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Photoinduced self-assembly of the supramolecular photochromic systems – photoinduced dimer formation of the inclusion complexes of an indolinospiropyran with CDs

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Abstract

The photochromic spiropyran with a long alkyl chain can form inclusion complexes with cyclodextrins (CDs) in aqueous solution. The complexes are axial inclusion complexes formed between the long alkyl chain and CDs, with the spiropyran head group located outside the cavities of CDs. Under UV irradiation, the inclusion complexes show normal photochromism. The coloured form(B) of the complexes can assemble into a dimer. Unlike the dimer formed in apolar solvents or in polymers, which consists of a coloured molecule (B) and a colourless molecule (A) with a composition of AB, the dimer consists of two coloured molecules (B) in the present system. Corresponding to its structure, the decolouration process can not be described by an exponential or a two-exponential kinetics, but obeys half-order kinetics very well. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photochromic spiropyran; Cyclodextrins; Photoinduced self-assembly

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6–8 D-glucose units (α-CD: six, β-CD: seven, γ-CD: eight). Cavities of CDs have slightly truncated-cone shape with the secondary hydroxyl sides broader than the primary hydroxyl sides. The interior cavities are apolar compared with water, and the exteriors of CDs are hydrophilic [1]. The most important characteristic of CDs is that they can form inclusion complexes in solutions with a wide variety of inorganic and organic guest compounds [1–7]. Such properties of CDs have aroused the enthusiasm of many groups to use them as building blocks in the construction of supramolecular systems [3,4]. With the formation of inclusion complexes, the microenvironment in which guests are located may be different and their properties may be changed. This can be used to regulate the physical and physiochemical properties of the functional guest molecules, such as proton transfer, energy transfer and bond rotation. In the recent work of Wenz's group [8], it was found that, the photochemical properties of stilbenes can be controlled effectively by formation of different inclusion complexes between stilbenes and CDs.

Spiropyrans are one of the most popular classes of photochromic compounds [9]. The photochromic reaction is caused by the reversible heterolytic cleavage of the pyranyl C(spiro)–O bond under UV irradiation, yielding the coloured form that can return to the colourless form by ring closing under visible light irradiation or in the dark. Since the discovery of photochromic properties of spiropyrans by Fischer and Hirshberg [10], great interests have been focused on these photochromic compounds that can be related to their applications in various fields, such as non-silver high resolution photography, optical filters and recording materials [9].

The coloured and colourless form of spiropyran are different species. The coloured form is a more polar species than the colourless form. The photochromic reaction is very sensitive to microenvironmental variation and can be regulated by many factors such as solvent polarity [11–13], viscosity, and ionic strength [14]. In the work of Tamaki et al. [15], they believed that 1′,3′,3′-trimethyl-6-nitro-spiro[2H,1-benzopyran-2,2′-indoline] can form inclusion complexes with γ-CD and modified γ-CDs in the solid states, and the complexes formed show normal photochromism. However, the structures of the complexes have not been clarified. In the recent work of Hamada et al. [16–18], it was found that the spiropyran-modified CDs show reverse photo-

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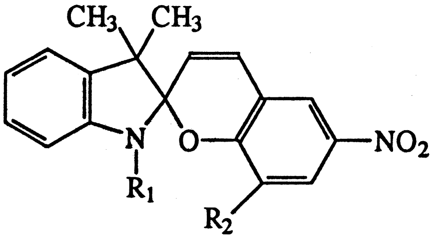


I R_1 = $-CH_3$, R_2 = - H

II R_1 = $-CH_3$, R_2 = $-OCH_3$

III R_1 = $-n-C_{16}H_{33}$, R_2 = $-OCH_3$

IV R_1 = $-(CH_2)_4-\overset{+}{N}Et_3$, R_2 = $-OCH_3$

Scheme 1. Compound I, II, III, IV.

chromism in water. In order to probe the structure of the inclusion complexes, the inclusion behaviours of spiropyrans of different structures with α-, β-, and γ-CDs in aqueous solutions are explored in detail in this work.

2. Experimental

II, **III** and **IV** (Scheme 1) are synthesized by the method of Gruda and Leblanc [19], and identified by suitable methods [12]. **IV** is a new compound identified by FT-ICRMS (Bruker APEX II) using an ion source of Cs^+ gun with 10 kV kinetic energy, and its molecular ion peak appears at 494.2990 (calculated for $C_{29}H_{40}O_4N_3$: 494.3013). α-, β- and γ-CDs are analytically pure and are used as received. The sample solutions are prepared by adding precise amount of acetone solutions (2.0×10^{-3} mol/l) of spiropyran into CD solutions under magnetic-stirred condition, and then sonicated with a bath-typed instrument (250 W) for 5 min. The absorption spectra are recorded by using a Hewlett-Packard HP8452 diode array spectrophotometer. The solutions are irradiated by a 150 W Xe lamp equipped with a grating monochromator or N_2 laser light source (337 nm). The experiment is performed at room temperature (12–15°C).

3. Results and discussion

3.1. *Photochromic behavior of the inclusion complex of* **III** *with* β*-CD*

CDs can form stable complexes with a large variety of compounds in water. Other solvents are less suitable, because the stability of the complexes in these solvents is much lower. In the work of Tamaki et al., the solid inclusion complexes of spiropyrans with γ-CD were obtained as precipitates by mixing acetone solution of **I** at high concentration (1.0×10^{-3}mol/l) with equimolar amount of γ-CD aqueous solution. Similarly, Hamada et al. believed the cavity of γ-CD should be large enough to include the indolinospiropyran [17] and they guessed that the isomerization from the closed form to the open form proceeded in the cavity of γ-CD [4]. In order to obtain a stable complex solution in the present work, aqueous solution is used in this work. When acetone solution of **I** or **II** is added to aqueous solution of CDs at low concentration, the system turns to be turbid and the dispersion solution obtained shows very weak photochromic behavior. This indicates that compounds **I** and **II** show little tendency to form inclusion complexes with α-, β-, and γ-CDs in aqueous solutions. The reason should come from the size limitation of the cavities of CDs. The i.d. of the cavities for α-, β- and γ-CDs are 4.7–5.2, 6.0–6.4 and 7.5–8.3 Å, respectively [1,2], and their colourless forms are apolar compared with water, therefore, they aggregate themselves. The solid complex of Tamaki et al. might be an association complex [15], in which the spiropyran molecule is located outside the cavity of CD.

Long-chain hydrocarbons fit the cavities of CDs very well, and they can form stable complexes with CDs. Because neutral groups at the end of long alkyl chains have little influence on the stability of the complexes formed [3], a long-chain alkyl group is introduced into the SP molecule. Spiropyran **III** obtained can not be dissolved in water, but a transparent solution can be obtained when it is added to aqueous solution of β-CD under supersonicated condition. This implies that an inclusion complex may have been formed. Because the cavity of β-CD can not include the spiropyran head group, the main driving force should be the hydrophobic inclusion interaction between the long alkyl chain and the relatively apolar cavity, and the head group is located outside the cavity. Fig. 1 shows the absorption spectrum of the aqueous solution of 4.0×10^{-5} mol/l **III**

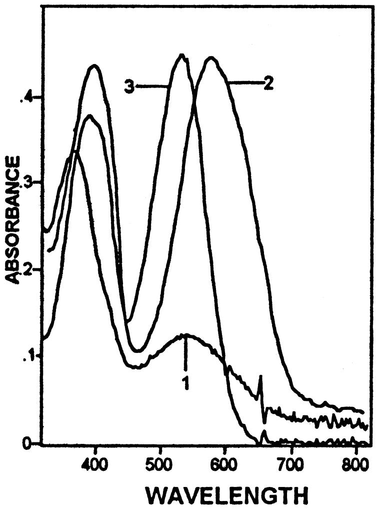


Fig. 1. The absorption spectra of 4.0×10^{-5} mol/l of **III** in the presence of 1.0×10^{-4} mol/l β-CD before (curve 1) and after (curve 2) UV irradiation. The curve 3 is the spectrum of the coloured form of **IV** in aqueous solution.

in the presence of 1.0×10^{-4} mol/l β-CD. It is similar to that of **III** in other solvents. Apart from the absorption band of the colourless form in UV region, a weak peak at 542 nm can be seen, which can be attributed to the coloured form that is in equilibrium with the ring-closed colourless form. The visible spectrum of the open coloured form of spiropyran is very sensitive to the polarity of the microevironment around it, and it shows a negative solvatochromic behavior. In order to elucidate this more exactly, **IV** is synthesized. Its structure is similar to that of **III**, but has a charged terminal group on the substituent of the N atom of indoline, which makes the compound easy to dissolve in water. From the spectrum of the coloured form of **IV** in the visible region, it can be seen that its λ_{max} appears at 530 nm in aqueous solution (as shown in Fig. 1, curve1), similar to that of the coloured forms of the inclusion complex of **III** with β-CD.Thus we may conclude that the coloured form of spiropyran should be located in a polar environment similar to that of **IV** in water. This is consistent with our viewpoint that the spiropyran head group is not included in the cavity of CD but excluded from it, existing in water. Unlike the spiropyran-appended CDs, which show reverse photochromic behavior in water [16–18], the inclusion complex of **III** with β-CD shows a normal photochromism under UV irradiation. λ_{max} of the coloured form formed after UV irradiation is 574 nm (curve 3), this means a red shift of more than 30 nm relative to that of the coloured form that is in thermal equilibrium with the colourless form before UV irradiation. Therefore, there are at least two coloured form species in the solution.

For more information, the decolouration process of the coloured form was investigated. Fig. 2(a) shows the spectral variations of the photoinduced coloured form during the thermal decolouration process after UV irradiation. The decolouration rate is very slow comparing with that in organic solvents. For example, the λ_{max} of the coloured form in acetone is nearly the same with the inclusion complex. The half-decay time for the coloured form in acetone is about 35 s, however, in the present system, it is difficult to observe any obvious decay in such a short time interval. Another characteristic is that an isosbestic point at 370 nm can be observed in the spectra and the E-diagram gives good linear relation between the absorbance at different wavelengths, which means that the decolouration process may be a simple process and only one linear independent process exists [20]. Another important char-

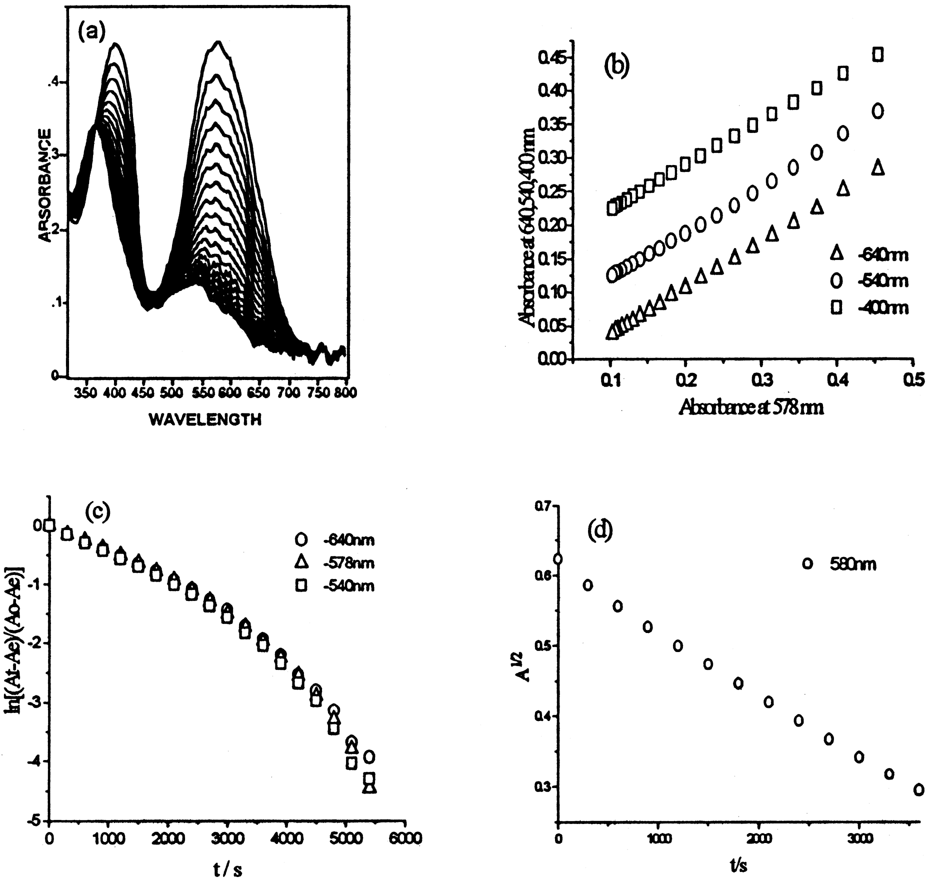


Fig. 2. (a) Spectral variations of the coloured form of inclusion complex formed from **III** (4.0×10^{-5} mol/l) and β-CD (1.0×10^{-4} mol/l) during the decolouration process after UV irradiation for 4 min, time interval between successive curves: 300 s, room temperature: 15°C; (b) E-diagram for the decolouration process of (a); (c). First-order decolouration plot of (a) at different wavelengths; (d) Half-order decolouration plot of (a).

acteristic is that hypsochromic shift in the spectra of the photoinduced coloured form can be observed during the decolouration process. Because the cavity of β-CD is too small for the UV-induced coloured form to fit in, it can not be used to interpret the spectral shift. A possible reason for this may come from the coexistence of several merocyanine isomers. If this is true, there must exist an equilibrium between different isomers. Because only one linear independent process can be observed during decolouration process, the decolouration process should be described well by first-order kinetics in this circumstance. Treating the decolouration process with first-order kinetics, no linear relation can be obtained. Thus, the coexistence of isomers can not be used to interpret the spectral shift and decolouration kinetics.

Similar to cyanine, merocyanine and other planar dyes [21], the photoinduced coloured form can form aggregates in apolar solvents [22–24], polymers [25] or L-B films [26,27]. By comparing the spectrum of the UV-induced coloured form with those of the dimer formed in apolar solvents [24], we find they are quite similar. Thus we suppose that the coloured form may assemble into a dimer further, as shown in Scheme 2.

For the aggregates formed in polymers after UV irradiation, when the first-order kinetics is used to describe the decolouration process, no satisfactory result can be obtained. The instantaneous rate turns to be lower and lower with time, therefore, the two-exponential approximation is used instead [25]. Such a process is interpreted by a step-by-step decolouration mechanism. For the two fractions in the two-exponential kinetic equation, the fraction with a large decolouration rate corresponds to the decolouration of aggregates with small aggregation numbers and the fraction with a small decolouration rate corresponds to the aggregate with large aggregation numbers. The increase in the concentration of spiropyran is favourable to the formation of large aggregate and causes the retardation of the decolouration rate. In our recent work [24], the decolouration process of the dimer formed in cyclohexane after UV irradiation under carefully controlled condition was investigated. The results indicated that there is an equilibrium between merocyanine monomer, colourless form and the dimer formed during this process. The decolouration of monomer causes the shift in the equilibrium, which can in turn cause the dissociation of the dimer. The increase in the concentration of the colourless form will result in the retardation in the decolouration rate of the dimer. In the present case, when first-order kinetics is used to treat the decolouration process, no linear relation can be found (Fig. 2(c)), and the deviation from the linearity is different from that of the aggregates formed in polymers. From Fig. 2(c), it can be seen that the instantaneous rate turns to be faster and faster with time, therefore, the two-exponential approximation is not suitable. These results imply that the decolouration process is not a single molecular process. If we suppose the dimer formed is not AB but B_2 in the present case, according to the decolouration mechanism of Scheme 2, the decolouration process may be treated in the following way:

$$K = \frac{[B_2]}{[B]^2} \quad \text{or} \quad [B] = K^{-1/2}[B_2]^{1/2} \tag{1}$$

$$\frac{d[A]}{dt} = -\frac{d[B]}{dt} - 2\frac{d[B_2]}{dt} \cong -2\frac{d[B_2]}{dt} = k_{dc}[B] \tag{2}$$

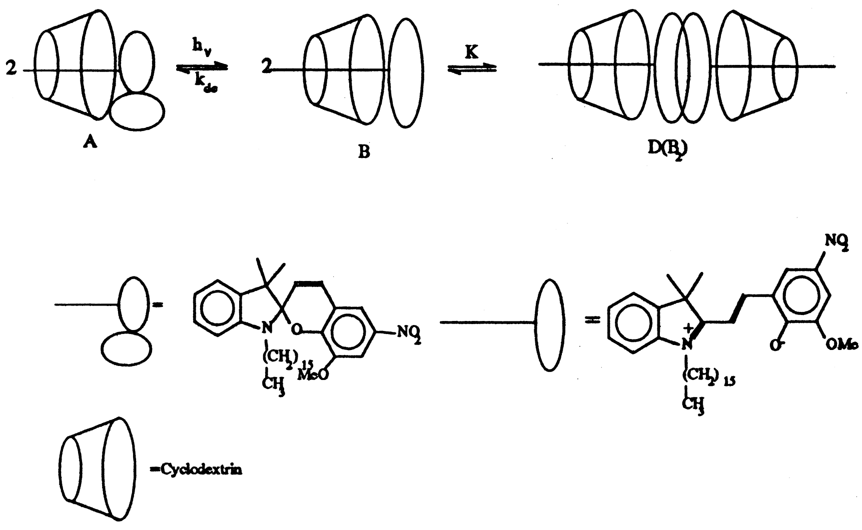
From Eqs. (1) and (2), we have

$$2\frac{d[B_2]}{dt} = -k_{dc[B]} = -k_{dc}K^{-1/2}[B_2]^{1/2} \tag{3}$$

As $A_{B_2}=\epsilon_{B_2}b[B_2]$ we have:

$$(A_{B_2})^{1/2} = -\frac{1}{4}k_{de}(\epsilon_{B_2}b/K)^{1/2}t + C \tag{4}$$

where b is the cell length. From Eq. (4), we know that there



Scheme 2. Dimer formation of the inclusion complex of **III** with CDs under UV irradiation.

should be a linear relation between $A_{B_2}^{1/2}$ and *t*. Fig. 2(d) shows the plot of $A_{B_2}^{1/2}$ against *t*. It can be seen that the process obeys half-order kinetics very well. This can be served as a direct evidence that the composition for the dimer formed in the present system is not AB but B_2.

Because there always exists an equilibrium between B and B_2, the species whose λ_{max} appear at 542 nm can not be assigned to the pure free B monomer, but a mixture of the free B monomer and the dimer (B_2). When the concentration of the coloured form turns to be lower and lower during the decolouration process, the relative ratio of the monomer (B) to dimer (B_2) will increase, and thus in turn causes a blue shift in the spectrum of the coloured form. If no dimer exists, the absorption maximum of the coloured form that is in equilibrium with the colourless form should show little spectral shift compared with that of the coloured form of **IV**. In fact, it appears at 542 nm in the present system, and shows a red shift of 12 nm compared with that of the coloured form of **IV** (530 nm). We believe one of the main reasons for this should come from the coexistence of B and B_2 even at low concentration of the coloured form.

3.2. The effects of the concentration of III

For the dimer (AB) and other aggregates (A_nB) formed in apolar solvents or polymer [23–25] the decolouration process of these complexes can be described by an exponential [24] or a two-exponential model [25]. Because the colourless form (A) is involved in structures of these aggregates, the concentration of A has a significant effect on the formation and decolouration rate of these complexes [23–25]. In the present system, from Scheme 2 it can be seen that the composition of the dimer formed is not AB but B_2, that is, the colourless form (A) is not involved in the structure of the dimer. From Eq. (4), we know that the concentration of the colourless form is not involved. Namely, the variations in the concentration of **III** should have no obvious effect on the slope of the plot between $A_{B_2}^{1/2}$ and *t*. To confirm this, the photochromic behaviours of different concentrations of **III** are investigated. The results indicate that the decolouration process cannot be described by an exponential decay process. Similarly, a two-exponential decay process cannot give a satisfactory result as well. Fig. 3 shows the plot of $A^{1/2}$ against *t*, it can be seen that the decolouration processes fit half-order kinetics very well and the concentration of **III** has little effect on the decolouration rate of the system. Thus the colourless form should not be involved in the kinetic equation. When the concentration of **III** is lower than 1.0×10^{-4} mol/l, the variations in the concentration of **III** have no obvious effect on the decolouration rate. When the concentration is higher than 1.0×10^{-4} mol/l, the system turns to be more complex, J-aggregates can be formed after UV irradiation and this will be discussed in detail in our later work.

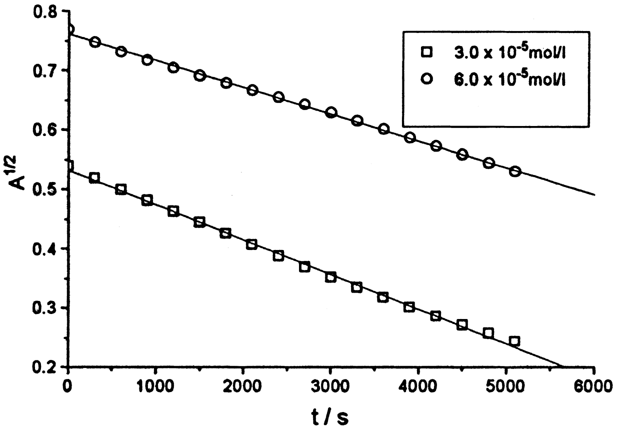


Fig. 3. Effects of concentration of **III** on the half-order decolouration plot at 12°C.

3.3. The effect of cavity diameter of CDs on the formation of inclusion complexes

The main driving force for the inclusion complex formation comes from hydrophobic inclusion interaction between the long chain substituent of **III** and the cavity of β-CD. The head group of **III** is too large to fit in the cavity. Because the cavity diameter of α-CD (4.2 Å) is smaller than that of β-CD (6.2 Å), the inclusion complex formed between α-CD and **III** should have similar structure with that of β-CD and **III**, and similar photochromic behavior should also be observed. The spectral variations of the coloured form of the inclusion complex formed between α-CD and **III** after UV irradiation are shown in Fig. 4(a). It can be seen that λ_{max} and the shape of the absorption spectra of the coloured form are similar to those of the inclusion complex formed between β-CD and **III**. From Fig. 4(c), we find that the first-order kinetics deviates from linearity, and an exponential decay model cannot be used to describe the decolouration process. From Fig. 4(d), we can see that the plot of ${A_{B_2}}^{1/2}$ vs. *t* coincides with linearity very well. This indicates that the decolouration process obeys half-order kinetics very well during the decolouration process and there is an equilibrium between the merocyanine monomer and photoinduced dimer of the inclusion complex.

Cavity diameter of γ-CD is 7.9 Å , which is about twice as wide as that of α-CD. In the work of Hamada et al. [16–18], it was found that for spiropyran-appended-β-CD and spiropyran-appended-γ-CD, the appending spiropyran moiety tends to be included in the cavity of γ-CD, and the small cavity of β-CD is favourable to increase the ratio of the coloured form to the colourless form. This is interpreted as steric hindrance of spiropyran-appended-γ-CD during the conversion from the coloured form to the colourless form due to the formation of intramolecular inclusion complex between spiropyran moiety and γ-CD (Fig. 5). The absorption band of the coloured form is very sensitive to the

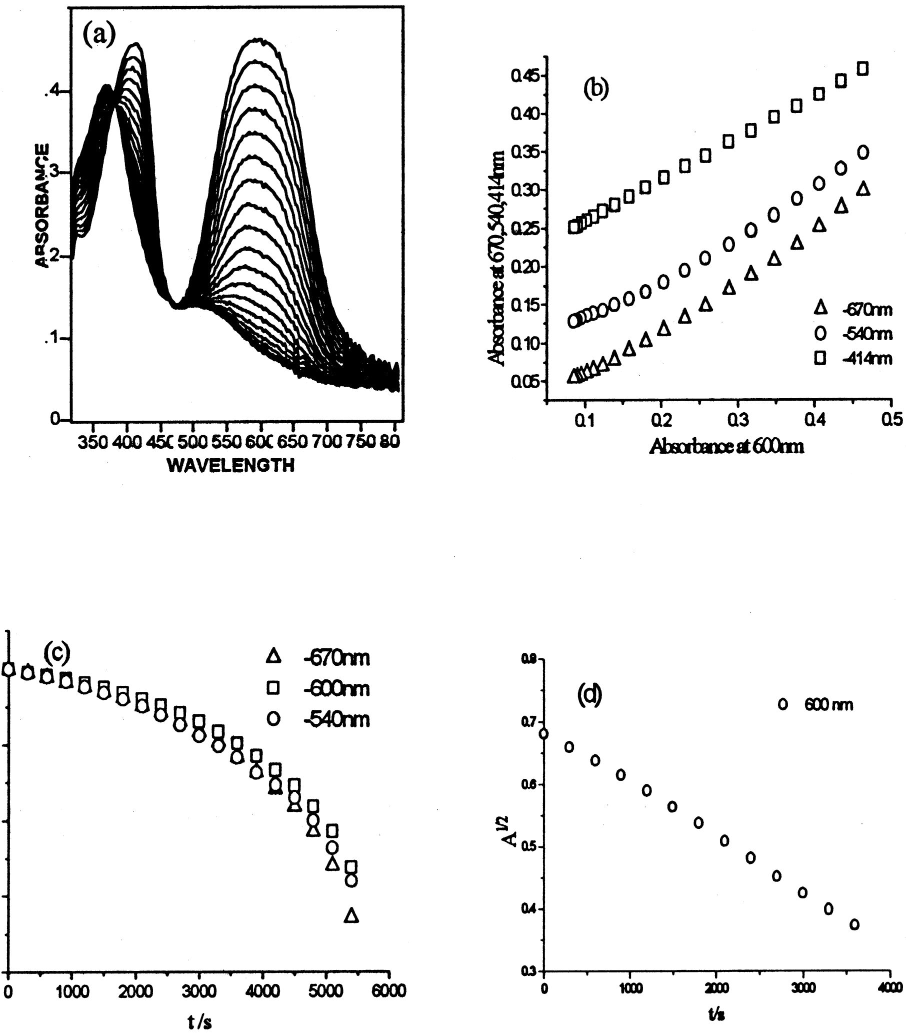


Fig. 4. (a) Spectral variation of the coloured form of inclusion complex formed from **III** (4.0×10^{-5} mol/l) and α-CD (5.0×10^{-4} mol/l) during the decolouration process after UV irradiation for 4 min, time interval between successive curves: 300 s, room temperature 14.0°C; (b) E-diagram for the decolouration process of (a); (c) First-order decolouration plot of (a) at different wavelengths; (d) Half-order decolouration plot of (a).

polarity of solvents and shows a typical negative solvatochromism. They reported a blue shift of more than 40 nm when dimethyl sulfoxide or 10 vol% ethylene glycol aqueous solution are used as solvents. Since the cavity of CD is apolar compared with water, a significant spectral shift should be observed for the coloured form of spiropyran moiety between the case inside and outside the cavity. But the λ_{max} of the coloured form of the two compounds mentioned above appear at 515 and 513 nm, respectively, in aqueous solutions, i.e., no significant shift in the absorption band can be obtained. This implies that both the coloured forms might be located in a similar microenvironment. In other words, the spiropyran moiety might not be included in the cavity of γ-CD. If there exists an intramolecular complex for the spiropyran-appended γ-CD, it should not be an inclusion complex but an association complex, in which most part of the spiropyran moiety is located in water.

Both spiropyran-appended-β-CD and spiropyran-appended-γ-CD show a reverse photochromic behavior in water. Because only normal photochromic behavior can be observed for spiropyran in apolar environment, this gives another evidence that the spiropyran moiety should locate in water. In this study, the photochromic behavior of the inclusion complex formed between γ-CD and **III** is also similar to that of the inclusion complex formed between β-CD and **III**. Its decolouration process fits half-order kinetics very well, that is, dimer is formed after UV irradiation. Because the cavity of γ-CD can not include two spiropyran molecules, the head group of **III** should not be included in the cavity of γ-CD, but located outside it. Thus, we conclude that, for the CDs used in the present system, the cavity diameter of CD has no obvious effect on the spectra and the decolouration kinetic characteristics of the coloured form. This result may be served as another evidence for the exclusion of **III** head group from the CD cavity.

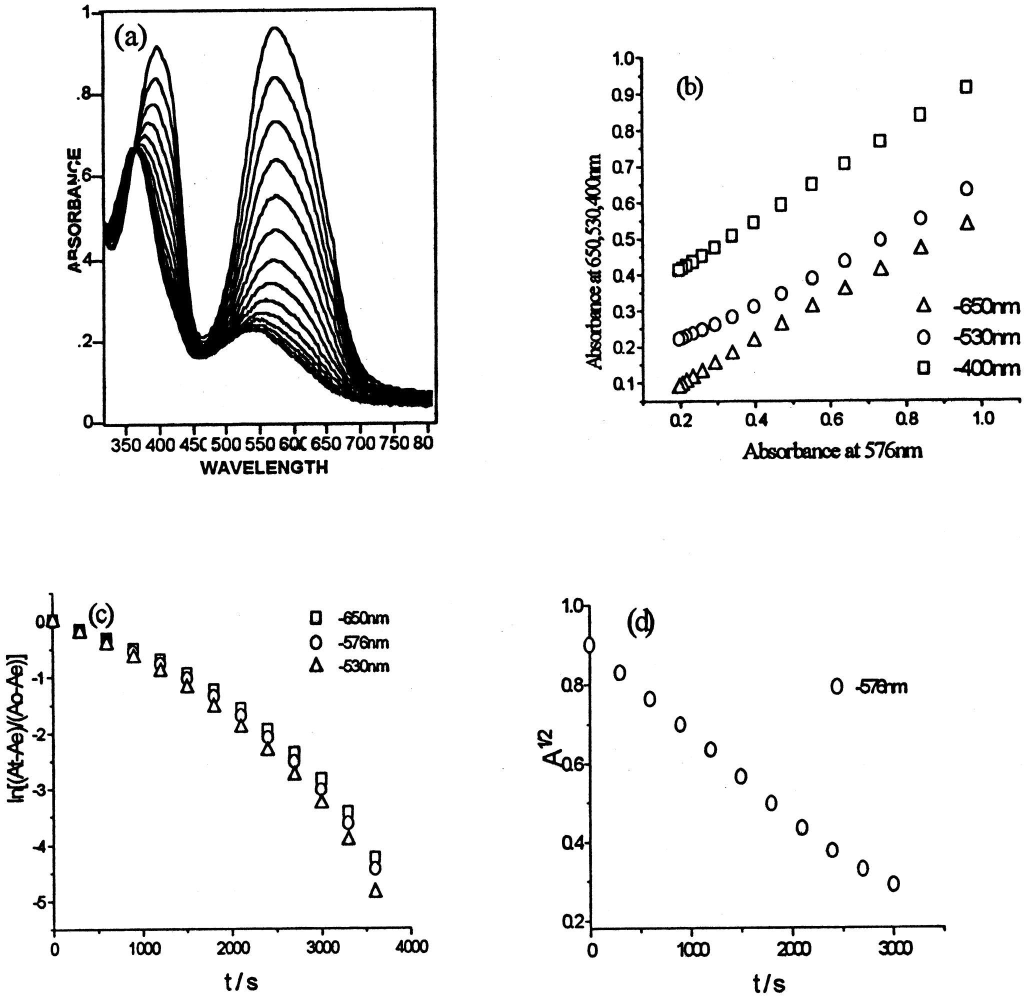


Fig. 5. (a) Spectral variations of the coloured form of inclusion complex formed from **III** (1.0×10^{-4} mol/l) and γ-CD ($1.\times10^{-4}$ mol/l) during the decolouration process after UV irradiation for 4 min, time interval between successive curves: 300 s, room temperature 14.0°C; (b) E-diagram for the decolouration process of (a); (c) First-order decolouration plot of (a) at different wavelengths; (d) Half-order decolouration plot of (a).

4. Conclusions

The inclusion behaviours of spiropyrans of different structures with α-, β-, and γ-CD in aqueous solutions are explored in detail in this work. The following results are obtained:

1. The photochromic spiropyran with a long alkyl chain can form inclusion complexes with α-, β- and γ-CDs. The complexes are axial inclusion complexes formed between the long alkyl chain and cavities of CDs, with the spiropyran head group located outside the cavities of CDs.
2. Under UV irradiation, the inclusion complexes show normal photochromism. The coloured form (B) formed can assemble into a dimer. With the formation of the dimer, the decolouration rate of the coloured form can be retarded significantly.
3. Unlike the dimers formed in apolar solvents or in polymers which consist of a coloured molecule (B) and a colourless molecule (A) with a composition of AB, in the present system, the dimer formed consists of two coloured molecules (B). Corresponding to its structure, the decolouration process of the dimer (B_2) can not be described by an exponential or a two-exponential kinetics, but obey half-order kinetics very well.
4. For the CDs used in the present system, the cavity diameter of CD has no obvious effect on the spectra and the decolouration kinetic characteristics of the coloured form.

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