Application of Cyclodextrin to the Textile Dyeing and Washing Processes

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Received 13 August 2003; accepted 16 May 2005
DOI 10.1002/app.22863
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cyclodextrins can form inclusion complexes with different molecules with the aid of their special chemical (molecular) structures. Physical and chemical properties of molecules can change after the formation of complex. This special feature enables the usage of dextrins in different industry areas. In this study, applicability of cylcodextrins in textile dyeing and washing processes was investigated. With this aim, β-cyclodextrin was used in direct dyeing of cellulosic fabrics and in rinsing processes of direct dyed fabrics. Retarder/leveling effect of β-cyclodextrin in dyeing process has been studied and the results were compared with that of a commercial product. In general, cyclodextrins were used in washing processes to remove the absorbed surfactants. It has been investigated whether this effect was the same for washing of dyed fabrics. Eight different direct dyes, for which the chemical structures are known, were used in dyeing and washing processes, and effect of β-cyclodextrin on different chemical structures was investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 208–218, 2006

Key words: biopolymers; dyes; fibers; processing

INTRODUCTION

Besides the efficient pretreatment of the goods, temperature, pH, and addition of electrolytes influence uniformity of dyeing. However, all these factors do not guarantee the production of an excellent product, and new special auxiliary products are used. During dyeing, auxiliary products have an influence by acting with dye solution on fiber interface or by acting with dye resolvent on dyestuff interface.

Various auxiliary products are used in wet finishing processes, especially in dyeing and washing. One of the dyeing auxiliary products is leveling agent. Leveling agents help to achieve a uniform dyeing by slowing down the dye exhaustion and by dispersing the dye taken by the fiber into and onto the fiber in a uniform way. Leveling agents are classified under two groups.

Agents having affinity to the fiber: These bond to the active zones of the fiber before the dyestuff and slow down the speed of dye uptake; thus, more homogenous dispersion onto the fiber and more penetration into the fiber can be achieved.

Agents having affinity to the dye: Leveling agents having affinity to dyes slow down the dyeing process by forming complex compound (loose agglomerate) with the dye; thus, they decrease the movement of dye and prevent rapid diffusion into the fiber. Complex compound, moving slowly, disintegrate at high temperature. In this way, dye is released and it is fixed to the fiber.

In washing, auxiliary textile products have the most important role in removing dyes that are not fixed to the fiber, soils, and foreign matters from the goods, with the aid of water and by keeping them in the form of colloid, emulsion, or dispersion in the washing liquor.

Besides certain organic molecules, cyclodextrins and their derivatives also form complexes in aqueous solutions with dyes used in textile dyeing. Cyclodextrins can be used as leveling agents having affinity to dyes because of this feature. It is stated that cyclodextrins can be used for dyeing of polyamide 6.6, cotton, and polyester, respectively, by Shibusawa et al. and Savarino et al., Denter et al., and Buschmann et al.[1–7]

On the other hand, for the use of cyclodextrins in washing process, experiments were carried out to remove the surface active agents remained on the fabric. Cyclodextrin form complex with the surface-active agent that has an appropriate molecular structure, and thus, it is removed from the fabric.

Cyclodextrins, which are shown in Figure 1, are cyclic oligosaccharides composed of α-D-glucopyranose building blocks that are bonded to each other with (α-1,4) bonds, and are obtained as a result of the enzymatic degradation of the starch.[8]

Cyclic structure is similar to a cone that is cut at the top and consists of an inner hydrophobic space and a hydrophilic outer wall. Hydroxyl groups, which are

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Journal of Applied Polymer Science, Vol. 100, 208–218 (2006)

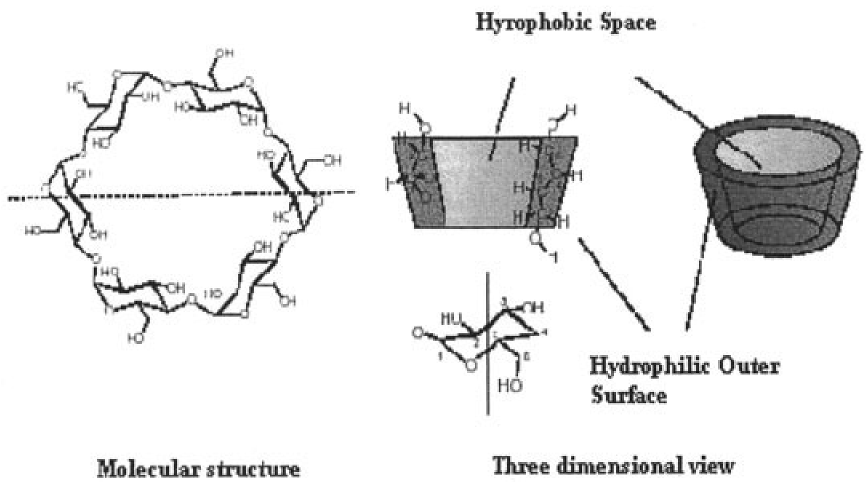


Figure 1 Molecular structure of cyclodextrins.

oriented outward, create a convenient surface for hydrophilic interactions and provide cyclodextrins the necessary solubility, by interacting with water.

The most frequently used cyclodextrins are α, β, and γ, and they contain 6, 7, and 8 glucopyranose units, respectively. Sizes of cyclodextrins are shown in Figure 2, and some of their physical properties are summarized in Table I.

Inclusion complex is the complex formed by another molecule (guest) filling out the space of cyclodextrin molecule (host).

When cyclodextrins are solubilized in water, polar water molecules in the space are repelled by apolar inner surface and it passes into unstable state from the energy viewpoint. Hydrophilic part of the guest molecule has fairly high hydratation, whereas the water molecules in the medium repel apolar aromatic cyclic part. A more stable inclusion complex is formed, as the guest molecule enters to the space of apolar cyclodextrin.[9]

Size of the "guest" molecule must be well suited to the space of cyclodextrin. This suitability is one of the most important factors in complex formation.[10]

Application of cyclodextrins as leveling agents having affinity to dyestuff has been investigated in dyeing of cellulose with direct dyes according to exhaust method. Additionally, it was aimed to determine the effect of cyclodextrin in washing of goods dyed with direct dyestuff. With this purpose, β-cyclodextrin was used as the cyclodextrin, and eight different dyes, for which the chemical structures are known and are practically used in the market, were selected as the direct dyestuff (Table II).

EXPERIMENTAL

Material

For the experiments, 100% bleached and mercerized cotton woven fabric (307 g/m^2) was used. Eight dif-

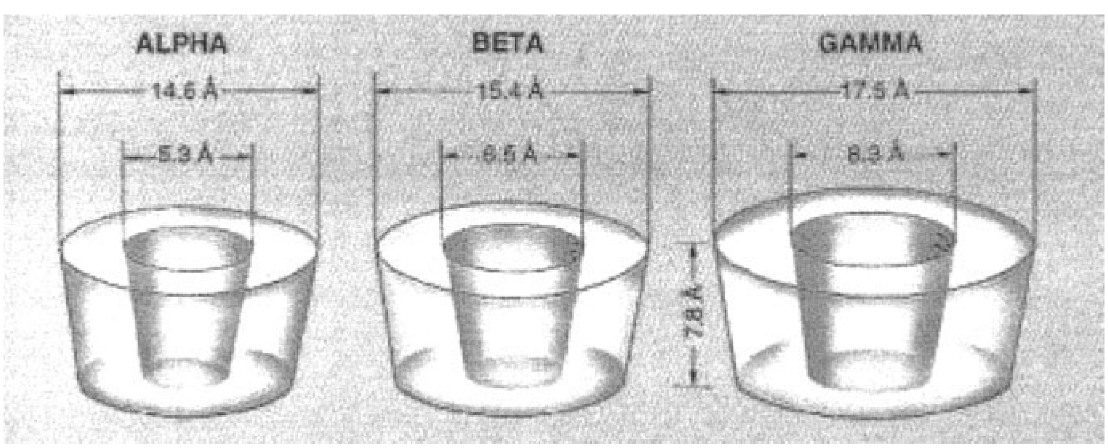


Figure 2 Dimensions of cyclodextrins.

TABLE I
Certain Physical Properties of Cyclodextrins

	α	β	γ
Number of glycopyranose building blocks	6	7	8
Molecular weight	972.00	1135.00	1297.00
Central diameter of space (Å)	4.7–5.3	6.0–6.5	7.5–8.3
Solubility at 25°C (g/100 mL)	14.5	1.85	23.2

ferent direct dyes (Dystar), for which chemical structures and color index numbers are given in Table II, were used in dyeing process. Dyeing process according to exhaust method was performed on Rapid™ IR Dyer (Hong Kong), and squeezing step after dyeing was performed on Rapid™ foulard (Hong Kong). Samples were washed on IR Dyer again, after 70–80% of the dyestuff was ensured to stay on the fabric. Color efficiencies of the dyed fabrics were measured on Minolta 3600d spectrophotometer. Other chemicals used in the experiments are β-cyclodextrin (Cavitron 82900 produced by Cerestar), Levegal® ED (nonionic leveling agent for direct dyestuff, produced by Bayer), and NaCl (industrial salt). Distilled water obtained by reverse osmosis method was used for all experiments. Dyeing chart is shown in Figure 3.

Dyeing recipe

The dyeing recipe is as follows: 0.2% Sirius dyestuff, 4 g/L NaCl, 0.5 and 4 g/L β-cyclodextrin, liquor ratio: 1/40. The same recipe was used for Levegal ED.

After dyeing, samples of each color processed with and without usage of an auxiliary product were washed with distilled water and dried at room temperature at the same time.

Washing experiments

Samples that are dyed at the same time according to dyeing chart given in Figure 3 and without usage of any auxiliary product in 1% depth of color were taken to washing process after they were centrifuged on the laboratory-type foulard, ensuring that pick up would be 70–80% after dyeing. Washing recipes and washing conditions are given in Table III.

Samples were washed three times successively, according to the recipe used. Samples were squeezed between the washings on laboratory-type foulard, ensuring that pick up would be 70–80%.

Evaluation of dyeing results

Spectrophotometric measurements were made and amount of dyestuff remained in the liquor after dyeing was determined. With this aim, maximum absorption–concentration relationship of each dyestuff that can be expressed as "simple linear regression model" in different concentrations of auxiliary products was defined.

$$A = mC + b \tag{1}$$

where, A is the maximum absorbance value in visible region and C is the concentration (g/L).

To determine the maximum absorbance–concentration relationship, as the first step, six different dyestuff concentrations within the range 0.01–0.05 g/L and calibration liquors containing salt and auxiliary product in the same amount used in dyeing liquor were prepared and their maximum absorbance values were determined at room temperature with spectrophotometer. Afterwards, linear relationship between maximum absorbance values obtained and concentration was designated with the aid of least square method. Distilled water containing salt and auxiliary products in the same amount utilized in dyeing was used as a reference for the calibration liquor measurements.

The "degree of exhaustion" of each dyestuff was calculated according to the formula given below.

$$\text{Degree of exhaustion} = \frac{(\text{Initial concentration} - \text{Concentration after dyeing})}{\text{Initial concentration}} \times 100 \tag{2}$$

Evaluation of washing results

Transmission values were measured on spectrophotometer after each washing, by taking samples from washing liquor. After measurements, absorbance values were determined at wavelengths at which maximum absorption was realized. On the other hand, reflectance measurements of the samples that were dried at room temperature were made on spectrophotometer in D-65 (daylight source) and at 10° measurement angle. Measurement results were evaluated according to CIELAB system.

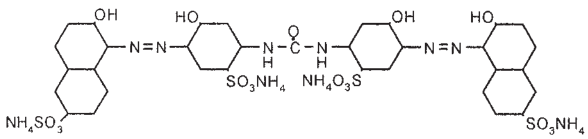
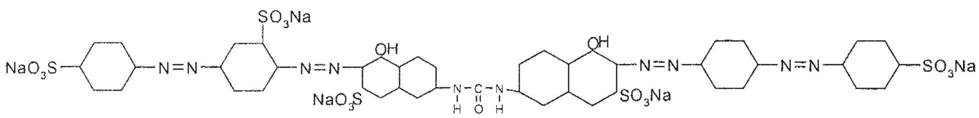
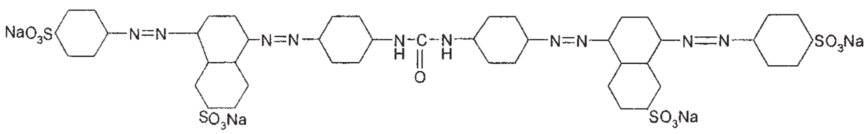
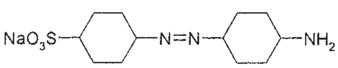
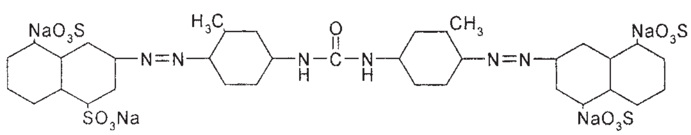
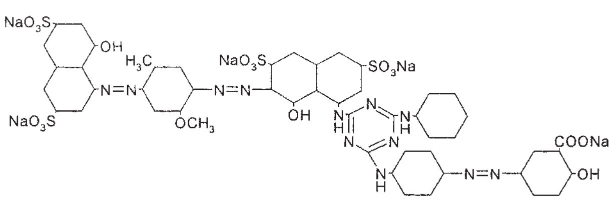
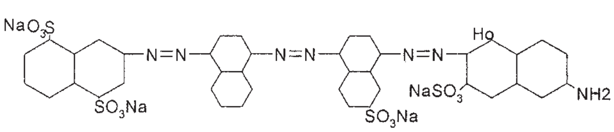
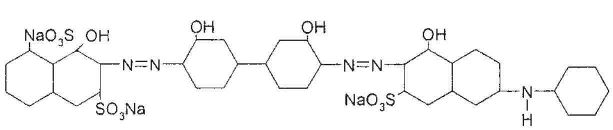
RESULTS AND DISCUSSION

Dyeing results in the presence of β-cyclodextrin

When dyeing according to exhaust method is carried on for a certain period of time, a dynamic balance is reached, and from this point, the amount of dyestuff taken by the fibers does not increase even though the dyeing continues.

$$\text{Dyestuff taken by the fibers} \leftrightarrow \text{Dyestuff remained in the liquor}$$

TABLE II
Direct Dyes Used

Dyestuff	Color Index	SDC Group
Sirius Red violet RL	Direct violet 47	A
		
Sirius Red F3B	Direct Red 80	B
		
Sirius Brown 3RL	Direct Red 83	C
		
Sirius Orange KCF	Direct Orange 46	B
		
Sirius Yellow R	Direct Yellow 50	A
		
Sirius Green S4B	Direct Green 26	B
		
Sirius Blue SBRR	Direct Blue 71	B
		
Sirius Blue FBGLN	Direct Blue 98	C
		

As a result of the interaction between the leveling agents and dyestuff, the amount of dye taken decreases and the balance that will be reached at the end of dyeing is in the favor of liquor.[11]

Results of dyeing made in the presence of β-cyclodextrin are shown in Figure 4. In this figure, the efficiency of dyeing performed without β-cyclodextrin has been accepted as 100%, and degree of exhaustion

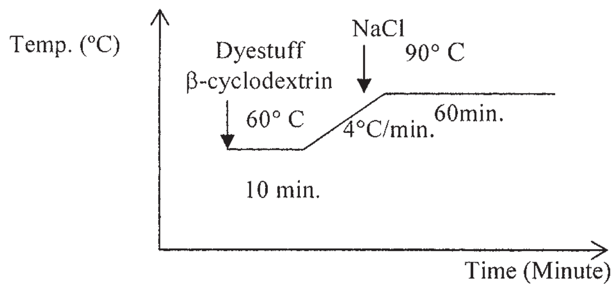


Figure 3 Dyeing chart.

that changes according to the concentration of β-cyclodextrin has been compared in relation with the dyeing realized without any auxiliary product.

The effect of β-cyclodextrin on the dyeing result can be seen clearly in Figure 4. In general, usage of 0.5 g/L β-cyclodextrin does not cause any big difference in dyeing efficiency; however, significant differences can be observed in 4 g/L concentration. The existence of 4 g/L β-cyclodextrin in the dyeing liquor generally has a negative effect on dyeing efficiency, and it can be seen that efficiency decreases in most of the dyestuff. The most distinct effect was obtained for Orange KCF, with a decrease of 20%. The change of 8% in Sirius Red F3B was the second biggest decrease.

When it is considered that cyclodextrins act as leveling agents having affinity to dyestuff, it is seen that β-cyclodextrin has the biggest effect on Sirius Orange KCF dyestuff and next on Sirius Red F3B. Changes in the degree of exhaustion obtained for the other dyestuff are fairly low, especially when Sirius Orange KCF is considered.

Results obtained from the usage of Levegal ED (which is a commercial leveling agent), using the same dyeing method, are shown in Figure 5. Degree of exhaustion is again expressed relatively.

Levegal ED is a leveling agent for direct dyes that has affinity to fibers. When we consider this fact, which is different from β-cyclodextrin having affinity to dyestuff from the influence of mechanism viewpoint, it is an expected result that Levegal ED has a certain effect on all dyes. It has an effect on all dyes, even at low amounts such as 0.5 g/L. It is seen from Figure 5 that degree of influence changes according to the type of the dyestuff.

When it is considered that producer recommends 0.1–0.4 g/L for 1/40 liquor ratio, it is seen that increasing amounts bring to light the fact that the dyestuff Levegal® is being selective.

It is seen that Levegal ED has an effect on almost all dyestuff, when the results are compared with the results obtained in the presence of β-cyclodextrin. The usage of Levegal ED in little amounts means that the same effect will be obtained for each dyestuff, especially in blend dyeing processes.

Washing results of dyed goods in the presence of β-cyclodextrin

Practically, it is recommended to use soft water for the first washing liquor, to enable the removal of the dyestuff that is not fixed to the fabric. For the following washings, it is recommended to realize the process in the existence of hard water or salt water, to ensure that dyestuff does not prefer the liquor. Dystar Company (producer of Sirius dyestuff) recommends in its Sirius catalogue soft water for the first washing liquor and usage of hard water or NaCl in the amount of 3 g/L for the other washing liquors, and reminds that washing temperature must be cold.

Samples dyed without any auxiliary product were washed with distilled water and salt water at the same time. β-Cyclodextrin was added to the other two liquors that contained distilled water and salt water, to observe the effect of β-cyclodextrin in the two washing mediums. Washing recipes used are given in Table III. In Figure 6, total absorbance values of three washing liquors for each recipe are given separately for each dyestuff.

In general, coloration of liquor in washings realized with salt is fairly lower than the coloration of washing liquor for which only distilled water is used.

When we compare washing liquors containing distilled water and addition of 5 g/L β-cyclodextrin (recipes A and B), it is seen that results are different according to the dyestuff used. Distinct increase in coloration of washing liquors of Sirius Orange KCF, Sirius Red F3B, Sirius Blue FBGLN, and Sirius Brown 3RL was noted, whereas for the other four dyestuffs, Sirius Red Violet RL, Sirius Green S4B, Sirius Blue SBRR, and Sirius Yellow R, no evident coloration was observed.

It is seen that addition of β-cyclodextrin influences the same dyes when washings are realized in the existence of salt. Generally, the change obtained by the addition of β-cyclodextrin to washing liquor is more distinct in washings with salt water. In each case, Sirius Orange KCF is the dyestuff affected most. Sirius Red F3B follows Sirius Orange KCF in the washings performed with and without salt. The effect of β-cy-

TABLE III
Washing Recipes and Washing Conditions

Recipes	
A	—
B	5 g/L β-cyclodextrin
C	5 g/L NaCl
D	5 g/L NaCl, 5 g/L β-cyclodextrin
Conditions	
Recipes used	A, B, C, and D
Washing liquor ratio	1/20
Washing temperature	Cold (20°C)
Washing time	10 min

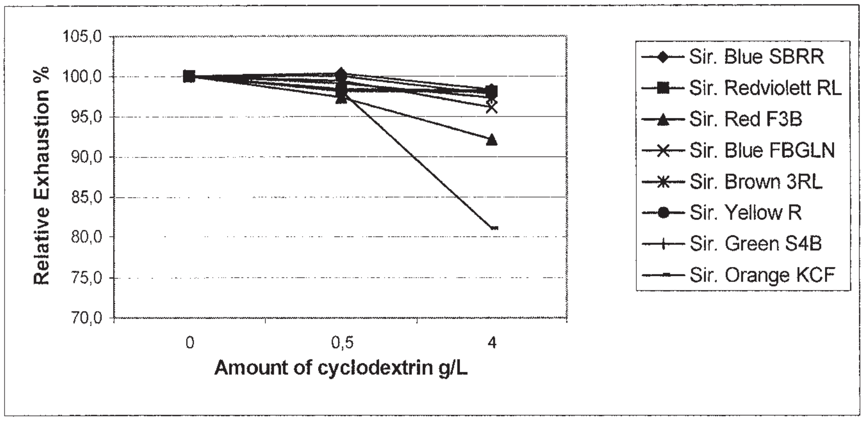


Figure 4 Relative degree of exhaustion in the existence of β-cyclodextrin.

clodextrin is also apparent for Sirius Red F3B, even though it is not as distinct as Sirius Orange KCF.

Dyestuff, which do not form covalent bonds with the fabric during application according to the exhaust method or which has not subjected to any after treatment to provide insolubility in water, shows tendency to set equilibrium again in the washing liquor. This principle can be applied to the direct dyestuff not subjected to after treatment. Additionally, washing conditions, having high ionic strength, decrease the desorption of direct dyes.[12]

In the experiments, transfer of the dyes (which are absorbed onto the fiber surface without any diffusion into the fiber) to the liquor and the tendency of dyed samples to set an equilibrium again when placed into distilled water after dyeing can be clearly seen, as mentioned earlier. As expected, liquor coloration of the washings realized in the existence of salt is fairly low, as a sign of the decreasing amount of dyestuff desorption.

The reason for increase in coloration together with the presence of β-cyclodextrin in the liquor is thought to be the destruction of the dyestuff oxidatively or

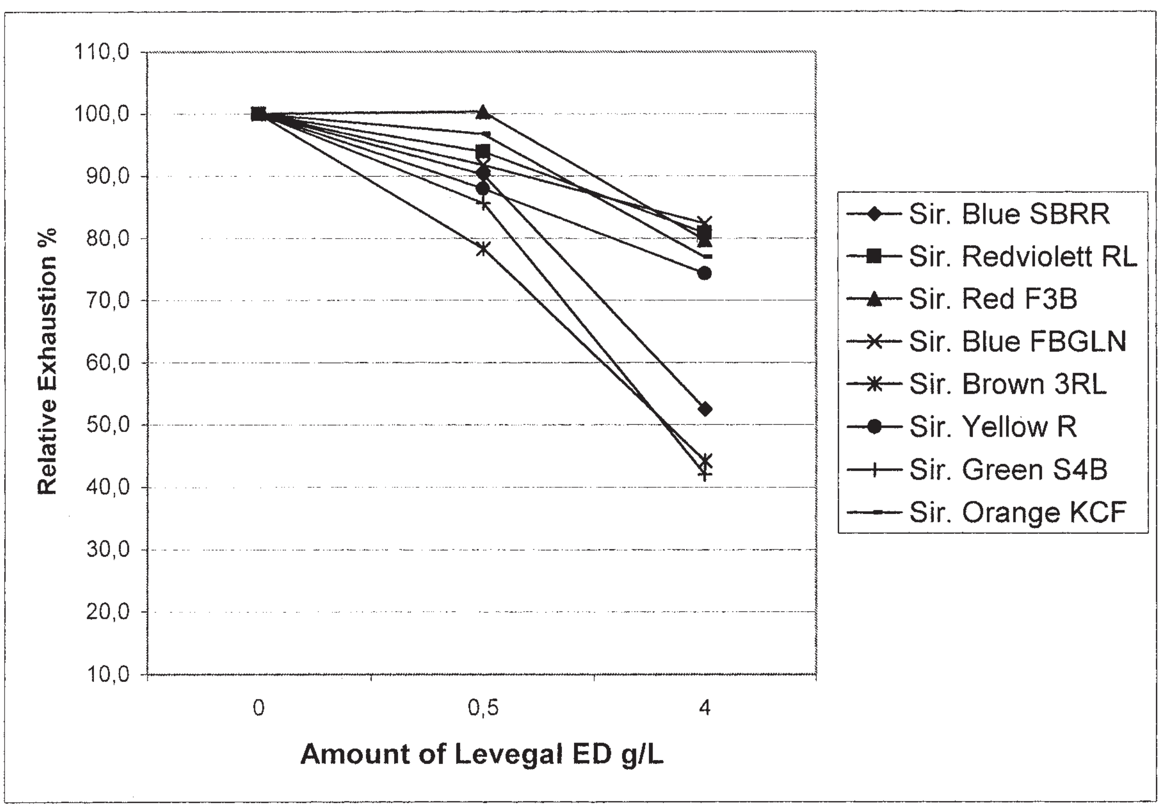


Figure 5 Relative degree of exhaustion in the existence of Levegal® ED.

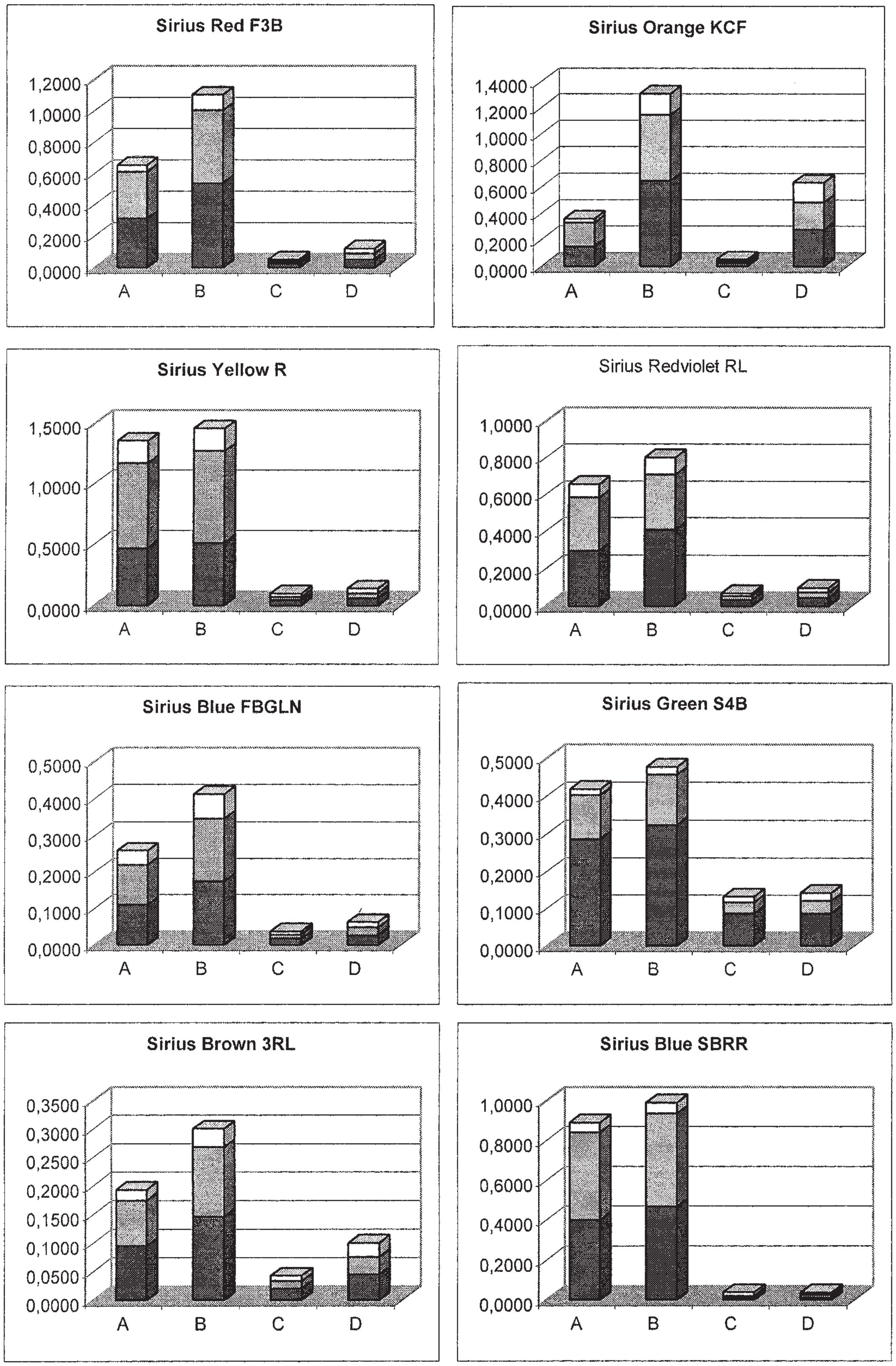
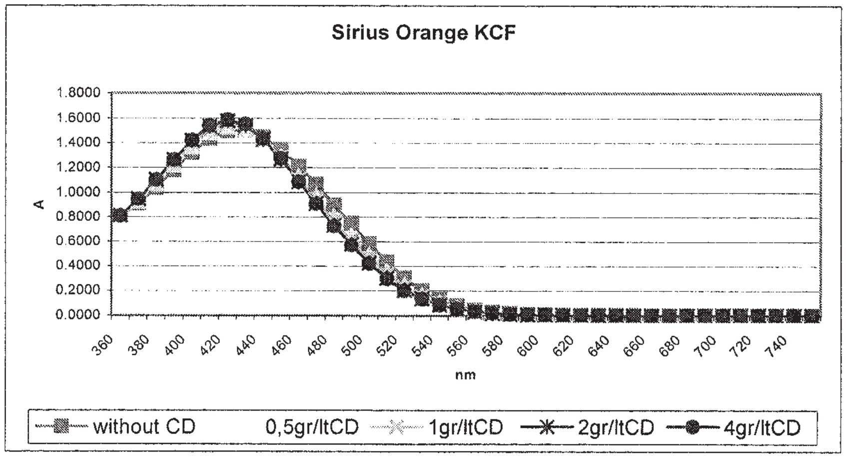
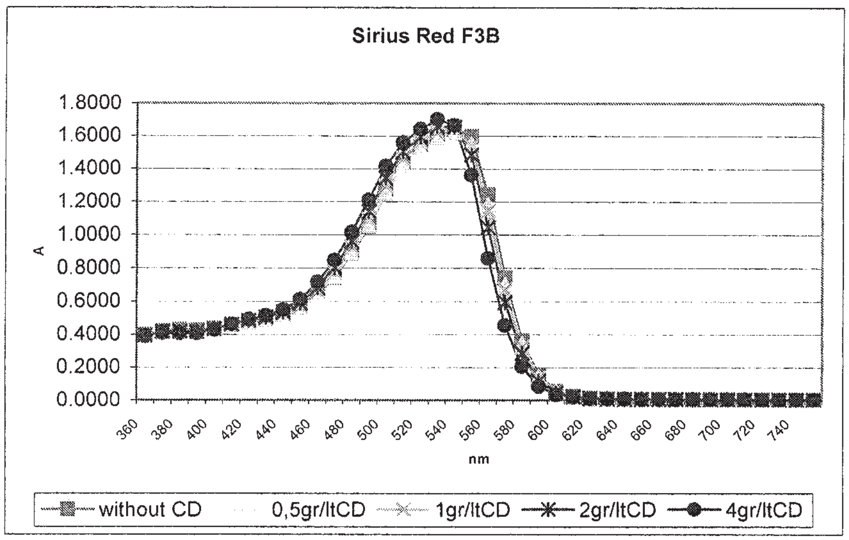


Figure 6 Total absorbance values of three washing liquors, ■ first washing ▩ second washing □ third washing.

reductively, that is, the effect of an equilibrium reaction took place with the aid of the attraction force that is not covalent between dyestuff and β-cyclodextrin, rather than the chemical stripping of the dyestuff. Measurements of color of washed samples and the influence of β-cyclodextrin, which is not in the same





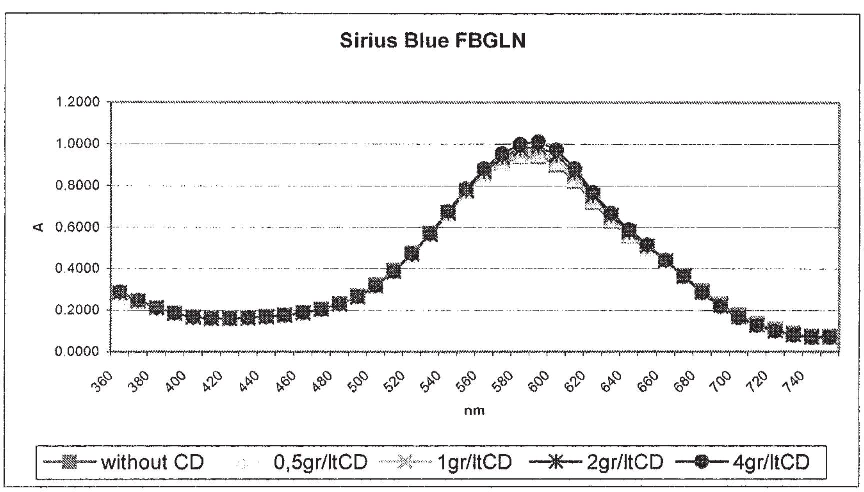


Figure 6 (*Continued from the previous page*)

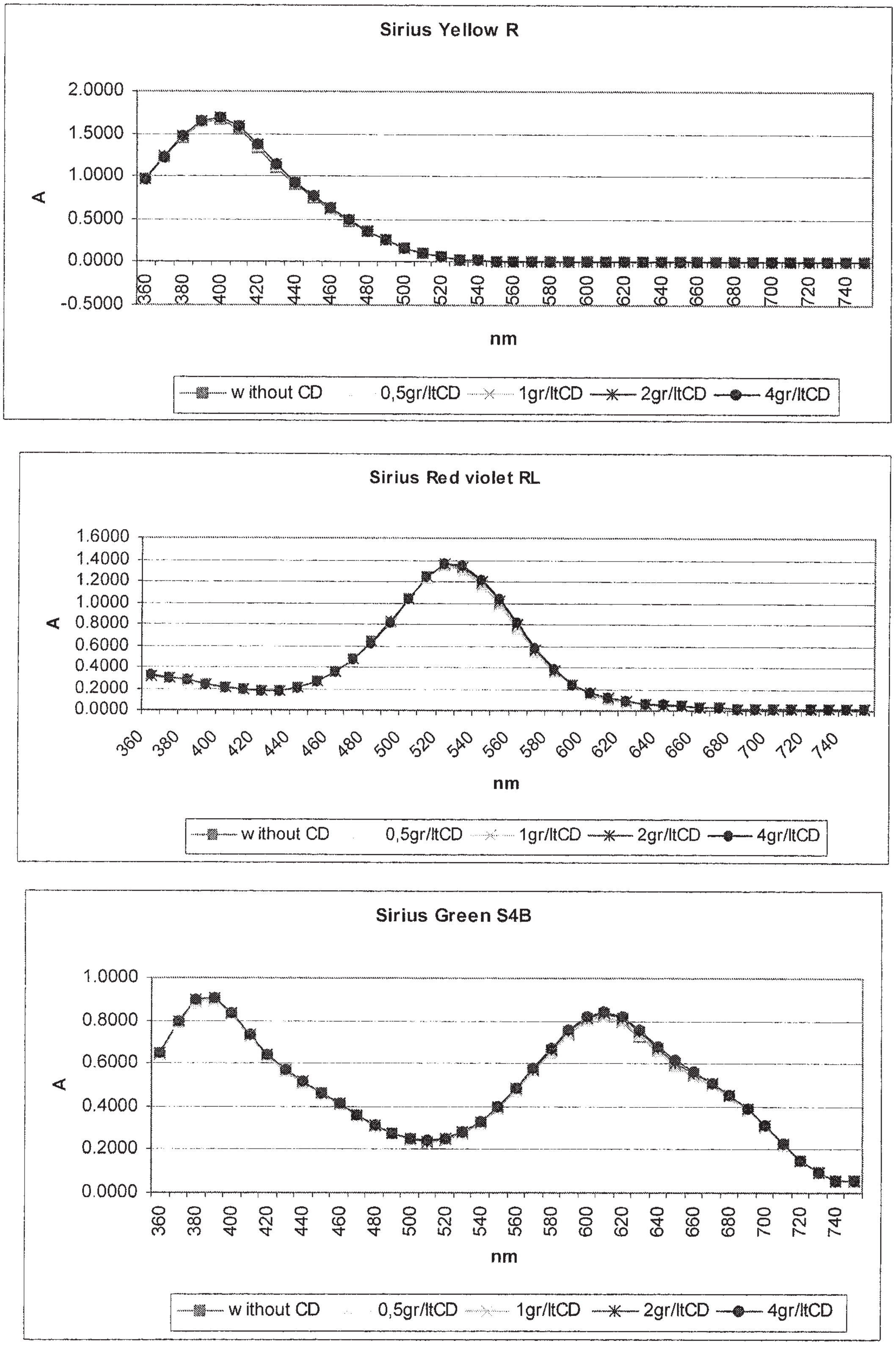


Figure 6 (*Continued from the previous page*)

degree for each dyestuff, support this opinion. Total color difference (ΔE) values of washed samples calculated from values of L^*, a^*, b^* of CIELAB system (eq. (3)) are shown in Table IV.

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (3)$$

where ΔE is the total color difference between reference and sample, ΔL^* is the difference of lightness coordinates

TABLE IV
Total Color Differences after Washings Realized with Different Recipes

Dyestuff	Total Color Differences[a] (Δ*E*)	
	Distilled Water (Reference: Recipe A, Sample: Recipe B)	Salt Water (Reference: Recipe C, Sample: Recipe D)
Sirius Red violet RL (520 nm)	0.3	0.4
Sirius Red F3B (540 nm)	0.4	0.5
Sirius Brown 3RL (470 nm)	0.4	0.1
Sirius Orange KCF (420 nm)	1.5	1.2
Sirius Yellow R (400 nm)	0.4	0.4
Sirius Green S4B (390 nm)	0.3	0.3
Sirius Blue SBRR (580 nm)	0.1	0.1
Sirius Blue FBGLN (590 nm)	0.6	1

[a] Δ*E* values are the average of three measurements.

between reference and sample, Δa^* is the difference of redness–greenness coordinates between reference and sample, and Δb^* is the difference of yellowness–blueness coordinates between reference and sample.

In Table IV, total color difference (Δ*E*) has been determined separately for the media with and without salt. Washed samples are compared within themselves, because shade deviation has been observed, after the washings had realized in the presence of salt.

Color differences, seen in Table IV, give an idea about the increase of the absorbance together with the addition of β-cyclodextrin into the washing liquor, that is, the influencing degree of the dyestuff amount transferred into the liquor on the color of the fabric. If "1" is accepted as the acceptable limit value for (Δ*E*), it is seen that addition of β-cyclodextrin does not cause big color differences. Naturally expected color change will be more visible in case of a chemical reaction.

Shao *et al.* and Cramer informed that the presence of a complex formation within a dyestuff and cyclodextrin gives significant differences in the UV and visible spectrum of the dyestuff solution.[13,14] The result of spectrum measurements of eight dyestuffs in the absence and presence of different β-cyclodextrin concentrations are given in Figure 7. All dyestuff solutions were prepared at a concentration of 0.05 g/L to have the maximum absorbance value as 2.

It is seen that the presence of β-cyclodextrin affects the maximum absorbance wavelength and the absorbance values of Sirius Orange KCF, Sirius Red F3B, and Sirius Blue FBGLN. These changes in the spectrum measurements can give an idea about an interaction between dyestuff molecules and β-cyclodextrin. Also, the selectivity of these interactions can be clearly seen from both dyeing and washing trials; β-cyclodextrin influences same dyestuffs.

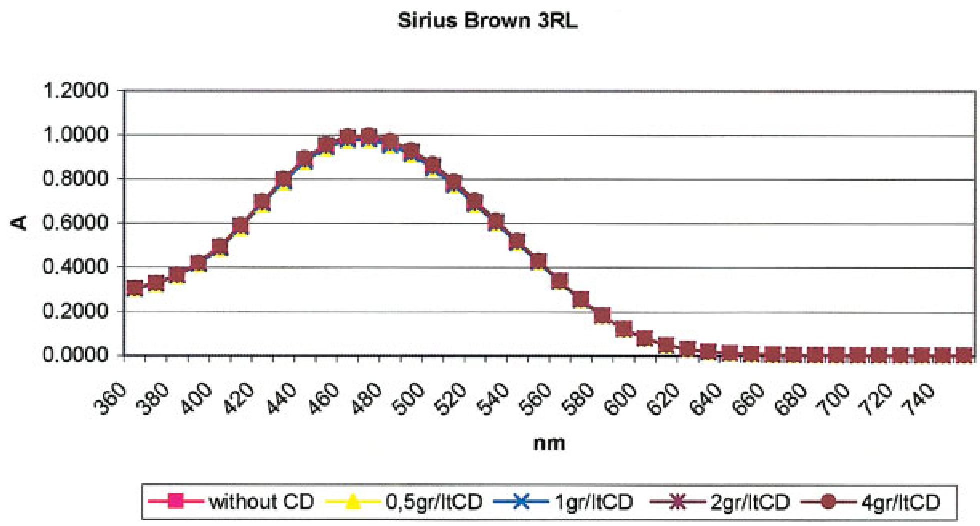
CONCLUSIONS

It is seen that, when cellulose is dyed with direct dyestuff according to exhaust method, usage of β-cyclodextrin affects the dyeing efficiency in a negative way. The reason for this is that β-cyclodextrin confines the dye molecules into its hydrophobic space in aqueous solutions, and that dye molecules in the space of cyclodextrin are released, as the dye molecules in free state are attracted by the polymers. Because of this property, cyclodextrins can be used as a leveling agent/retarder having affinity to dyestuff. However, this effect is not observed when cyclodextrin does not form complex with dyestuff. Consequently, usage of β-cyclodextrin is limited to several dyestuffs, in the area under consideration.

When the chemical structures of dyes are examined, it is seen that Sirius Orange KCF has the smallest structure, and the other dyes have long and planar structures, which is the characteristic of direct dyestuff. β-Cyclodextrin does not form complex by settling into the hydrophobic inner region of these dyes because of their molecular size and substituents on the ends. As a result of this, it is observed that there is not an important change in the degree of exhaustion when β-cyclodextrin exists. Even though Sirius Red F3B has a big structure, the reason of β-cyclodextrin having an effect on its degree of exhaustion in a certain degree can be explained by the nonexistence of substituents that prevent complex formation on both ends of the molecular structure. Shao *et al.* (1996) have showed that β-cyclodextrin molecules settle on both ends of Direct Red 80 (Sirius Red F3B) during complex formation.[13]

It is observed that commercial leveling agent having affinity to fiber has a more uniform effect with regard to β-cyclodextrin, even though the effect is not the same for all dyes. The amount of β-cyclodextrin used to obtain the same effect for certain dyes are much more than that for the commercial product. When the prices of β-cyclodextrin and commercial product are compared, it is seen that β-cyclodextrin is far away from being an alternative product because of its price.

Addition of β-cyclodextrin to the washing liquor causes the dyestuff to prefer the liquor in spite of the presence of salt, when dyes that interact with β-cyclodextrin are used. Secondary attraction forces are thought to take place in this case. Naturally, results will differ in



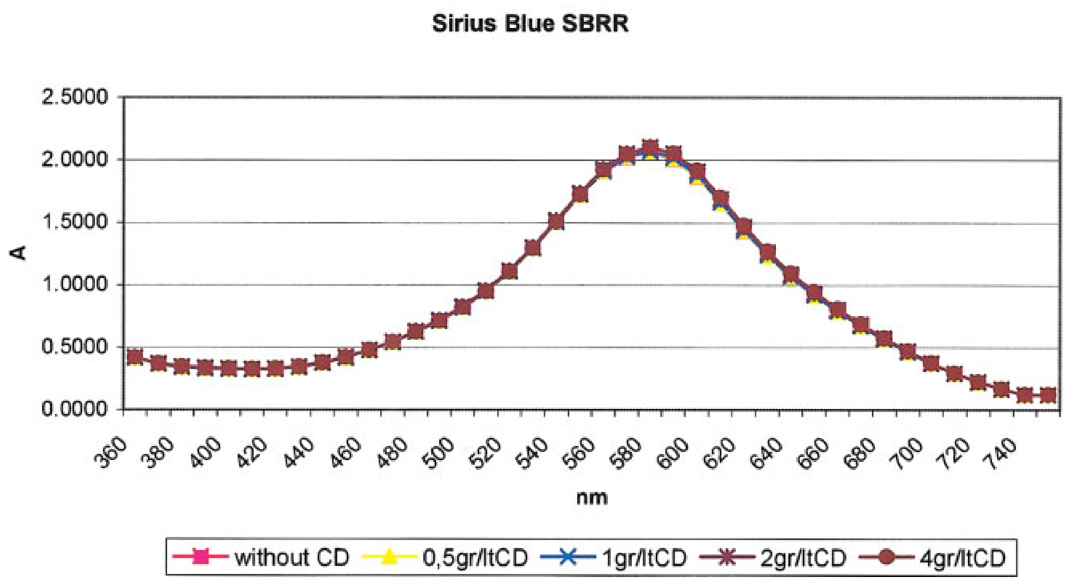


Figure 7 Absorbance measurements results of dyes at various β-cyclodextrin concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

connection with the concentrations of β-cyclodextrin and salt. β-Cyclodextrin must interact with the dyestuff for equilibrium. Degree of the change in equilibrium towards liquor is related with the interaction between β-cyclodextrin and dyestuff, in other words, with the degree of formation of complexes.

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