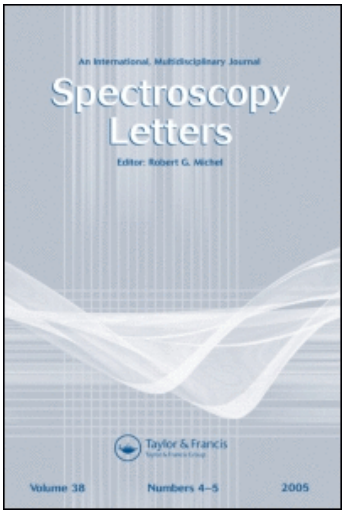

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Interaction of Cyclodextrins with Brooker's Merocyanine in Aqueous Solution

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ABSTRACT The UV-Vis spectroscopic behavior of the solvatochromic dye 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (Brooker's merocyanine) was investigated in aqueous solution (pH 10.55) in the presence of increasing amounts of native (α- and β-) and modified (methyl-β- and hydroxypropyl-β-) cyclodextrins. The data obtained showed that a bathochromic shift occurs in the dye solution after the addition of the cyclodextrins, indicating that the probe is transferred to a low-polarity microenvironment with the addition of the cyclodextrin. Experimental data also suggest the occurrence of a 1:1 dye:cyclodextrin inclusion complex.

KEYWORDS Brooker's merocyanine, cyclodextrins, hydrophobic effect, inclusion complexes

INTRODUCTION

Cyclodextrins (CyDs), or cycloamyloses, are cyclic polysaccharides composed of glucose units (6, 7, or 8 for α-, β-, and γ-CyD) connected at the 1 and 4 carbon atoms and have hydrophobic cavities with hydrophilic external walls in aqueous solution, with the diameter of the cavities (4.7–8.3 Å) being determined by the number of glucose units. These cyclic molecules are versatile receptors for many substrates,[1,2] and their ability to form inclusion complexes in solution and in the solid state has led to a great variety of research due not only to their industrial applications[3] but also to recent developments in many fields.[4]

It is well known that CyDs have an external polar moiety whereas their cavities are hydrophobic.[2,5] Several studies have been carried out by many authors in the search for estimates of the micropolarity of CyDs.[2] These investigations are very important to understanding many questions concerning, for instance, the nature of receptor–substrate interactions, the solubility of CyDs in different media, and their ability to improve the solubility of many classes of organic compounds in water.

Physicochemical investigations of medium polarity are commonly performed by means of solvatochromic probes,[6–9] which indicate, through a modification in the medium polarity, changes in the position of the band in the visible region of the spectrum and sometimes also in the position of the emission fluorescence band. An important example is the dye 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**1**), which is one

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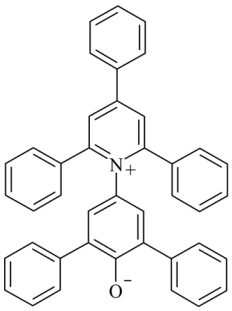
of the most commonly employed solvatochromic dyes in studies in solution.[6,9] Another well-known solvatochromic dye is 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one (**2**), better known as Brooker's merocyanine.[6,10]



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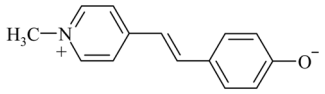

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These dyes have been used in recent years in several studies related to solvatochromism,[6,7,9,10] halochromism,[11–13] mixed solvents,[14–19] and microheterogeneity in solution.[20] Despite the number of studies on the behavior in solution of some classes of dyes in the presence of CyDs,[2,21–25] we can find very few similar studies related to solvatochromic dyes, for instance, with the well-known probes **1** and **2**. Recently, a study of the effect of the addition of methyl-β-CyD on the solvatochromic bands of **1** and **2**, using the UV-Vis technique and several media, showed that the dyes interact strongly with CyD by means of hydrogen bonding and hydrophobic effects.[26] In water, the results indicated that bathochromic shifts occur in the solvatochromic band of the dyes with the addition of CyD due to their inclusion in the CyD, revealing the lipophilic nature of the cavity of the CyD. These data are in agreement with recent studies using other merocyanine dyes.[27] In this paper, we describe the investigation by UV-Vis spectroscopy of the behavior of dye **2** in aqueous solutions containing α- and β-CyD. In addition, we also show how probe **2** interacts in aqueous solution with two modified CyDs, methyl-β-CyD and hydroxypropyl-β-CyD (HP-β-CyD).

MATERIALS AND METHODS

Materials

α-CyD [Cavitron 80000, batch no. G8071, water content 8.6%], β-CyD [Cavitron 82000, batch no. 1Q0011, water content 10.7% (Karl Fischer titration)], and hydroxypropyl-β-CyD [Cavitron 82005, batch no. H3M288P, water content 3.0% (Karl Fischer titration)] were kindly donated by Cerestar/Cargill (Minneapolis, MI, USA) and used as received. Methyl-β-CyD [Cavasol W7M, batch no. 71T023, 10% (wt) water (Karl Fischer titration)] was kindly donated by Wacker Chemie GesmbH (München, Germany) and used as received. Deionized water was used in all measurements. This solvent was boiled and bubbled with nitrogen and kept under nitrogen atmosphere to avoid the presence of carbon dioxide. The experiments were performed in buffered medium at pH 10.55 (prepared by mixing 50 cm^3 Na_2CO_3 0.1 mol dm^{-3} with 10 cm^3 HCl 0.1 mol dm^{-3}; ionic strength, $I = 0.216$ mol dm^{-3}) in order to avoid the protonation of the dye. In the studies in unbuffered medium, the pH value of 10.0 was obtained by the addition with a microsyringe of drops of sodium hydroxide solution (1.0 mol dm^{-3} in water) into the aqueous solution of **2**. Dye **2** was synthesized according to the method described in the literature,[28] recrystallized three times from hot water, and dried under vacuum.

UV-Vis Spectra of the Dye in the Solutions Containing CyDs

UV-Vis measurements were performed with a Varian Cary Bio 50 spectrophotometer at 25°C, using a 1-cm quartz, square cuvette. The maxima on the UV-Vis spectra (λ_{max}) were calculated from the first derivative of the absorption spectrum.

A general procedure was used to make spectral measurements with the dye solutions in the presence of the CyDs. Solutions of **2** (1.0×10^{-5} mol dm^{-3}) were freshly prepared in aqueous medium using a 50 cm^3 volumetric flask. A part of this solution was used in the preparation of a CyD stock solution in a 25 cm^3 volumetric flask. The concentration of CyDs was 1.14×10^{-2} mol dm^{-3} for α- and HP-β-CyD, and concentrations for β- and methyl-β-CyD were 7.05×10^{-3} and 3.0×10^{-2} mol dm^{-3}, respectively. The solution of dye **2** was placed in a quartz cuvette hermetically closed with a rubber septum to avoid the entrance of carbon dioxide. Small amounts of the CyD stock solution were then added by means of a microsyringe, and the spectral readings were performed.

Measurements of Binding Constants

The spectral data collected in water with dye **2** were analyzed according to the method described by Connors[25,29] with Equation (1),

$$\Delta A/b = [\text{dye}]K_{11}\Delta\varepsilon_{11}[\text{CyD}]/(1 + K_{11}[\text{CyD}]) \qquad (1)$$

where b is the path length, [dye] is the dye concentration, $\Delta\varepsilon_{11}$ is difference in molar absorptivities of the complexed and free dye, K_{11} is the binding constant for a 1:1 complex formation, and ΔA is the change in absorbance at a fixed wavelength for the solution containing the dye when the concentration of the CyD changes from zero to [CyD]. The binding constants were calculated using the ORIGIN 5.0 program.

RESULTS AND DISCUSSION

Dye **2** exhibits a negative solvatochromism with an increase in the polarity of the medium (i.e., a displacement of its solvatochromic band to low wavelengths with an increase in the medium polarity can be experimentally observed). This occurs due to the greater stability of the ground state of the dye structure in relation to its excited state.[6,7,9,10] Considering the pK_a value of the protonated dye **2** of 8.37, as estimated by Davidson and Jencks,[30] it can be expected that dye **2** is fully protonated in water at pH 7.0. Therefore, this study was performed at pH 10.55. Figure 1 shows plots of the variation in the maximum of the solvatochromic band for dye **2** as a function of the concentration of the different CyDs added in aqueous solutions at pH 10.55. With increasing CyD concentration, bathochromic shifts were registered for all CyDs, indicating that the dye was transferred to a less polar microenvironment with the addition of the CyD and suggesting that inclusion of the dye in the hydrophobic cavity of the CyD occurred. It was also verified that the modified CyDs displayed the largest red shifts, 20.0 and 24.3 nm for HP-β-CyD and methyl-β-CyD, respectively. Substantial shifts were also observed for α-CyD (11.2 nm) and β-CyD (11.0 nm until the solubility limit of the CyD in aqueous solution).

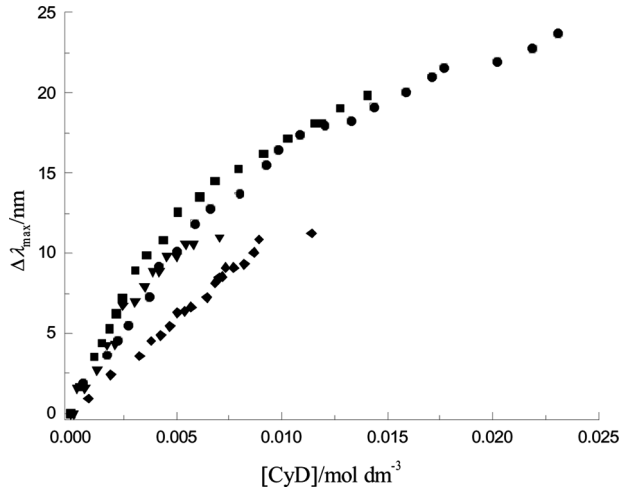

FIGURE 1 **Variations in the maximum of the solvatochromic band for dye 2 (1.0×10^{-5} mol dm^{-3}) in aqueous solutions (pH 10.55) with the addition of increasing concentrations of α-CyD (◆), β-CyD (▼), methyl-β-CyD (●), and HP-β-CyD (■) at 25°C.**

Titration of Dye 2 with the CyDs

The experimental data shown in Fig. 1 provide evidence for the formation of inclusion complexes of dye **2** and the CyDs. Thus, a study was performed to investigate in more detail the influence of an increasing concentration of each CyD on the UV-Vis spectrum of the dye.

Figure 2 displays a sequence of UV-Vis spectra of **2** as a function of the concentration of α-CyD. Analysis of the plot reveals a well-defined isosbestic point at 458.1 nm and bathochromic shifts of the solvatochromic band of the dye with an increase in CyD concentration, suggesting the formation of a 1:1 dye: CyD inclusion complex.[29]

Figure 3 shows the influence of the addition of methyl-β-CyD on the spectrum of **2** in aqueous solution. It can be seen that the solvatochromic band of the dye at 444.0 nm is bathochromically shifted up to 469.0 nm with the addition of the CyD. In addition, the set of UV-Vis spectra revealed the presence of an isosbestic point at 457.1 nm. A similar behavior was observed for the UV-Vis spectra of dye **2** in the presence of increasing concentrations of β-CyD and HP-β-CyD. In the experiments with β-CyD, an isosbestic point at 455.0 nm and a shift of the solvatochromic band of **2** at 444.0 nm to 455.0 nm was observed. With HP-β-CyD, the presence of an isosbestic point at 457.0 nm and bathochromic shifts with an increase in CyD concentration again suggest the formation of a 1:1 inclusion complex of **2** and the CyD.

The absorbance values of **2** at 444.0 nm were plotted as a function of the CyD concentration. Plots

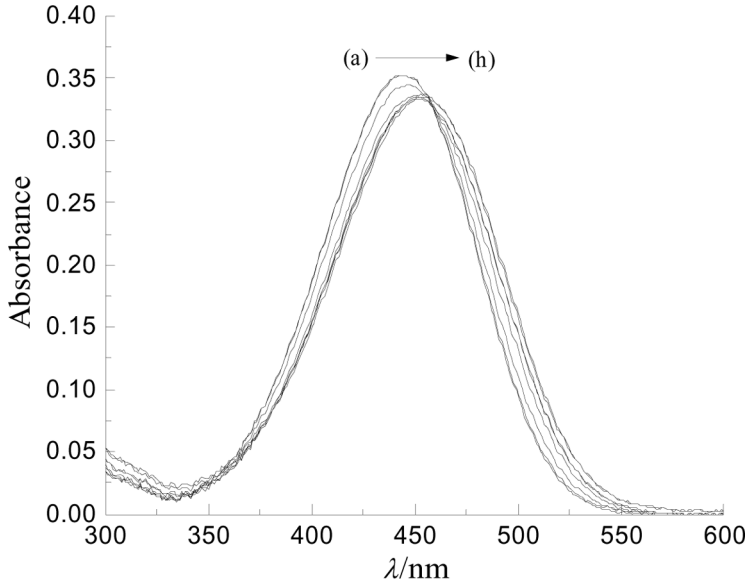

FIGURE 2 UV-Vis spectra at 25°C of aqueous solutions of dye 2 (1.0×10^{-5} mol dm^{-3}) at pH 10.55 containing α-CyD in concentrations of (a) zero, (b) 2.24×10^{-4}, (c) 1.19×10^{-3}, (d) 4.69×10^{-3}, (e) 6.44×10^{-3}, (f) 6.65×10^{-3}, (g) 8.23×10^{-3}, and (h) 8.81×10^{-3} mol dm^{-3}.

of the variations in the absorbance of free **2** as a function of the CyD concentration are shown for α-CyD (Fig. 4) and β-CyD (Fig. 5). All experimental data were fitted through a nonlinear regression according to Equation (1). The results are displayed in Table 1 and show that for all CyDs, Equation (1) fitted the experimental data very well (standard deviations below 9.97×10^{-6}). It can be observed from the data obtained in this study (Table 1) that β-CyD seems to possess the most adequate cavity size for the inclusion of dye **2**. The formation of inclusion complexes involving **2** and the modified CyDs was possible, with the substitution of the hydroxyl groups by methyl or hydroxypropyl groups giving the β-CyD a higher flexibility.[31,32] This substitution also increases the solubility of CyDs in aqueous medium due to the breaking of the internal rigidity attributed normally to β-CyD in view of the

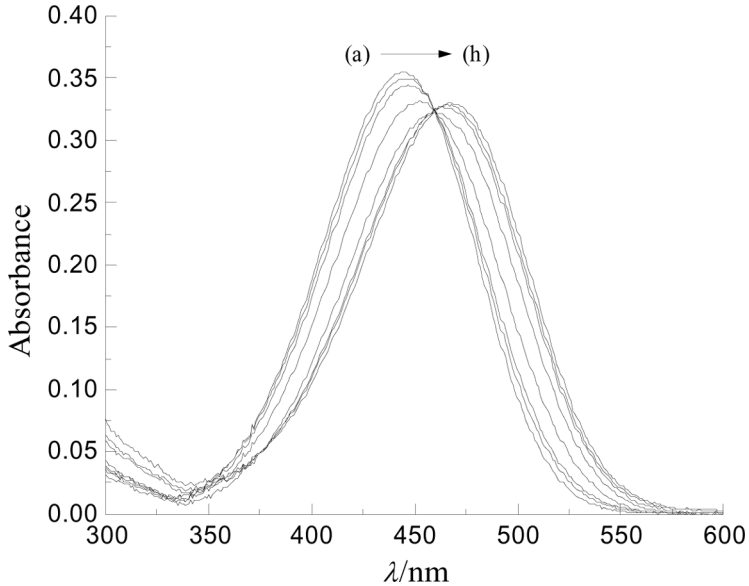

FIGURE 3 UV-Vis spectra at 25°C of aqueous solutions of dye 2 (1.0×10^{-5} mol dm^{-3}) at pH 10.55 containing methyl-β-CyD in concentrations of (a) zero, (b) 5.94×10^{-4}, (c) 1.17×10^{-4}, (d) 3.72×10^{-3}, (e) 9.26×10^{-3}, (f) 1.51×10^{-2}, (g) 1.77×10^{-2}, and (h) 2.34×10^{-2} mol dm^{-3}.

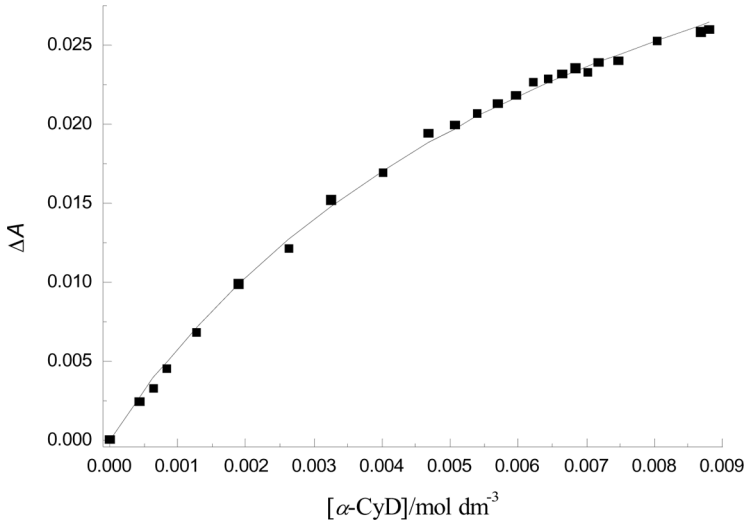

FIGURE 4 **Variations in the absorbance of the solvatochromic band of dye 2 in water (pH 10.55) with the addition of increasing amounts of α-CyD. The concentration of 2 was 1.0×10^{-5} mol dm^{-3}, and absorbances were collected at 444.0 nm. (–) Curve fitted with Equation (1).**

formation of intramolecular hydrogen bonding.[33,34] As expected, the diminution in the preorganization of the β-CyD by structural modification makes difficult a tight and space-filling accommodation of dye **2**, so that its mobility within the cavity is higher, reducing substantially its binding to the substrate.[33]

In order to analyze the influence of the ionic strength on the affinity of the dye to the CyD cavity, methyl-β-CyD was also used in unbuffered medium at pH 10.0. The addition of the CyD to the dye solution caused a bathochromic shift of the solvatochromic band of the dye, and an isosbestic point was observed at 456.2 nm. Data treatment gave a K_{11} value of 68.4 ± 3.3 dm^3 mol^{-1}, with a very good fit. A study in unbuffered medium was also carried out at pH 11.0, and it was verified that the increase in the pH of the aqueous solution under these experimental conditions did not have any effect on the binding constant value. A comparison of the results from the experiments with methyl-β-CyD at pH 10.0 with those in unbuffered medium showed that the increase in the ionic strength of the medium resulted in an increase in the stability of the complex, which is consistent with other studies reported in the literature.[35]

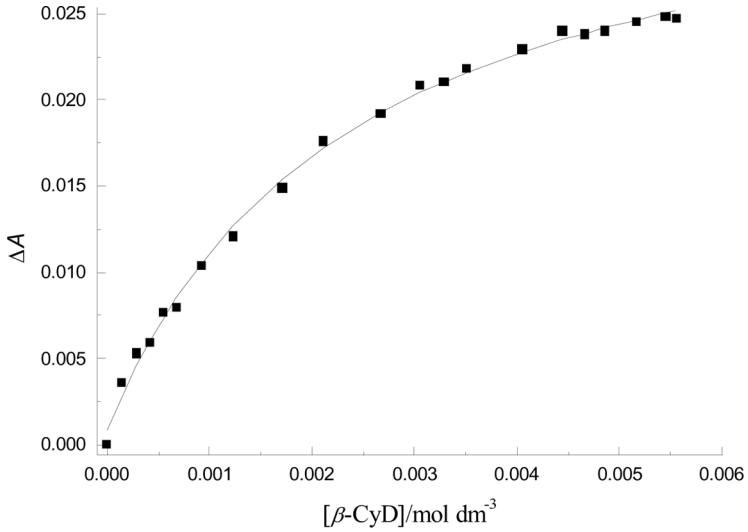

FIGURE 5 **Variations in the absorbance of the solvatochromic band of dye 2 in water (pH 10.55) with the addition of increasing amounts of β-CyD. The concentration of 2 was 1.0×10^{-5} mol dm^{-3}, and absorbances were collected at 444.0 nm. (–) Curve fitted with Equation (1).**

TABLE 1 **Binding Constants for the Inclusion Complexes of Dye 2 with CyDs at 25°C in Aqueous Solutions[a]**

CyD	Isosbestic point (nm)	K_{11} $(dm^3\,mol^{-1})^b$	Standard deviation
α-CyD	458.1	133.6 ± 6.8	1.29×10^{-7}
β-CyD	455.0	424.2 ± 32.8	2.27×10^{-7}
Methyl-β-CyD	457.1	108.2 ± 2.9	1.08×10^{-6}
Methyl-β-CyD[c]	456.2	68.4 ± 3.3	9.97×10^{-6}
HP-β-CyD	457.0	205.8 ± 7.4	1.65×10^{-6}

[a]pH 10.55 and $I = 0.216\,mol\,dm^{-3}$.
[b]Calculated with Equation (1).
[c]pH 10.0, unbuffered medium.

CONCLUSIONS

Data obtained for dye **2** in aqueous solution in the presence of the CyDs revealed that they formed 1:1 inclusion complexes under the experimental conditions of this study. These observations can be explained by the fact that the proper fit of the substrate to the cavity of the CyD receptor represents a very important contribution to the formation mechanism of the inclusion complex.[36]

The study of the inclusion of **2** in methyl-β-CyD in unbuffered (lower ionic strength) and buffered (higher ionic strength) media demonstrated that a medium with increased ionic strength favors the inclusion, mainly because the higher polarity of the medium increases the affinity between the lipophilic dye and the hydrophobic cavity of the CyD through hydrophobic effects.[37]

Because dye **2** exhibits a negative solvatochromism, the bathochromic shifts in the presence of the CyDs indicate that the dye was transferred from a more polar to a less polar environment (the cavity of the CyD). In principle, from a comparison of the data it can be stated that the greater the variation in the λ_{max} by inclusion of the dye in the CyD, the more apolar the microenvironment of the interior of the cavity. In fact, these differences may only reflect the extent of interaction of the CyDs with the dye. Another interesting aspect related to the use of solvatochromic dyes is their potential to allow naked-eye detection of CyDs by means of a selective recognition. This study demonstrated that the CyDs that interacted more strongly with **2**, the modified β-CyDs, caused more accentuated color changes in the solutions (orange color) than did the other CyDs (yellow color). Although we observed relatively small color changes and also a low selectivity of dye **2** for the different CyDs, the careful design of merocyanine dyes able to be selectively recognized through using a certain CyD may help in the development of the field of chromogenic and fluorescent sensors for different CyDs.

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