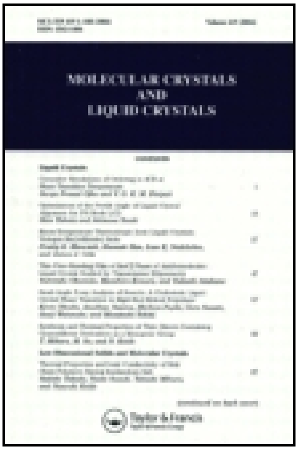

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Multichromic Dye Synthesis and Its Absorption Properties with Cyclodextrins

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The inclusion complex properties of the multichromic dye in DMSO with three different type of cyclodextrins, namely α-, β- and γ-cyclodextrin were studied by absorption spectra measurements. The first order fading rates were also calculated by decoloration properties of the three inclusion complex conditions. Futhermore, the inclusion complex of different sizes of cyclodextrins was compared, which showed the evident decoloration data for interaction of the multichromic dye and cyclodextrins.

Keywords: absorption spectra; cyclodextrin; inclusion complexes; multichromic dye

INTRODUCTION

The properties of inclusion complex by cyclodextrins [1–7] on the coloration and decoloration behaviors were the subject of this study. Cyclodextrins are macrocyclic compounds built from oligosaccharides units which have the ability to include organic molecules into their capacity. Cyclodextrins (CDs) are chemically and physically stable molecules formed by the enzymatic modification of starch. The most commonly used cyclodextrins are α-, β- and γ-cyclodextrins which consist

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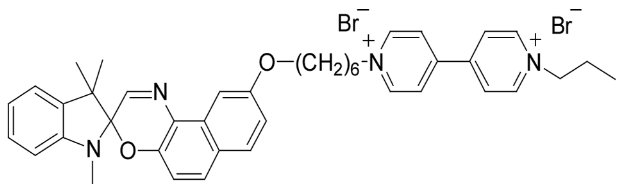


FIGURE 1 Structure of the multichromic dye.

of 6–8 glucopyranose units, respectively [1–3]. The cyclodextrins are of great importance as useful host molecules to make an inclusion complex with various guest molecules which enter partly or entirely into the relatively hydrophobic cavity of CDs simultaneously expelling the few high-energy water molecules from inside, a property that enables them to be used in a variety of different chemistry applications. Thus, the physical, chemical and various important properties of guest molecules, which are encapsulated by CDs, may be drastically modified.

In the previous article [8], the dye showing multichromic effect within single dye molecular structure was synthesized and characterized to study their reversible coloration and decoloration properties whose molecular structure is shown in Figure 1 [9–16]. In this context, another important experimental attempt was considered to investigate the host-guest inclusion complexes between the novel multichromic dye and α-, β- and γ-cyclodextrins. The reaction mechanism of the host-guest inclusion is given in Scheme 1. The study clearly reveals that cyclodextrins could indeed form inclusion complexes with the prepared multichromic dye. Especially, this work focuses on the coloration-decoloration properties in terms of absorption spectral measurements. In addition, the first-order decoloration rate constants were also calculated and discussed.

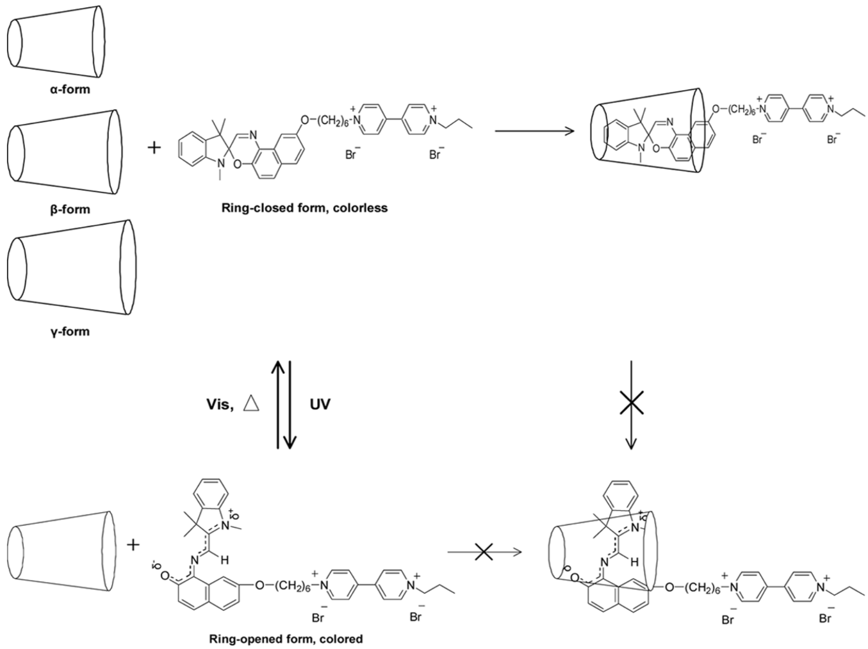
EXPERIMENTAL

Synthesis of Multichromic Dye

The multichromic dye was prepared from the method described in previous work [8]. Using spiroxazine and viologen compound, this dye shows both the photochromic and electrochromic absorption properties within single molecular structure.

Spectral Behavior and Property

Chromism properties, namely reversible coloration and decoloration systems were measured. UV energy (365 nm) for photochromism and



SCHEME 1 Effect of three cyclodextrin inclusion complexes.

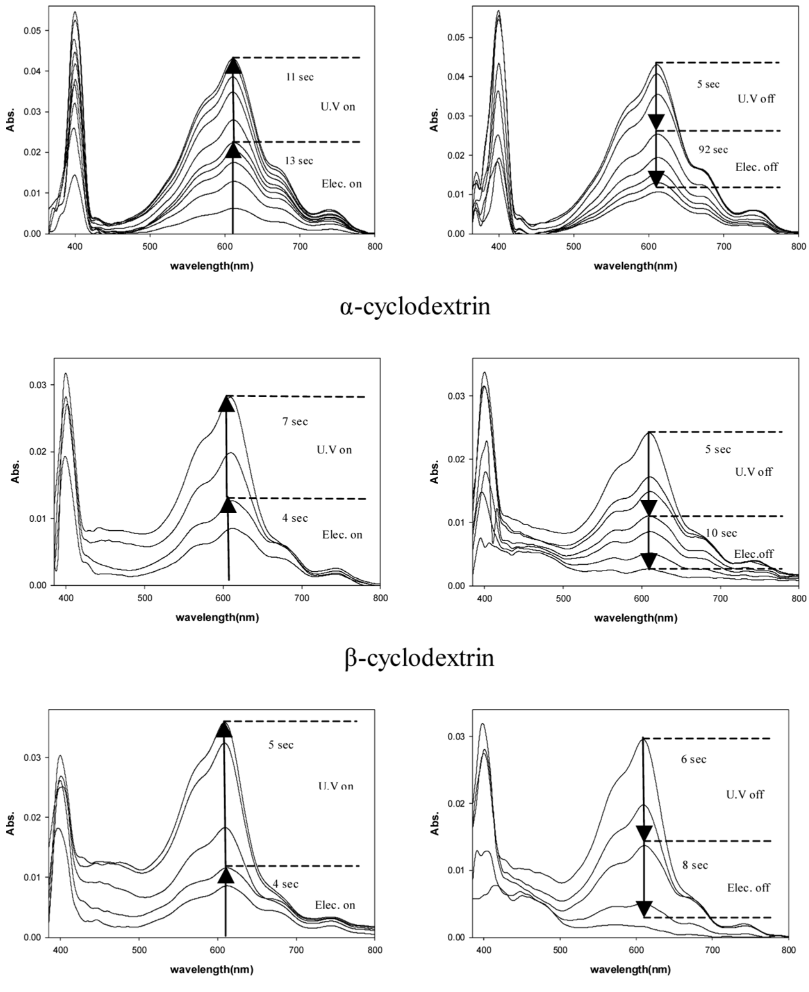
electric energy (2 V) were given to the dye solution in DMSO. First-order kinetic model was fitted with the experimental data and rate constants were evaluated. The properties occurred by cyclodextrin inclusion complexes was investigated in detail.

First Order Decoloration Kinetics of α-, β- and γ-Cyclodextrin Inclusion Complex

Using three types of cyclodextrin having different size of cavity diameter, the experiments were performed. With the experimental data, the first order decoloration kinetic model was plotted and results were analyzed.

RESULTS AND DISCUSSION

The cyclodextrin inclusion experiments with the multichromic dye were carried out. For spectral behaviors between the prepared multichromic dye and the three cyclodextrins, Figure 2 represents that the spectral absorption intensity increases with increasing induced light



γ-cyclodextrin

FIGURE 2 Effects of α-, β-, γ-cyclodextrin inclusion complex on absorption spectral change and spontaneous decoloration behaviors in DMSO: dye concentration 6.35×10^{-4} mol/l, α-, β-, γ-CD concentration 1×10^{-3} mol/l.

and electric energy engagement. These absorption peaks are responsible for the ring-open merocyanine structure of spiroxazine and electron redox system of viologen moiety. After removing energy engagement, spontaneous decoloration behaviors of the absorption spectra were also determined. Figure 2 shows the resulting decoloration changes with viewpoint of α-, β- and γ-cyclodextrin admixture media in DMSO. Due to different size of inner cavity diameter of cylcodextrins, the inclusion complex between cyclodextrins and multifunctional dye shows different host-guest interactions. These corresponding results could give interesting properties in terms of reversible color forming system and its kinetics.

As shown in Figure 2, when the energy engagement onto multichromic dye was removed, the absorption intensity at 605 nm gradually decreased. In the context of three cyclodextrin inclusions, this finding allowed the absorption to be monitored at $\lambda_{\max}$ (605 nm) as a function of time to obtain the color fading rate (k) in α-, β- and γ-cyclodextrin admixture media: a first-order fading rate can be obtained by the decoloration properties of the spiroxazine and viologen parts, which is given by Eq. (1) [8]:

$$(A_t - A_\infty)/(A_i - A_\infty) = k \tag{1}$$

where A_i is the absorbance at 605 nm, A_t is the absorbance at 605 nm at any time t after UV irradiation. A_∞ and k refer to the absorbance at 605 nm after 1 h and first-order color changing rate constant, respectively. In this color changing process, the kinetic analysis predicts the logarithm of the difference between A_∞ and A_t at time t to be linear with time, the slope giving the decoloration rate constant, k. First-order plots according to Eq. (1) for the multichromic dye are shown in Figure 3.

Figure 3 shows that the first-order decoloration rate constants of the dye in the viologen part from α-, β- and γ-cyclodextrin admixture conditions were lower than those of spiroxazine part, which indicate that the open-to-close reaction of spiroxazine occurs more rapidly than the redox system reaction of viologen. In addition, the decoloration rate constants of α-, β- and γ-cyclodextrin inclusion conditions were $k = 0.764$ for α-cyclodextrin, $k = 0.574$ for β-cyclodextrin and $k = 0.467$ for γ-cyclodextrin, respectively. In the case of α-cyclodextrin admixture condition, the host-guest inclusion complex could be restricted due to the small cavity diameter size. Thus, the large amounts of spiroxazine moiety still remains in DMSO solution and the corresponding reversible decoloration behavior could proceed rapidly. In other words, in the case of γ-cyclodextrin admixture condition, some amount of spiroxazine dye could make inclusion complexes and the corresponding complexed dye was relatively restricted to proceed the reversible conversion to the its original dye structure.

CONCLUSIONS

From the viewpoint of chromism effect, the optical functions with photochromism and electrochromism are very interesting subjects.

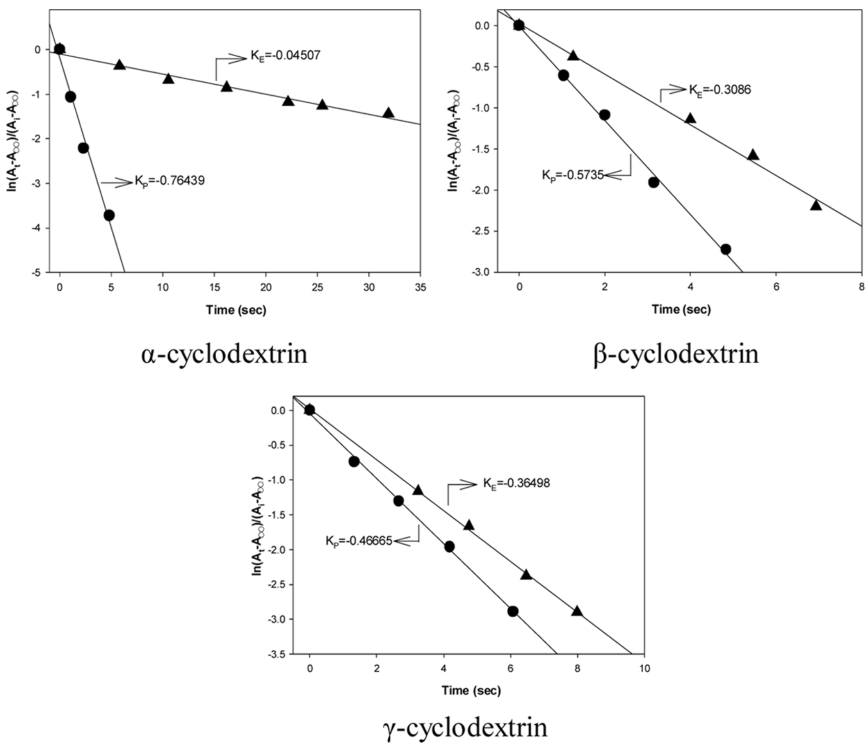


FIGURE 3 First-order decoloration kinetic plot of the dye and α-, β-, γ-cyclodextrin in DMSO.

Thus, the multichomic dye showing both photochromic and electrochromic spectral changes, was synthesized. In addition, the different chromism properties of the inclusion complex i.e., multichomic dye were, observed using three different types of cyclodextrins as an encapsulating agent. The encapsulation of the multichromic dye into the inner cavity of the different sizes of α-, β- and γ-cyclodextrin shows adverse effects on chromism behaviors of the inclusion complexes.

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