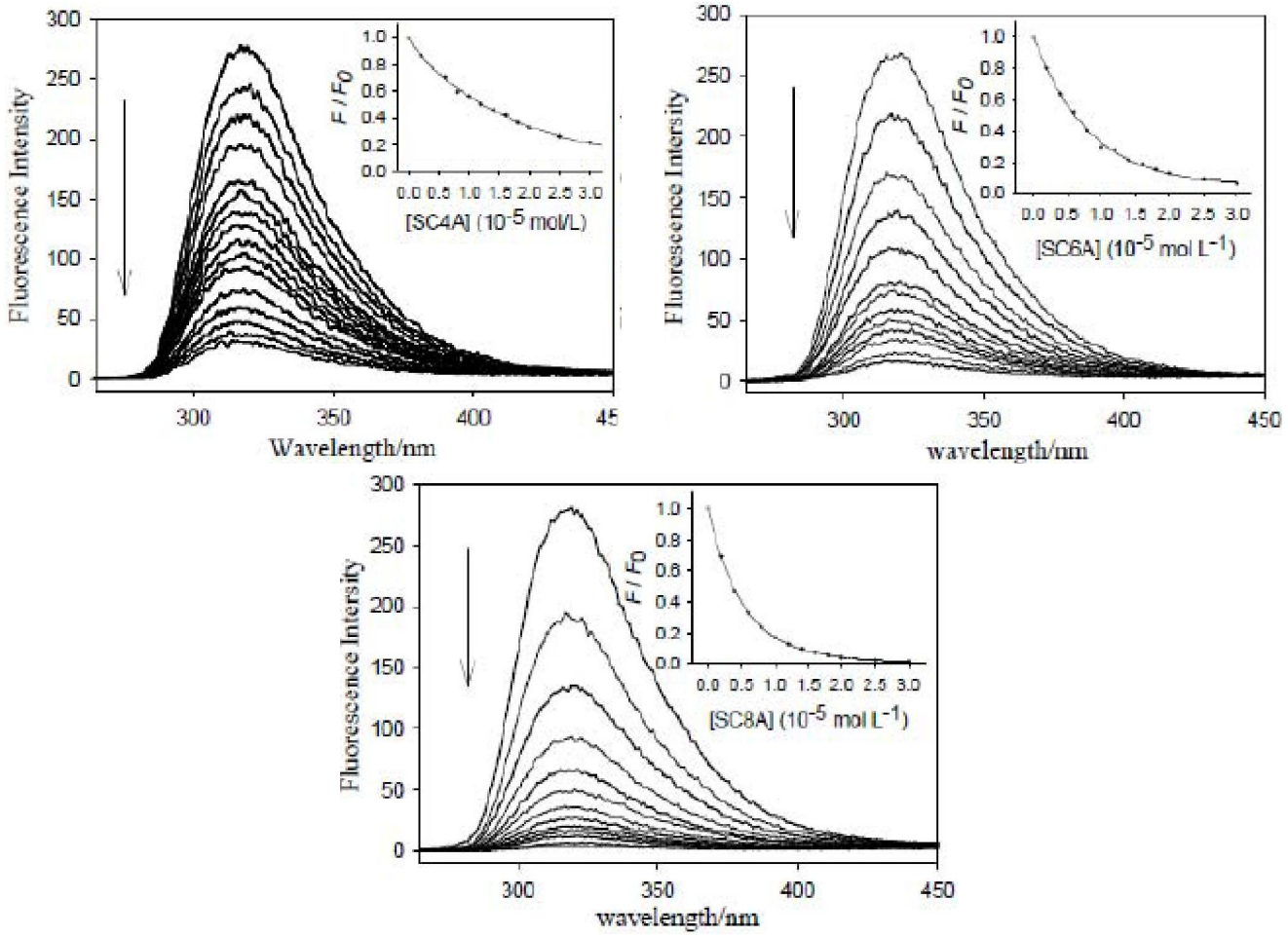

Figure 2 : The fluorescence emission spectra of CH with different concentration of SC*n*A (*n* = 4, 6, 8); The concentration of SC*n*A (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5)×10^{-5} mol L^{-1}, [CH] = 1.0×10^{-5} mol/L)

Stoichiometry and association constant of the inclusion complex

In the work, the stoichiometry and association constant of the inclusion complex were studied by the following method: assuming that SC*n*A (*n* = 4, 6, 8) and CH formed a 1:1 ratio complex, the following expression can be written as follows:

CH+SC□ CH–SC*n*A **(1)**

If the equilibrium concentrations of CH and SC*n*A were C_{SCnA} and C_{CH}, respectively, the concentration of complex at equilibrium was $C_{CH-SCnA}$, then:

$$K = \frac{C_{CH\text{-}SCnA}}{C_{CH} \times C_{SCnA}} \quad \textbf{(2)}$$

The association constant value for the inclusion complex can be determined by the typical double reciprocal (or Benesi – Hildebrand) plots:

$$\frac{1}{F - F_0} = \frac{1}{(F_\infty - F_0)KC_{SCnA}} + \frac{1}{F_\infty - F_0} \quad \textbf{(3)}$$

where F_∞ is the fluorescence intensity of the system when the guest has been completely encapsulated by the host SC*n*A (*n* = 4, 6, 8); C_{SCnA} is the concentration of host SC*n*A (*n* = 4, 6, 8) and F_0 is the fluorescence intensity of CH without SC*n*A; while *F* is the fluorescence intensity at each SC*n*A (*n* = 4, 6, 8) concentration. And *K* is the binding constant of the complex.

As shown in Figure 3, a good linear relationship was obtained when $1/(F - F_0)$ was plotted against $1/C_{SCnA}$, which supports the existence of a 1:1 complex. The result showed that the apparent association constants for these 1:1 complexes at pH 7.5 were determined to be 6.93×10^4, 9.60×10^4, and 2.10×10^5 L mol^{-1} in presence of SC4A, SC6A and SC8A, respectively, and the large association constants indicated the strong interaction of the SC*n*A (*n* = 4, 6, 8) and CH.

The 1:1 complex stoichiometry was also evidenced by Job's method. The solution of SC*n*A (*n* = 4, 6, 8) and guests were mixed in different mole ratio keeping

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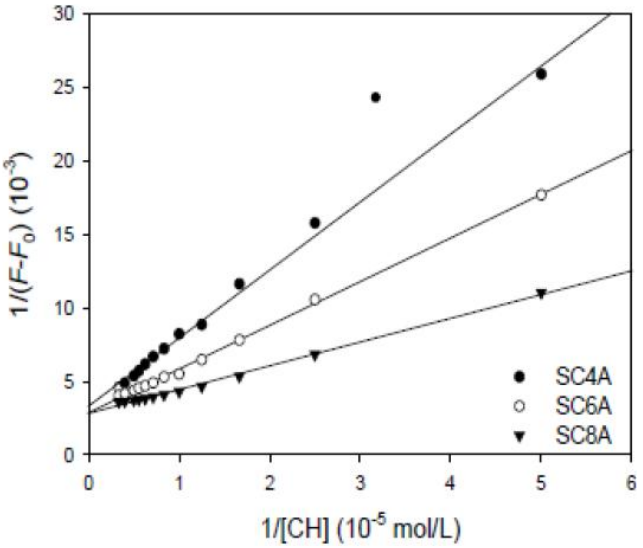

Figure 3 : Plot of $1/(F-F_0)$ vs. $1/C_{SCnA}$ of CH-SC*n*A complex. [CH] = 1.0×10^{-5} mol/L

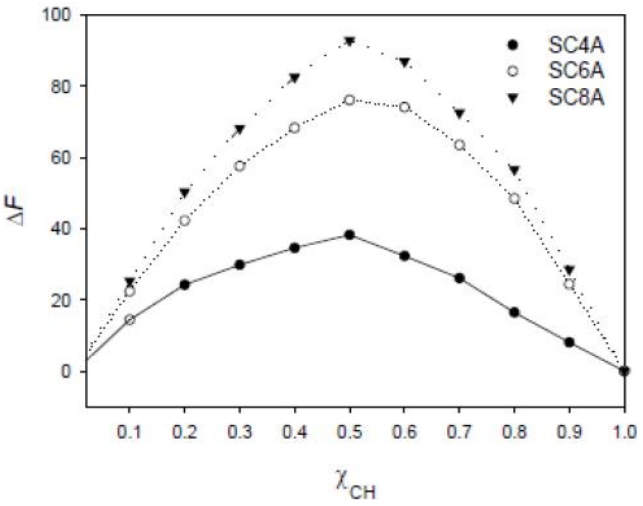

Figure 4 : Job's plot for the complexation of CH with SC*n*A (*n* = 4, 6, 8) in Britton-Robinson buffer solution (pH = 7.5) at 25°C. ([CH] + [SC*n*A]) = 1.0×10^{-5} mol L^{-1}

the sum of the SC*n*A and guests concentration a constant, and the maximum relative fluorescence intensity was observed when [SC*n*A]/([SC*n*A]+[CH])= 0.5, means that the stoichiometry of the complex is 1:1. This is in agreement with the double reciprocal plot. A typical plot for SC*n*A–CH complex is shown in Figure 4.

Influence of pH

The value of pH was known as one of the most important factors affecting the stability of inclusion complex. The influences of pH value of solution on the spectrum and fluorescence intensity were investigated over the range 2.00–12.00. As shown in Figure 5, the fluorescence intensities variation (Δ*F*) of CH in the presence of SC*n*A (*n* = 4, 6, 8) increased with the increase of pH and reached the highest at pH 7.5, however, it decreased with further increase of pH. The formation of inclusion complex between CH and SC*n*A (*n* = 4, 6, 8) was also measured by fluorescence spectra at different pH and the stability constants were calculated to use the nonlinear curve fitting method and shown in TABLE 1. From TABLE 1, it is noted that inclusion constants at pH = 6–7.5 were slightly bigger than at pH < 6 or pH > 7.5, implying that the inclusion interactions of CH with SC*n*A (*n* = 4, 6, 8) were not basically impacted by pH values. Only take into consideration the optimal inclusion condition of SC*n*A (*n* = 4, 6, 8) (6.0–8.5) and physiological environment of drug action, the buffer of pH 7.5 was chosen in the following study.

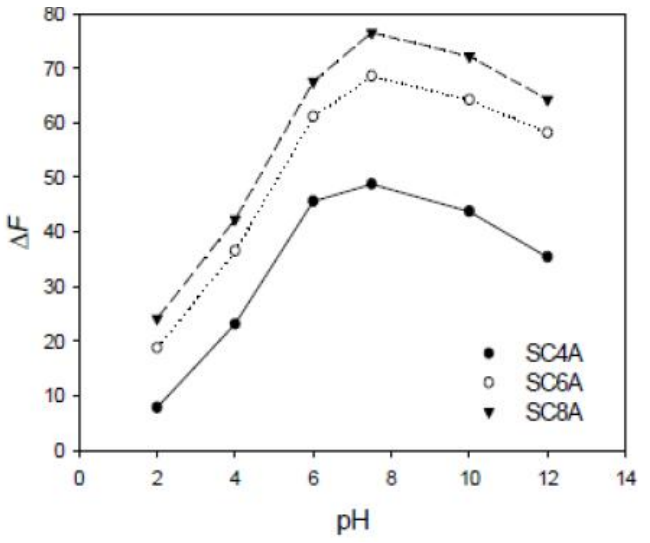

Figure 5 : Dependence of fluorescence intensity of CH-SC*n*A inclusion complex on pH: [CH] = 1.0×10^{-5} mol/L, [SC*n*A] = 4.5×10^{-4} mol/L

Influence of ionic strength

To probe the driving force for inclusion of CH by SC*n*A (*n* = 4, 6, 8), the effect of NaCl ionic strength on the inclusion process was examined. If the addition of NaCl solution had no obvious effect on the inclusion process, the main driving force should be not the electrostatic interaction between CH and the electron rich aromatic ring of SC*n*A (*n* = 4, 6, 8). As shown in TABLE 1, there is remarkable change of inclusion constant in the absence and presence of 0.25 mol/L NaCl. It could be seen that NaCl ionic strength has obvious effect on the inclusion process, which implies that the electro-

TABLE 1: *K* values for 1:1 inclusion complexes of CH with SC*n*A (*n* = 4, 6, 8) in the absence and presence of NaCl at different pH

		pH	2	4	6	7.5	10	12
SC4A	Without NaCl	*K* (L/mol)	2.42×10^4	4.63×10^4	5.16×10^4	6.93×10^4	1.15×10^4	8.23×10^3
		R^2	0.9997	0.9978	0.9985	0.9939	0.9956	0.9956
	With NaCl	*K* (L/mol)	7.56×10^3	1.26×10^4	2.10×10^4	3.28×10^4	9.57×10^3	4.59×10^3
		R^2	0.9991	0.9971	0.9956	0.9995	0.9973	0.9980
SC6A	Without NaCl	*K* (L/mol)	3.07×10^4	4.51×10^4	9.19×10^4	9.60×10^4	6.97×10^4	5.16×10^4
		R^2	0.9940	0.9990	0.9987	0.9985	0.9987	0.9969
	With NaCl	*K* (L/mol)	3.44×10^3	8.01×10^3	1.44×10^4	2.36×10^4	1.62×10^4	7.59×10^3
		R^2	0.9991	0.9982	0.9950	0.9970	0.9979	0.9980
SC8A	Without NaCl	*K* (L/mol)	5.20×10^4	7.20×10^4	1.76×10^5	2.10×10^5	1.16×10^5	3.58×10^4
		R^2	0.9979	0.9981	0.9960	0.9962	0.9990	0.9911
	With NaCl	*K* (L/mol)	3.75×10^3	1.26×10^4	1.38×10^4	1.50×10^4	1.32×10^4	5.35×10^3
		R^2	0.9991	0.9979	0.9981	0.9980	0.9993	0.9980

static interaction has some contribution for the formation of inclusion complex between CH and Sc*n*A (*n* = 4, 6, 8). The result is consistent with the lomefloxacin-p-sulfonated calix[4]arene system, where electrostatic interaction was thought to play important part in the inclusion process[34].

Influence of SC*n*A concentration

The influence of SC*n*A (*n* = 4, 6, 8) concentration on the fluorescence quenching intensity of CH was examined under the conditions established above. CH concentration was held constant at 1.0×10^{-5} mol/L, while the concentration of SC*n*A (*n* = 4, 6, 8) varied from 0 to 4.5×10^{-4} mol/L. The experimental results showed that remarkable quenching effect of CH was observed with the addition of $0 - 3.0 \times 10^{-4}$ mol/L SC*n*A (*n* = 4, 6, 8), and the fluorescence quenching intensity reached maximum when the concentration of SC*n*A (*n* = 4, 6, 8) is 3.0×10^{-4} mol/L. This means that in this concentration range of SC*n*A (*n* = 4, 6, 8), a stable host–guest complex has formed and the inclusion process has got to the equilibrium condition when the concentration of SC*n*A (*n* = 4, 6, 8) is 3.0×10^{-4} mol/L.

Influence of temperature

The influence of temperature on the fluorescence intensity of Sc*n*A (*n* = 4, 6, 8) — CH systems was examined on the basis of the experimental conditions of inclusion process. The binding constants at various temperatures were investigated and the results were summarized in TABLE 2. As can be seen in TABLE 2, the inclusion constants were little sensitive to temperature, suggesting that the SC*n*A (*n* = 4, 6, 8) — CH system was relatively stable in the temperature range of 293 to 313 K. This is favorable for the delivery of drug in the body.

Influence of surfactants

Three kinds of surfactants: the cationic surfactant

TABLE 2 : Effect of temperature on inclusion constants (*K*) of CH with SC*n*A (*n* = 4, 6, 8)

		T (K)				
		293	298	303	308	313
SC4A	*K* (L/mol)	3.65×10^4	6.93×10^4	6.06×10^4	5.67×10^4	4.64×10^4
	R^2	0.9944	0.9939	0.9975	0.9969	0.9962
SC6A	*K* (L/mol)	7.45×10^4	9.60×10^4	1.09×10^5	9.53×10^4	9.02×10^4
	R^2	0.9953	0.9968	0.9974	0.9962	0.9972
SC8A	*K* (L/mol)	1.78×10^5	2.10×10^5	1.47×10^5	1.43×10^5	1.39×10^5
	R^2	0.9982	0.9974	0.9991	0.9976	0.9989

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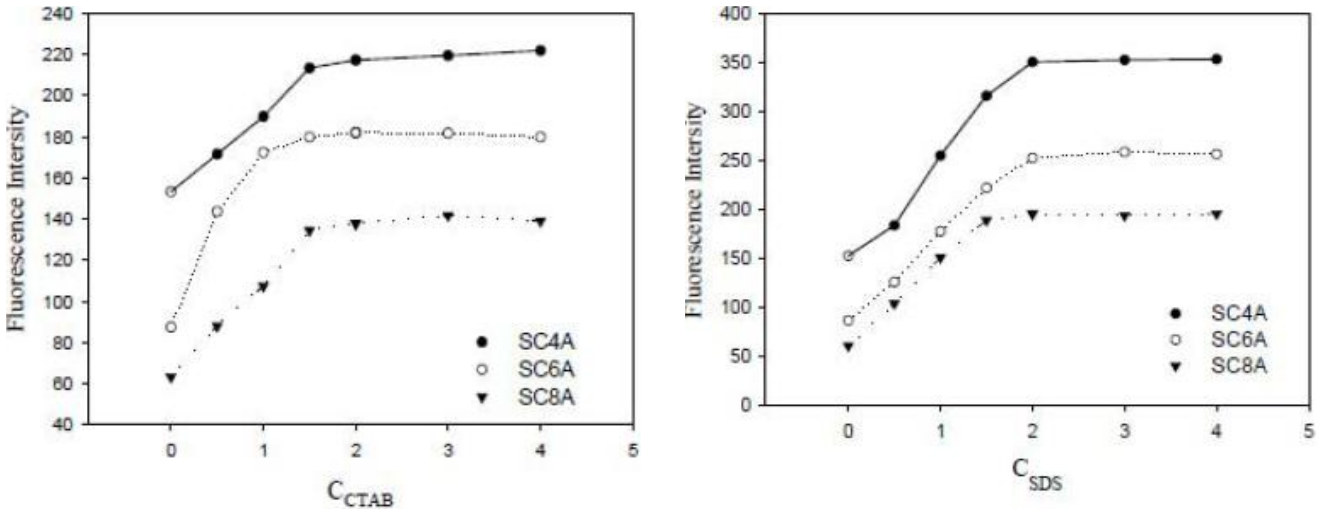

Figure 6 : Influence of surfactants concentration on the fluorescence intensity of CH–SC*n*A, [CH] = 1.0×10^{-5} mol/L, [SC*n*A] = 4.5×10^{-4} mol/L

cetyltrimethyl ammo-nium bromide (CTAB), the non-ionic surfactant Triton X-100, and the anionic surfactant sodium dodecyl sulfate (SDS) were chosen to study their effect on SC*n*A (*n* = 4, 6, 8)–CH inclusion complex. As shown in Figure 6, the fluorescence intensity of SC*n*A (*n* = 4, 6, 8)–CH inclusion complex increased upon the addition of CTAB, and SC4A–CH inclusion complex experience a more obvious increase. According to the previous report[35], trimethyl ammonium cations can insert into the hydrophobic cavity of SC*n*A. CTAB molecules are trimethyl ammonium cationic surfactants, so CTAB compete with CH in SC*n*A–CH inclusion, release a fraction of CH and lead to fluorescence intensity enhancement. It is confirmed that SC*n*A and CH had formed host–guest complexs.

Non-ionic surfactant Triton X-100 had no notable effect on SC*n*A–Phen inclusion complex.

When SDS was added, the fluorescence intensity of SC*n*A (*n* = 4, 6, 8)–CH inclusion complex also increased. The result is consistent with the investigation of Spectrofluorimetric study on the inclusion interaction between lomefloxacin and p-sulfonated calix[4]arene and its analytical application reported by Yunyou Zhou et al[36]. It is proved that electrostatic interaction was the main driving force for the SC*n*A–CH inclusion complex.

Influence of reaction time

The effect of reaction time was studied. As shown in Figure 7, the results showed that the fluorescence intensity reached a minimum after the reagents had been

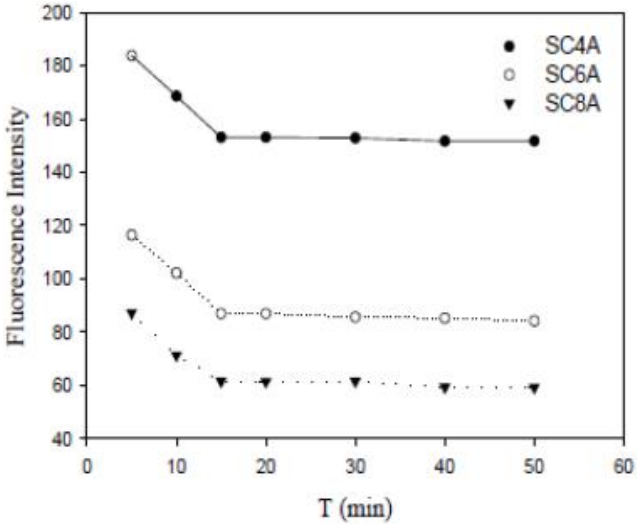

Figure 7 : Effect of reaction time on fluorescence intensity of the complex. [CH] = 1.0×10^{-5} mol/L, [SC*n*A] = 4.5×10^{-4} mol/L, pH = 7.5

added for 15 min. Hence, the reaction was carried out for 15 min, the subsequent fluorescence measurements were made 15 min later.

Influence of the addition order of reagents

The effect sequence of adding reagents on the fluorescence recovery was studied, and the order: CH, SC*n*A (*n* = 4, 6, 8) and buffer solution was proved to be the best suitable.

Molecular modeling calculations

The formation of inclusion complexes between CH and SC*n*A (*n* = 4, 6, 8) was also confirmed by molecular modeling calculations optimized at the B3LYP/

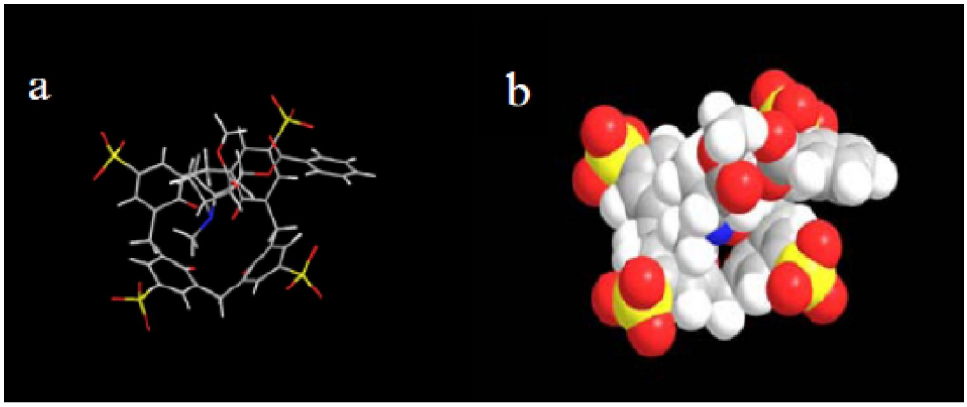

Figure 8 : Energy-minimized structure of CH-SC*4*A complexes in the ground state using balls and tubes for the rendering of atoms. Color codes: nitrogen, blue; sulfur, yellow; oxygen, red; carbon, white

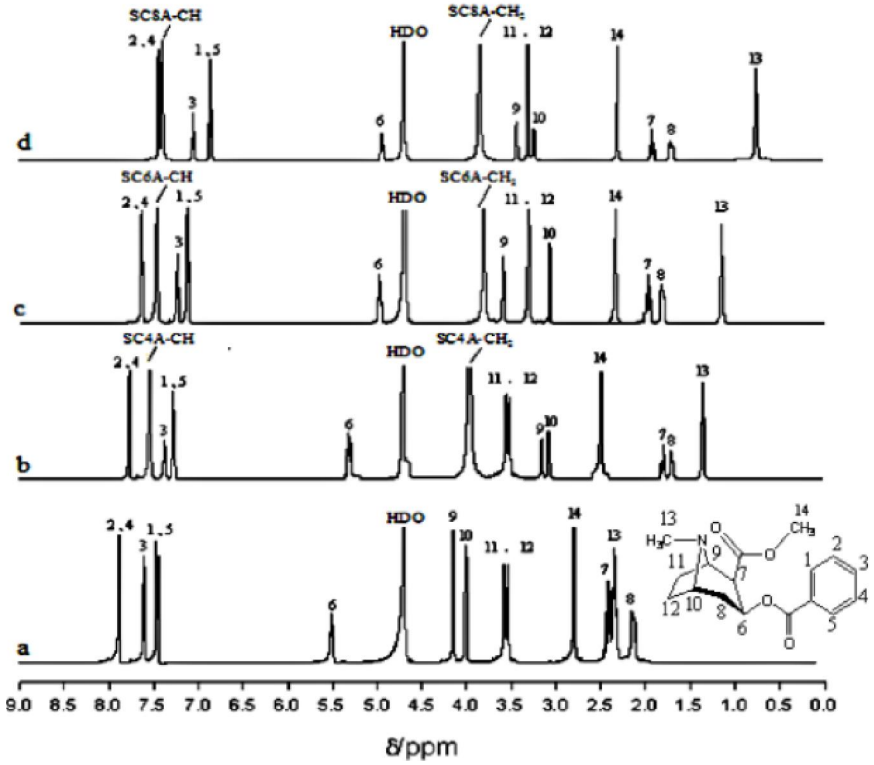

Figure 9 : ^{1}H NMR spectra (600 MHz) of CH (a), SC*4*A-CH complex (b), SC*6*A-CH complex (c), SC*8*A –CH complex (d) in D_2O

6-31G (d) level of the density functional theory using the Gaussian 03 program. The optimized conformation of the host–guest complex is shown in Figure 8, Take SC4A–CH complex for example, in the energy-minimized structure of CH, its bridge-ring part of N-CH_3 penetrated into the hydrophobic cavity of SC4A because of the spatially matched effect. Moreover, a repelling interaction existed between the oxygen lone-pair electrons of the benzoyl methoxyl group and the lone-pair electrons of the negatively charged sulfonyl groups on SC4A. Consequently, the conjugate plane of benzoyl methoxy on CH was damaged, leading to fluorescence quenching.

^{1}H NMR studies

^{1}H NMR spectroscopy is a powerful tool for studying the formation of inclusion complexes between host and guest molecules, especially their interaction mechanisms[37]. Chemical shift variations of specific host or guest nuclei could provide evidence for the formation of inclusion complexes in solution because significant changes in microenvironment are known to occur be-

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tween the free and bound states[38]. For the ^{1}H NMR experiment, the chemical shift of the guest molecule was obtained first and then compared with those in the host-guest complexes. The H-chemical shifts in both free and complex state are reported in Figure 9. All H protons were found to shift upfield, whereas H protons on the benzoyl methoxyl group were deshielded upon complexation. The bridge-ring part of N-CH_3 was confirmed to partially penetrate the cavity of SC*n*A and thereby exert shielding effect, which caused the H proton on N-CH_3 to shift upfield. Given the repulsive interactions of the lone-pair electrons on the benzoyl methoxyl group, the density of the electron cloud on the benzoyl methoxyl group increased to undermine its conjugated system, which also caused the H proton on the benzene ring to shift to a high field. This result agreed with that obtained from molecular dynamic calculations.

CONCLUSIONS

In this paper, the supramolecular inclusion complex of CH with SC*n*A (n = 4, 6, 8) were investigated by fluorescence and ^{1}H NMR technique in pH 7.5 B-R buffer solution. The stoichiometry and the association constant of the inclusion complex were evaluated. The interaction mechanism of the host–guest complex was discussed. The various factors affecting the inclusion process were examined in detail. The results approved that electrostatic interaction and structural matching effect were thought to play important roles in the formation of the host–guest complex. The possible inclusion model of CH with SC*n*A (n = 4, 6, 8) were proposed by ^{1}H NMR. Apparent chemical shift variations of H proton on benzoyl methoxyl grou validated that the bridge-ring part of N-CH_3 may be partially penetrated into the cavity of SC*n*A (n = 4, 6, 8) to form host–guest complex. Molecular dynamic calculation is in agreement with the result obtained from ^{1}H NMR. It provided the useful information for the determination of CH and stimulated further investigation to exploit the interactions between CH and other calixarenes. The inclusion complexes show potential for biological and medical applications. This method also can be used in a fluorescence sensor for the detection of fluorescent substances.

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