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INCLUSION COMPLEXES WITH A SYMMETRICAL DISAZO DYE WITH α- AND β-CYCLODEXTRINS

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ABSTRACT:
The results for the synthesis of a disazo dye with symmetrical structure derived from 4, 4'-diaminobenzanilide and its inclusion complexes (IC) with α- and β-cyclodextrins is reported. The free azo dye was prepared by the bis-diazotisation of 4,4'-diaminobenzanilide and the coupling reaction of the obtained bis-diazonium salt with alkaline solutions of the salicylic acid. The free azo dye and its inclusion complexes with α- and β- cyclodextrins were purified by gravity and flash column chromatography. Further, UV-VIS, FTIR and thin-layer chromatography (TLC) studies of the synthesized compounds were performed.

KEYWORDS:
Azo dye, Cyclodextrins, Inclusion complexes

1. INTRODUCTION

Cyclodextrins (CD) are macrocyclic compounds built from glucopyranose units linked by α-(1,4)-glycosidic bonds. CD can be obtained by enzymatic degradation of starch; in this process compounds with 6-12 glucopyranose units per ring are produced. Depending on the enzyme and the way in which the reaction is controlled, the main product is α, β or γ-cyclodextrin (6, 7 and 8 glucopyranose units, respectively).

Cyclodextrins can form inclusion complexes with a large number of organic molecules, a property that enables them to be used in a variety of different textile applications [1]. Through the incorporation, the physical and chemical proprieties of the "guest" compounds are changing. Their toxicity is lower, and they became biodegradable [2].

Azo dyes represent a major group of all the synthetic dyes and have extensive applications in textile industry, paper industry, additives, food, cosmetics and pharmaceutic industry [3]. The encapsulation of the disazo dye with cyclodextrins is a procedure that has been investigated as a method of controlling their stability, solubility and aggregation. It was found that rotaxane structure offers the protection of the dye which is encapsulated inside the cavity of the cyclodextrin, without forming covalent bonds [4].

In this work, the synthesis of a disazo dye and its inclusion complexes in α- and β-cyclodextrins is presented.

2. THE STUDY

The chemicals used in this study were of analytical grade and were obtained from Merck Co., Aldrich and Chimopar Bucharest. 4,4'-diaminobenzanilide was synthesized according to reference [5].

The thin layer chromatographic (TLC) data were taken from silica gel plates (Merck 60F-254) using isopropanol: methyl-ethyl-ketone: ammonia 25% = 4:3:3 as eluting system for the free azo dyes, respectively buthanol-ethanol-water = 4:3:5 as eluting system for their inclusion complexes.

For the gravity and flash column chromatography we used silica gel (Merck) as stationary phase and buthanol-piridine-water = 3:3:3 and buthanol-ethanol-water = 4:3:5 as eluting systems.

The FTIR spectroscopy was recorded on JASCO FT/IR -4200 from KBr pellets.

The UV-VIS spectra were recorded on a Cecil CE-7200 spectrophotometer from 1 mol/L NaOH aqueous solutions for the free disazo dyes, and from aqueous solutions in the case of the inclusion complexes.

General mode of synthesis of the azo dye AS

0.06 g 4,4'-diaminobenzanilide (0.26 mmol) was bis-diazotised using the direct method of diazotization, in mineral acid solution, with natrium nitrite. The reaction was maintained at 0÷5 ^{0}C for 1 hours and the pH in the range of 0.5÷1 [8]. The bis-diazonium salt thus obtained was coupled in a 1:2 molar ration with alkaline solutions of the salicylic acid (dye AS). The pH of the reaction mixtures was maintained in the range of 8.5÷9 by periodic addition of Na_2CO_3. The obtained dye was separated by filtration and was purified by gravity and flash column chromatography.

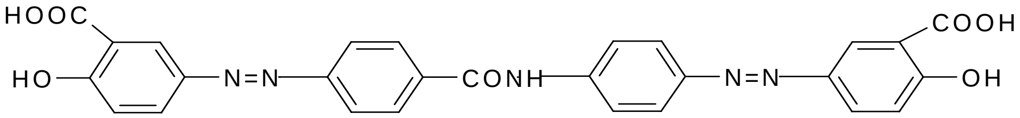
General mode of synthesis of the azo dyes/cyclodextrins complexes

0.06 g 4,4'-diaminobenzanilide (0.26 mmol) was bis-diazotised by the direct method. To the bis-diazonium salt thus obtained, aqueous solutions of the corresponding cyclodextrins (α, and respectively β) were added dropwise. The reaction mixture was maintained under vigorous stirring at 0÷5 °C for 30 minutes. The encapsulated bis-diazonium salt was subjected to the coupling reaction with alkaline solutions of salicylic acid in the case of the β-cyclodextrin. In the case of the synthesis of the α-cyclodextrin complexe, the alkaline solution of salicylic acid was added to the encapsulated bis-diazonium salt. The coupling reaction was monitored by the conventional method and by TLC. The reaction mixture was maintained under stirring at 7.5÷8 pH, at 20 °C for 2 hours. The final products were separated by centrifugation and the rotaxane complexes were isolated by evaporation from the supernatant.

The synthesized dyes and their inclusion complexes were purified by gravity and flash column chromatography and were characterized by thin-layer chromatography (TLC), FTIR and UV-VIS spectroscopy.

3. DISCUSSIONS

The first step of this work was to prepare the disazo dye with structure (I), and further its complexes with α- and β-cyclodextrins.



I

From previous work [6], it was noticed that the bis-diazotization of 4,4'-diaminobenzanilide occurred with better yields when the direct method of bis-diazotisation is used. The temperature was maintained in the range of 0÷5°C and the pH of the mixture around 1. In the coupling step, 3 % excess of coupling component was used. In order to avoid the formation of undesirable by-products, the bis-diazonium salt was quickly added to the alkaline solution of the coupling components and the pH was maintained and adjusted in the range of 8÷9 by periodic addition of Na_2CO_3.

For the preparation of the inclusion complexes of the model dye (I) with α- and β-cyclodextrins, a simple procedure using the hydrophobic effect to direct rotaxane formation was developed. According to this procedure, 4, 4'-diaminobenzanilide was bis-diazotizated by the direct method, and to the bis-diazonium salt thus obtained, an aqueous solution of α- and then β-cyclodextrin was added. The symmetric coupling reaction of the encapsulated bis-diazonium salt with alkaline solution of the coupling component (salicylic acid), in the case of the α-cyclodextrin, was obtained by 2 methods: firstly, the encapsulated bis-diazonium salt was added to the alkaline solution of the coupling component (SA) as described in reference [7]. Secondly, the alkaline solution of the coupling component is added to the encapsulated bis-diazonium salt. In the case of the β-cyclodextrin the encapsulated bis-diazonium salt was subjected to the coupling reaction with alkaline solutions of salicylic acid. Further, the coupling reaction of the encapsulated bis-diazonium salt with salicylic acid was carried-out.

It was noticed that when the bis-diazonium salt is added to the alkaline solution in the presence of α-, respectively β-cyclodextrin, the solution immediately turns yellow. Thin layer chromatography reveals the formation of the rotaxane, respectively the non-rotaxanated dye, which is rather insoluble in water and can be separated from the rotaxane by centrifugation. The progress of the coupling reaction was monitored by the usual way (drop reaction with an alkaline solution of 1-amino-8-hydroxy-3,5-naphthalene disulphonic acid and with the diazonium salt of p-nitroaniline) and by TLC.

The synthesized dyes and their inclusion complexes were purified by gravity and flash column chromatography, and were characterized by thin-layer chromatography (TLC), FTIR and UV-VIS spectroscopy. The results are shown in Table 1 and Figure 1.

Table 1. Yields of reaction, chromatographic mobilities R_f, and spectrophotometric properties of the disazo dye I, non-encapsulated dye and rotaxane complexes.

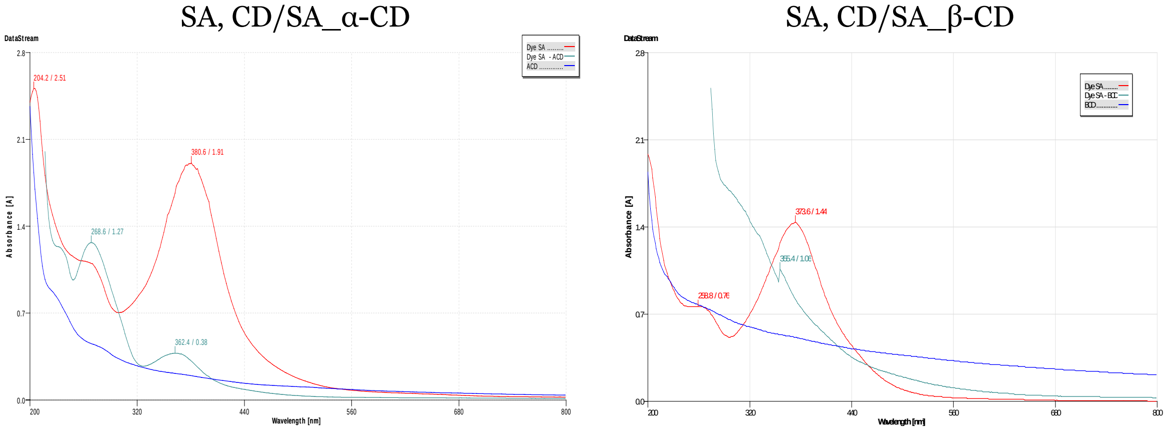
Dye and dye_CD	η [%]	Rf*	λ_{max}** [nm]	lgε
AS	82	0.88	441	1.8
AS_α-CD	13	0.65	269	2.3
AS_β-CD	23	0.68	355	1.9

*Silicagel plates, iso-propanol:methy-ethyl-ketone:ammonia 25% = 4:3:3 as eluent of the synthesized dyes, respectively eluent: buthanol: ethanol: H_2O = 4: 3: 5 of the rotaxane complexes.

**λ_{max} – wavelenght of maxim absorbance, from dye solution in 1 mol/L NaOH, respectively aqueous solutions in the case of the inclusion complexes, CECIL 7200 spectrophotometer.

The FTIR study: KBr pellets, for the disazo dye and inclusion complexes are showed a difference among the initial α- and β-cyclodextrins, free disazo dye and its complexes. IR: for α-CD was found: OH, 3403 cm^{-1}; CH_2, 2925 cm^{-1}; CH, 1337 cm^{-1}; COC, 1079 cm^{-1}; for β-CD: OH, 3383 cm^{-1}; CH_2, 2927 cm^{-1}; CH, 1337 cm^{-1}; COC, 1079 cm^{-1}; for dye SA: OH, 3377 cm^{-1}; CH, 1590 cm^{-1}; CO, 1635 cm^{-1}; for SA/α-CD complex: OH, NH, 3438 cm^{-1}; CONH, 2241 cm^{-1}; N=N, 1414 cm^{-1}; CO, 1641 cm^{-1}; CH, 1561 cm^{-1}; COC, 1021 cm^{-1}; and for SA/β-CD complex: OH, NH, 3425 cm^{-1}; CONH, 2241 cm^{-1}; N=N, 1415 cm^{-1}; CO, 1638 cm^{-1}; CH, 1576 cm^{-1}; COC, 1030 cm^{-1}.

In Figure 1 the UV-VIS spectra for the disazo dye, cyclodextrins and inclusion complexes are shown. The absorption spectra in the 200÷700 nm region of the disazo dye and cyclodextrins were comparated with inclusion complexes, and differences in the spectra were observed. It was noticed that both obtained inclusion complexes show a hipsochromic shift of their absorptions maxima in comparison to the free azo dye (SA).


SA, CD/SA_α-CD

SA, CD/SA_β-CD

Figure 1. The UV-VIS spectra for the diazo dye, ciclodextrins and inclusion complexes

4. CONCLUSIONS

Two inclusion complexes of a symmetrical disazodye with α- and β-cyclodextrin have been obtained and characterized by UV-Vis spectra, FTIR and Thin Layer Chromatography.

The direct route to a rotaxane encapsulated azo dye will facilitate investigations into consequences of chromophore encapsulation.

REFERENCES

[1] Bojana Von_cina, Vera Vivod, Darja Jausˇovec, β-Cyclodextrin as retarding reagent in polyacrylonitrile dyeing, *Dyes and Pigments*, *74*, 642-646, 2007.

[2] Wenz G., Cyclodextrins as Building Blocks for Supermolecular Structures and Functional Units, *Angew. Chem. Int. ed. Engl., 33, 803-822, 1994.*

[3] Aydan Yilmaz, Elif Yilmaz, Mustafa Yilmaz, Richard A. Bartsch, Removal of azo dyes from aqueous solutions using calix[4]arene and β-cyclodextrin, *Dyes and Pigments*, *74*, 54-59, 2007.

[4] Anderson S., Claridge T.D.W., Anderson H. L., Azo-Dye Rotaxanes. Angew.*Chem. Int. ed. Engl.*, 12, 36, 1997.

[5] Simu G. M., Chicu A., Morin N., Schmidt W., Sisu E., Direct Dyes Derived from 4,4'-Diaminobenzanilide. Synthesis, Characterization and Toxicity Evaluation of a disazo symmetric direct dye. *Turkish Journal of Chemistry*, 28, 1-7, 2004.

[6] Simu G., Funar-Timofei S., Hora S., Schmidt W., Kurunczi L., Sisu E., Morin N., Coloranti Directi Derivati ai 4,4'-Diaminobenzanilidei. I. Sinteza si Studiul Izotermelor de Adsorbtie pe Bumbac ale unui Colorant Disazoic Direct cu Structura Asimetrici, *Revista de Chimie – Bucharest*., 53, 826- 829, 2002.

[7] Agrigoroaie G., Simu G. M., Paşka O., UV-VIS and TLC study of some direct azo dyes and their inclusion complexes with α- and β-cyclodextrin, *Proceedings of The 15th Symposium on analytical and environmental problems,* Szeged, Ungaria, 238-241, 2008.