Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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Online publication date: 29 October 2010

To cite this Article Wang, Xiao-ping , Pan, Jing-hao , Shuang, Shao-min and Zhang, Yong(2002) 'Determination of the Inclusion Constants for the Inclusion Complexes between meso-Tetrakis (4-sulfonatophenyl) Porphyrin and Cyclodextrins by Three Methods', Supramolecular Chemistry, 14: 5, 419 — 426
To link to this Article: DOI: 10.1080/1061027021000002224
URL: http://dx.doi.org/10.1080/1061027021000002224

Supramolecular Chemistry, 2002 Vol. 14 (5), pp. 419–426

Determination of the Inclusion Constants for the Inclusion Complexes between meso-Tetrakis (4-sulfonatophenyl) Porphyrin and Cyclodextrins by Three Methods

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(Received 15 October 2001; Revised 10 December 2001; In final form 11 January 2002)

In this paper, the interactions of meso-Tetrakis (4-sulfonatophenyl) porphyrin ($TPPS_4$) and six cyclodextrins have been studied, respectively, by fluorescence spectroscopy, polarography and thin-layer chromatography. The inclusion constants of different methods are determined and the comparison of inclusion capacity of various cyclodextrins indicates that for the ionic cyclodextrins the charge interaction plays an important role in the inclusion procedure. The thermodynamic parameters of interaction imply that the inclusion process shows the enthalpy–entropy compensation effect. Cyclodextrin, being regarded as an artificial analogue of proteinoid of heme, provides a protective sheath for porphyrin. However, the $TPPS_4$, encapsulated within this saccharid-coated barrier, its solubility is enhanced prominently, which exhibits that this interaction may modify the biological properties of $TPPS_4$ that owned the similar properties as hematoporphyrin.

Keywords: $TPPS_4$; Cyclodextrin; Fluorescence spectroscopy; Thin-layer chromatography; Polarography

INTRODUCTION

Water-soluble porphyrins and metaloporphyrins are interesting materials in many applied fields. $TPPS_4$ is the most accessible water-soluble porphyrin. It is used not only as catalyst [1] but also as photosensitizer in photodynamic therapy for curing cancer [2]. The ability of cyclodextrins (CDs) and modified CDs to form inclusion complexes with various molecules is well known [3]. The formation of inclusion complex changes the physical and chemical properties of guest. CDs are used to enhance the solubility and bioavailability of hydrophobic drugs in aqueous media [4]. The chemical modification of CDs is a new branch of research [5,6]. The chargeable CDs differ from other modified CDs in inclusion effect, such as it can sustain the release rate of drug [7] and enhance the peak concentration of drug in blood [8]. It has been reported that the $TPPS_4$ can form inclusion complex with CDs [9,10]. Hamai *et al.* [11] gave a detailed study about the inclusion complexation of $TPPS_4$ with TM-β-CD and γ-CD by means of electronic absorption, fluorescence and circular dichroism method. Moisinger's study [12] confirmed that a new type of efficient $TPPS_4$- HP-β-CD sensitizer was formed. The nuclear magnetic resonance technique has shown that porphyrins can form inclusion complexes with CDs by its meso-phenyl group [13]. In our previous studies, $TPPS_4$-CD and $H_2TPPS_4^{2+}$-CD supramolecular system were studied by Spectroscopy [14]; TAPP-CD supramolecular system was studied by polarography [15]. However, few data were reported about $TPPS_4$ interacting with CDs by means of electrochemical methods and thin-layer chromatography.

In this paper, the inclusion complexations of $TPPS_4$ with two ionic derivatives Sulfurbutylether-β-CD(SBE-β-CD)and Caboxymethyl-β-CD(CM-β-CD) have been studied by fluorescence spectroscopy, polarography and thin-layer chromatography besides α,β,γ-CD and Hydroxypropyl-β-CD(HP-β-CD). Among these measurements, 0.1 mol/l phosphate buffer is selected and inclusion constants of different CDs are calculated. The $TPPS_4$, encapsulated within this saccharid-coated barrier provided by cyclodextrins, its solubility is enhanced promi-

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ISSN 1061-0278 print/ISSN 1029-0478 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/1061027021000002224

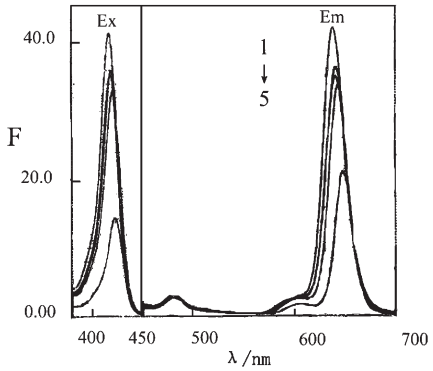

FIGURE 1 The flurescence spectroscopy of $TPPS_4$ in presence of different CDs. (1) $TPPS_4$, (2) β-CD + 1, (3) γ-CD + 1, (4) SBE-β-CD + 1, (5) HP-β-CD + 1

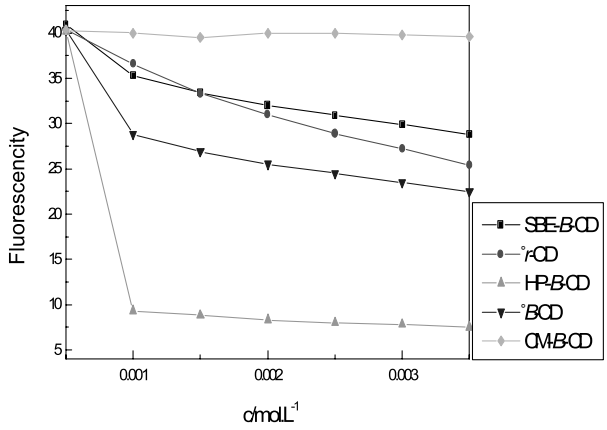

FIGURE 2 The change of fluorescence intensity of $TPPS_4$ in different CD media

nently, which exhibits that this interaction may modify the biological properties of $TPPS_4$ that owned the similar properties as hematoporphyrin. At the same time, cyclodextrin, being regarded as an artificial analogue of proteinoid of heme, offers a protective sheath for porphyrin.

EXPERIMENT

Reagents

$TPPS_4$ was purchased from Emeishan Yahua Drug Institute (China); β-CD (Yunan Gourment Factory, China) was purified by recrystallization in double distilled water. γ-CD, HP-β-CD, (degree substitution = 0.6) were purchased from Aldrich, CM-β-CD, SBE-β-CD were synthesized employing the paper written by Jacques Reuben [16]. All other reagent were of analytical reagent grade, water was doubly distilled.

Apparatus and Methods

The fluorescence measurements were performed on RF-540 spectrofluorimeter (Shimdazu, Japan). Both excitation and emission slits were set at 10 nm. All experiment were carried out at 20 ± 1°C via a model 501 superthermostat circulating water bath. The $TPPS_4$ solution (1×10^{-6} mol/l) in phosphate buffer (pH = 7.0) was excited at 426 nm and the emission intensity of the mixture of $TPPS_4$-CD solution (the concentrations of CD are varied from 0.5 to 5×10^{-3} mol/l) was measured at 636 nm.

In TLC measurements, the NaH_2PO_4–Na_2HPO_4 buffer (pH = 9.7, 20°C) containing various CDs and polyamide plates were selected, respectively, as mobile and stationary phases. $TPPS_4$ were dissolved separately in methanol at a concentration of 1 mg/ml and 1 μl of this solution was plotted on the plates. Developments were carried out in chambers ($6.8 \times 10\,cm^2$ height) at room temperature, the distance of development being about 8 cm. The final position of the solutes was detected under UV lamp. Both the UV_{254} lamp and pH meter were made by Leici Instrument Factory (Shanghai, China).

The polarography measurements were performed at a BAS-100A electrochemical analyzer with a PAR 303 electrode system serving as the working electrode. A saturated calomel electrode was used as a reference electrode and a platinum wire as auxiliary electrode. All figures were drawn with a DMP-40 digital platter. The $TPPS_4$ solution (1×10^{-4} mol l^{-1}) in phosphate buffer (pH = 7.0) was fixed. An appropriate amount of cyclodextrins whose concentration are varied from 1 to 5×10^{-3} mol l^{-1} was added. Shake these solutions thoroughly and allow to equilibrate at 20 ± 1°C for 15 min.

RESULTS AND DISCUSSION

Fluorescence

To fix the concentration of $TPPS_4$ at 1×10^{-6} mol/l and the concentration of cyclodextrin was varied from 5×10^{-4} to 5×10^{-3} mol/l. Addition of different cyclodextrins (β-CD, γ-CD, HP-β-CD, SBE-β-CD) to an aqueous solution of $TPPS_4$ produces a decrease in the emission intensity of fluorescence. Furthermore, both the emission wavelength and excitation wavelength shift to longer wavelength (Fig. 1.). These remarkable changes are due to the interactions between $TPPS_4$ and cyclodextrins. The fluorescence excitation and emission spectra of $TPPS_4$ in the absence and presence of CDs indicate that the $TPPS_4$ can form inclusion complexes with cyclodextrins. However, in the presence of CM-β-CD the intensity of fluorescence changes slightly, which means it is difficult for the CM-β-CD to form inclusion complex with $TPPS_4$. When the concentration of cyclodextrin is 3×10^{-3} mol/l, the fluorescence intensity

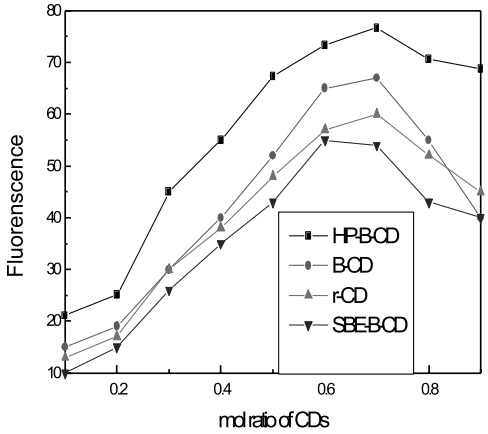

FIGURE 3 The inclusion stoichiometry of $TPPS_4$-CD complexes

gradually level off, implying the inclusion process trends to equilibrium. (Fig. 2).

The inclusion constants of complexes are estimated according to the double-reciprocal method [17] and the stoichiometry of complex is assessed by equimolar variation method. A plot of fluorescence intensity versus mole fraction of CDs is provided in Fig. 3. Under the equilibrium: **porphyrin** $+ n$**CD** $=$ **porphyrin**$-$(**CD**)n, the mole fraction of CD ($f = 2/3$), inducing a maximal fluorescence intensity in Fig. 3 proves that a 2:1 (CD:porphyrin) complex is formed. It is in good agreement with the result obtained by Hamai [11], however, is different from that reported by Mosinger [12]. The inclusion constants can be obtained by the following equation [17].

$$\frac{[G_0]}{\Delta F} = \frac{1}{K \cdot k \cdot Q} \cdot \frac{1}{[\mathrm{CD}]^n} + \frac{1}{k \cdot Q}$$

Where, $[G]_0$ is the initial concentration of $TPPS_4$, [CD] is the equilibrium concentration of cyclodextrin. ΔF is the change of fluorescence intensity in the presence of cyclodextrin, k is an instrumental constant, n is the stoichiometry of inclusion complex, K is the inclusion constant and Q is the quantum yield for the complex. K can be calculated from a plot of $1/F$ vs. $1/[\mathrm{CD}]^n$. With a result that 2:1 complex is formed between CD and $TPPS_4$. Plot $1/F$ vs. $1/[\mathrm{CD}]^2$, a good linearity of the plots verified the 2:1 complexation stoichiometry. The inclusion constants of $TPPS_4$ for different CDs are calculated by the ratio of intercept over slop.

Thin Layer Chromatography

TLC measurements indicate that β-CD, HP-β-CD, SBE-β-CD and γ-CD are effective agents for increasing R_f value of $TPPS_4$ on polyamide plates. However, it is worth pointing out that CM-β-CD cannot increase R_f value distinctively. We employ the following equation [18] to estimate the inclusion constants.

TABLE I The inclusion constants at different temperature

	293 k	303 k	313 k	323 k
HP-β-CD	8.5×10^7	7.1×10^6	1.5×10^6	6.9×10^4
β-CD	4.4×10^5	8.0×10^4	2.7×10^4	4.6×10^3
SBE-β-CD	3.5×10^5	8.5×10^4	2.3×10^4	1.9×10^3
γ-CD	3.8×10^5	1.3×10^5	4.4×10^4	4.2×10^3

$$\frac{R_f}{1 - R_f} = \frac{1}{\Phi K[A]} + \frac{K_f}{\Phi K[A]}[\mathrm{CD}]^n$$

where, Φ is the phase ratio and R_f is the retardation factor of a solute in thin-layer chromatography, A is a stationary phase adsorption, [CD] is the concentration of cyclodextrin, equilibrium constant between drugs and stationary phase is K, and K_f is the inclusion constant, n is the stoichiometry of inclusion complex. Curve of $R_f/1 - R_f$ vs. $[\mathrm{CD}]^n$, in which the slope corresponds to $K_f/\Phi K[A]$ and the intercept is $1/\Phi K$[A] shows linear behavior. From the ratio of slope over intercept, we can calculate K_f. The inclusion constants determined by TLC method are listed at Table IV.

At different temperature (from 293 to 323 k), the inclusion constants of $TPPS_4$-CD inclusion complexes are obtained. The value of inclusion constant decreases with the increasing of temperature (Table I). That means the high temperature is not suitable for inclusion procedure. Some thermodynamic parameters such as ΔG, ΔH, ΔS are calculated by van't Hoff equation $(\Delta G/T) = (\Delta H/T) - \Delta S$. The plot of $(\Delta G/T)$ vs.$(1/T)$ gives a curve with the slope of ΔH and the intercept of $-\Delta S$. Using all the thermodynamic data obtained in this experiment and reported elsewhere [19], the ΔH and ΔS value of inclusion procedure demonstrate that the inclusion complexation of $TPPS_4$ with CDs are exclusively exothermic

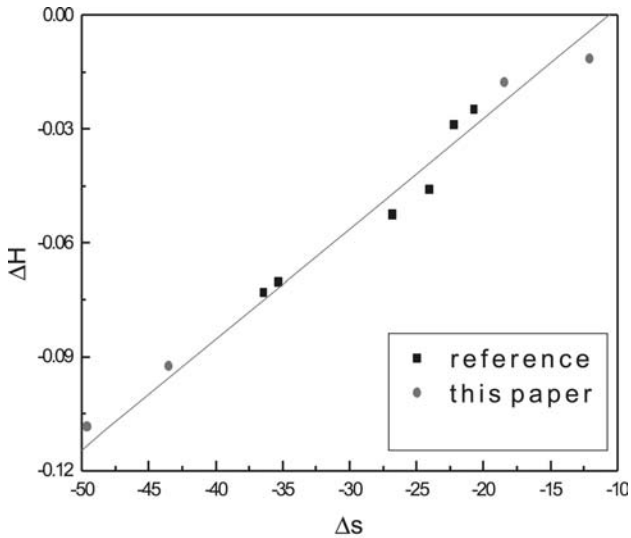

FIGURE 4 Entropy-Enthalpy compensation plot

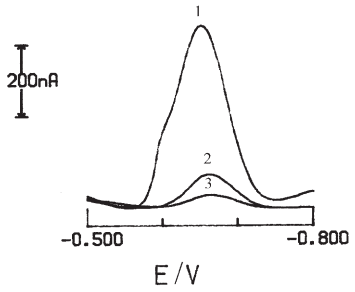

FIGURE 5 Linear sweep voltammogram of 1.0×10^{-4} mol/L $TPPS_4$ in the absence (1) and presence (2, 3) of HP-β-CD

and mostly enthalpy driven. Plot of ΔH vs. ΔS gives a good linear relationship, which displays that the inclusion interaction consists with entropy–enthalpy compensation effect [20]. The slope of the curve is the compensation temperature, here, $T = 309$ k (Fig. 4).

The R_M value characterizing the molecular hydrophobicity in reversed phase thin layer chromatography is calculated for $TPPS_4$ in each mobile phase. It can be calculated by the equation below [21].

$$R_M = \log(1/R_f - 1)$$

The effect of the concentration of CDs on the R_M value can be seen in Table II. It is suggested that the hydrophobicity of $TPPS_4$ decrease with the increasing of the concentration of CD, which proves that CDs can enhance the solubility of $TPPS_4$.

Polarography

The effect of the supporting electrolyte on the current, e.g. acetic acid–sodium acetate buffer (pH = 6.62), ammonia–ammonium chloride buffer (pH = 7.0), phosphate buffer (pH = 7.0) and sodium chloride solution, was examined. The experiment results show that a reduction peak is obtained for $TPPS_4$ in all cases. However, the peak at -0.640 V (vs. SCE) is more clear and sensitive in phosphate buffer. With the increase of the concentration of CDs, the peak current (i_p) of $TPPS_4$ decreases and the peak potential (E_p) shifts to more negative potentials (Fig. 5). The effect of cyclodextrin on both the i_p and the E_p is more remarkable in phosphate buffer than in others. So in this paper, 0.1 mol/l phosphate buffer was selected as supporting electrolyte.

The inclusion interactions of $TPPS_4$ by four CDs give rise to a decrease of the i_p and to a negative shift

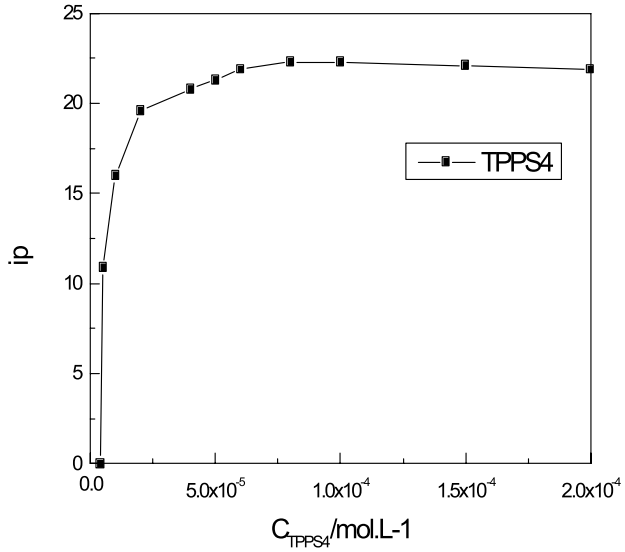

FIGURE 6 The change of i_p with the increased concentration of $TPPS_4$

of the E_p, suggesting that β-CD,HP-β-CD, CM-β-CD and γ-CD can form inclusion complexes with $TPPS_4$ in phosphate buffer. The decrease of the peak current is attributed to the decrease of apparent diffusion coefficient of $TPPS_4$, which has been formed inclusion complexes with CDs. The negative shift of the E_p suggests that the reduction of the inclusion complexes at the Hg electrode needed more activation energy.

The lowest concentration of CDs (1×10^{-3} mol/l) in the experiment is much higher than the analytical concentration of $TPPS_4$. It can make the complexation reaction remain at equilibrium in everywhere and the adsorption of CD has no influence on the peak current of $TPPS_4$ that is coated at maximum surface coverage of CDs.

The polarographic method of calculating the inclusion constants is based on the diffusion coefficient (D_f) of the free guest molecule and the observed diffusion coefficient (D_{obs}) of the guest in the presence of CDs. On the condition that the variation of i_p of $TPPS_4$ is controlled by diffusion, changes in D_{obs} are duo to the forming inclusion complexes of $TPPS_4$ with CDs.

With the increase of the concentration of $TPPS_4$, the i_p value remains constant (Fig. 6). When the concentration of $TPPS_4$ is above 1×10^{-4} mol/l, i_p is proportional to the square root of scan rate ($\nu^{1/2}$).

TABLE II The R_M value of various mobile phases containing different CDs

	c_{CD} (mol/l)	0.002 (mol/l)	0.004 (mol/l)	0.005 (mol/l)	0.006 (mol/l)	0.008 (mol/l)
HP-β-CD	1.953	0.749	0.408	0.255	0.168	0.089
β-CD	1.995	1.380	1.211	1.078	1.004	0.963
SBE-β-CD	1.556	0.799	0.739	0.739	0.673	0.512
γ-CD	1.609	1.151	0.973	0.853	0.810	0.743

TABLE III The inclusion constants of $TPPS_4$ with five CDs at pH = 7.0 (polarography)

	β-CD	γ-CD	HP-β-CD	CM-β-CD
K	$6.6 \times 10^5 \pm 5.2 \times 10^3$	$9.0 \times 10^5 \pm 3.0 \times 10^3$	$5.2 \times 10^7 \pm 4.7 \times 10^6$	$5.5 \times 10^5 \pm 2.5 \times 10^4$
K_1	1426 ± 119	2358 ± 45	4854 ± 1600	452 ± 17
K_2	460 ± 21	446 ± 65	16250 ± 550	1226 ± 345
i_{P_x} (Cal.)	35.4	13.7	41.9	14.8
i_{P_x} (Exp.)	37.3	13.8	42.0	13.2

The first derivative curve shows that the height of up branch is greater than that of down branch. All these data depict that the variation of i_p is controlled by diffusion. Fix the concentration of $TPPS_4$ is 1×10^{-4} mol/l and add the amount of CDs in solution by degrees. The formation of $TPPS_4$-CD inclusion complexes changes the D_{obs} of $TPPS_4$ and then makes the i_p of $TPPS_4$ vary accordingly. The inclusion constants can be calculated by "electric current method" [22].

When a complex of 1:1 stoichiometric ratio is formed, the inclusion constant K and the diffusion coefficient of complex (D_c) can be calculated according to Eq. (1) [23]

$$D_{obs} = \frac{(D_f - D_{obs})}{K_1[CD]} + D_c \quad (1)$$

Using Ilkovic equation, in reversed procedure: $ip = (2.69 \times 10^5)^2 n^{2/3} A D^{1/2} v^{1/2} c$ and in irreversed procedure: $i_p = (2.99 \times 10^5)^2 n^{2/3} A D^{1/2} v^{1/2} c$. Because i_p^2 is proportional to the diffusion coefficient D, substitute D with the corresponding i_p^2 in Eq. (1), the above equation is obtained as Eq. (2).

$$i_p^2 = \frac{1}{K_1} * \frac{(i_{px}^2 - i_p^2)}{[CD]} + i_{P_{x-CD}}^2 \quad (2)$$

Where i_p is the observed diffusion current of guest molecule; i_{P_x} is the limited diffusion current of guests in the absence of CDs; $i_{P_{x-CD}}$ is the limited diffusion current of inclusion complex which $TPPS_4$ is coated at maximum surface coverage by CDs; K_1 is the inclusion constant. Plots of i_p^2 vs. $(i_{P_x}^2 - i_p^2)/[CD]$ give curves in which the slope is $1/K_1$ and the intercept is $(i_{P_{x-CD}}^2)$. From the reciprocal of slope, the inclusion constant can be calculated easily.

When the 1:2 stoichiometric ratio inclusion complex is formed, the following Eq. (3) is obtained [23].

$$D_{obs} = \frac{D_f + D_c K[CD]^2}{1 + K[CD]^2} \quad (3)$$

Replace D with the corresponding i_p^2 in Eq. (3), we have Eq. (4)

$$i_p^2 = \frac{i_{P_x}^2 + i_{P_{x-CD}}^2 K[CD]^2}{1 + K[CD]^2} \quad (4)$$

and Eq. (5)

$$i_p^2 = K(i_{P_{x-CD}}^2 - i_p^2)[CD]^2 + i_{P_x}^2 \quad (5)$$

From the plots of i_p^2 vs. $(i_{P_{x-CD}}^2 - i_p^2)[CD]^2$, the slope corresponds to K and the intercept is $i_{P_x}^2$. The $(i_{P_{x-CD}}^2)$ used here is calculated from Eq. (2) and if the i_{P_x} obtained by Eq. (5) is approximate to the experiment data, the assumption of 1:2 stoichiometric ratio is reasonable.

From Table III, as far as these four CDs are concerned, the i_{P_x}, which is calculated by Eq. (5), is cohering with the i_{P_x} obtained from experiment. The K_2 value that is calculated by the ratio of K and K_1 shows that the K_2 value is relatively large. It is implied that 1:2 inclusion complexes are formed between $TPPS_4$ and four CDs. This result is consistent with the result of equal mole continuous variations method. Table IV shows the inclusion constant of $TPPS_4$ calculated by above three methods.

As can be seen from Table III, for the substituted cyclodextrins, the K_2 values are generally larger than the K_1 values, however, for the parent CD(β-CD)K_1 is very close to the value of K_2, the difference between K_1 and K_2 is very small, indicating the derivatives of cyclodextrins prefer form the 1:2 inclusion complexes with porphyrin. On another hand, when the edge of cyclodextrin is linked by hydrophilic groups and modified into a new kind of CDs, these new CDs universally have stronger inclusion abilities than that of his parent CD, just because of the enhancement of

TABLE IV The formation constant of $TPPS_4$ with five CDs obtained by three methods

	β-CD	γ-CD	HP-β-CD	SBE-β-CD	CM-β-CD
Fluorescence	3.8×10^5	4.7×10^5	2.9×10^7	1.9×10^5	–
TLC	4.4×10^5	3.8×10^5	8.5×10^7	3.6×10^5	–
Polarography	6.6×10^5	9.0×10^5	5.2×10^7	–	5.5×10^5

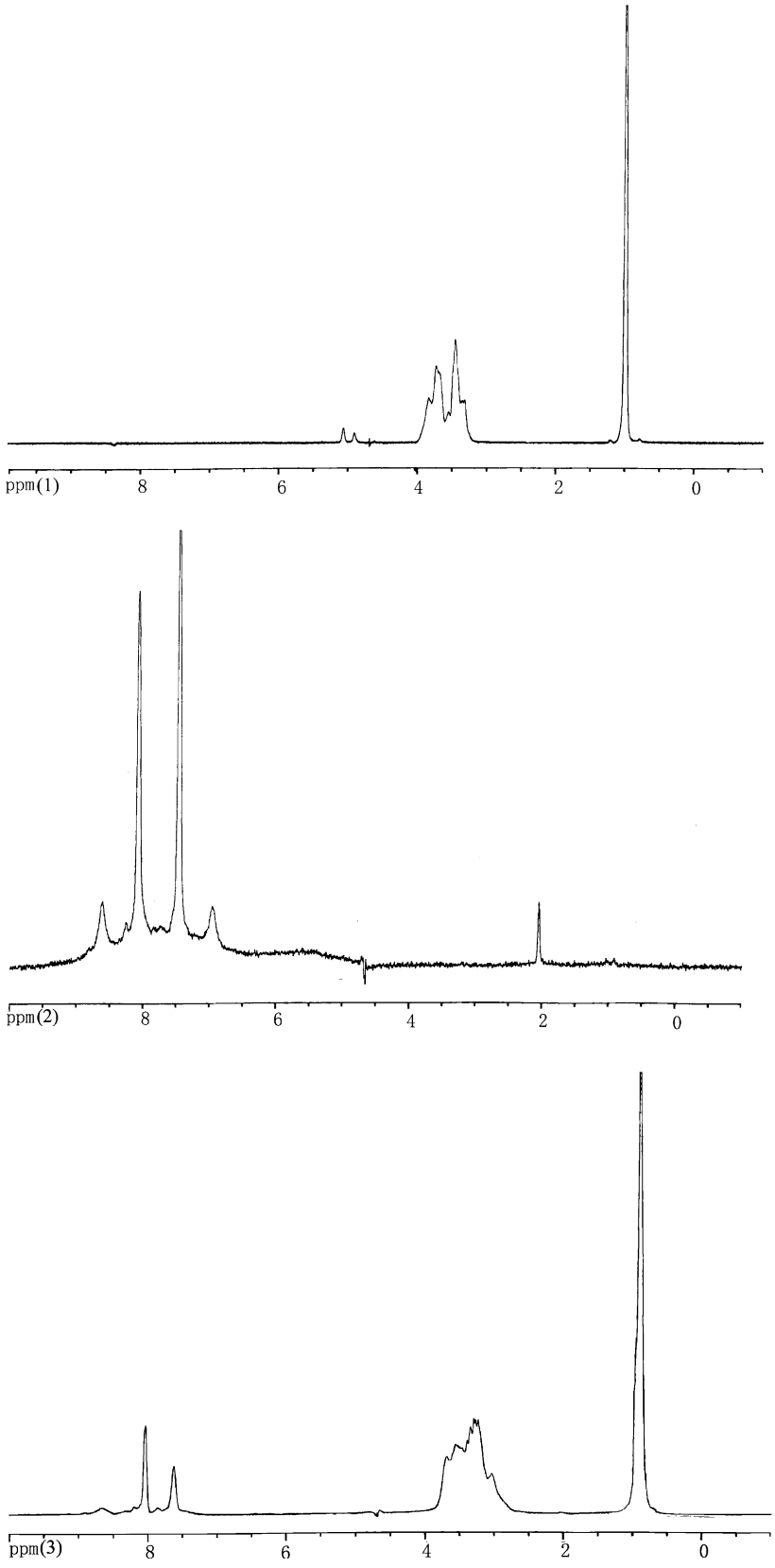

FIGURE 7 ^{1}HNMR spectra of HP-β-CD and $TPPS_4$ in D_2O (1) 2×10^{-3} M HP-β-CD (2) 1×10^{-3} M $TPPS_4$ (3) HP-β-CD containing 1×10^{-3} M $TPPS_4$

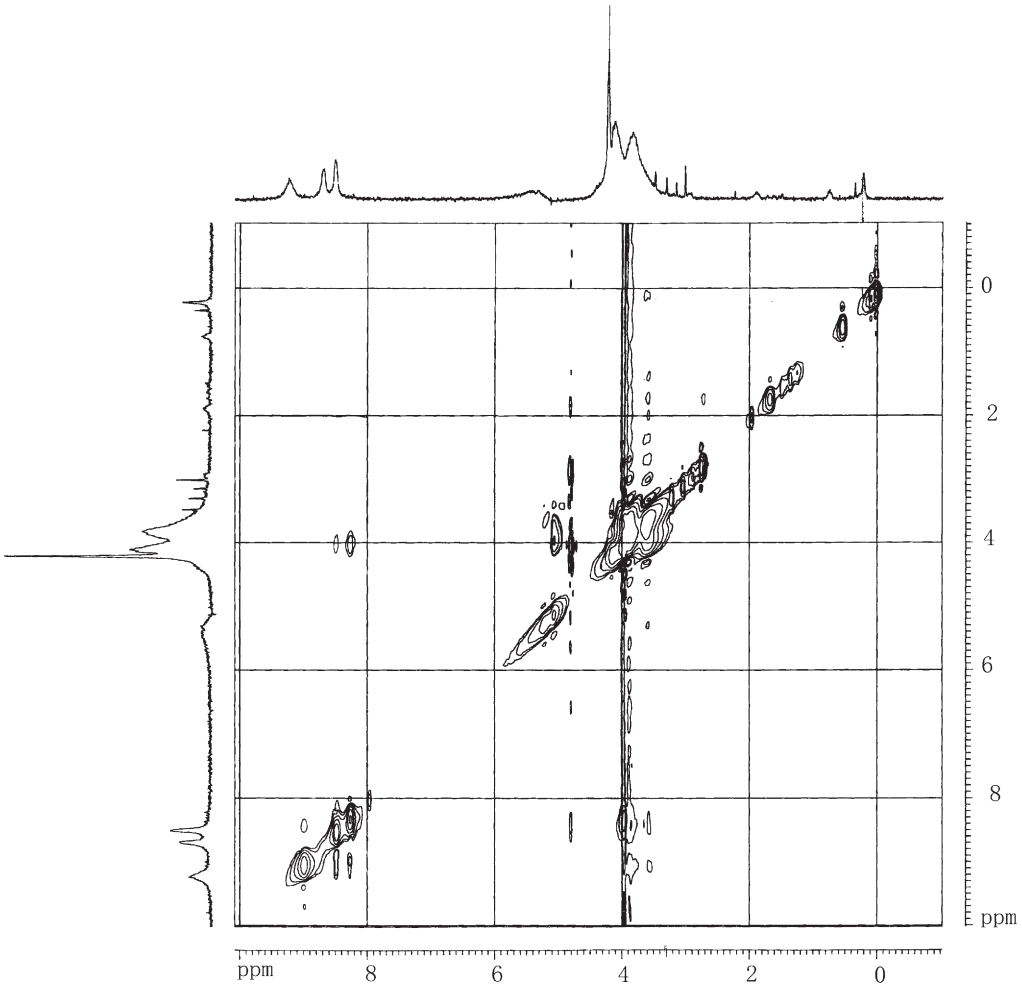

FIGURE 8 The Roesy spectra of $TPPS_4$-HP-β-CD supramolecular system

hydrophilicity and the easy distortedness of their cavity. The possible reason for the large K_2 value obtained by substituted cyclodextins is that it is just the modified structure of these CDs that make them have the more excellent ability than β-CD to give the further complex with porphyrin (two cyclodextins bind with one porphyrin).

Conformation Analysis by NMR Spectroscopy

Additional evidence for the formation of $TPPS_4$-CD complex can be obtained from changes of the chemical shifts of ^{1}HNMR spectra at 300 MHZ in D_2O solution. The ^{1}HNMR spectrum of HP-β-CD,$TPPS_4$ and their complex are shown in Fig. 7. As shown in Fig. 7, the chemical shift of the interior protons H-3, H-5, move upfield by 0.20 and 0.15 ppm, which is perhaps owing to the direct interaction of these protons with $TPPS_4$ molecule. By contrast, the chemical shifts of outer protons H-2 and H-4 are relatively unchanged, indicating the interaction occurs inside the cavity instead of exterior of the torus. Furthermore, the downfield (0.06 ppm) chemical shift of β-pyrrole protons and the upfield (0.17 ppm) chemical shift of phenyl protons indicate the meso-phenyl groups of $TPPS_4$ entered the cavity of HP-β-CD.

For the $TPPS_4$- HP-β-CD system, the results of two-dimensional rotating nuclear Overhauser enhancement spectroscopy (Roesy) also reveal that the $TPPS_4$ has been incorporated within the interior of the cyclodextrin cavity (unbuffered D_2O pD 4.0). Figure 8 shows that the proton–proton through-space interaction between the cyclodextrin and porphyrin are as follows: H^3(HP-β-CD) → β-pyrrole; H^3(HP-β-CD) → phenyl H meta; H^3(HP-β-CD) → phenyl hydrogen ortho; H^5(HP-β-CD) → phenyl hydrogen ortho (porphyrin). These results shed light on that the HP-β-CD has encapsulated the $TPPS_4$ via the secondary face first; and they are in good agreement with the model produced by Mankan [24].

DISCUSSION

Considering the advantages and drawbacks of these three methods involved in this study, the variations

of fluorescence intensity between free and complexed $TPPS_4$ are large so the determination of K_f is easy and accurate. This measurement requires only a quite low $TPPS_4$ concentration, as a result, it is less reagent consuming. However, the drawbacks of this method are the slight shift in emission wavelength and the narrow span of CD concentrations ($0.5-5\times 10^{-3}$ mol/l) influencing the fluorescence spectra. Furthermore, this method requires that the guest should only be fluorescence reagent.

The thin-layer chromatography is proved to be available, easy to perform less time consuming, not reagent consuming for the study of the inclusion interaction. However, the value of K_f lacks precision because the performance is easily influenced by other conditions such as temperature, vibration and so on.

For polarography, the procedure is easy to operate and the change of i_p is remarkable. But just on the condition that the variation of i_p must be controlled by diffusion, the inclusion constant can be calculated by "electric current method", the concentration of $TPPS_4$ is higher than other methods.

To compare the formation constants of different CDs in various methods, it can be concluded that the consequence of inclusion capacity of different CDs is HP − β − CD > γ − CD > β − CD > SBE-β-CD (or CM-β-CD). It is displayed that the hydrophilic derivatives of β-CD(HP-β-CD) has remarkably strong inclusion capacity, γ-CD which have a bigger cavity that can match with the size of meso-phenyl group of $TPPS_4$ shows higher inclusion capacity than that of β-CD. However, the charges repel interaction decreases the inclusion capacity of SBE-β-CD and CM-β-CD, which suggests that for the ionic cyclodextrins the charge interaction plays an important role in the inclusion procedure.

Acknowledgements

This work was supported by the National Natural Science Foundation of China and by the National Natural Science Foundation of Shanxi province of China.

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