The effect of nonionic surfactant treatment on dyeing of cotton fabrics

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The effect of nonionic FN-10 surfactant treatment on dyeing characteristics of cotton fabrics dyed with direct and reactive dyes was studied. Using different methods, the presence of nonionic surfactants on the surface of treated samples and the possibility of surfactant to interact with the used dyes were investigated. The treated samples have better wettability and absorb more dye than untreated sample. Intensities of direct and reactive dyes are the highest on treated samples dyed in a solution with standard amount of salt, and the intensity increase can be considered as mutual contribution of salt effect and that of deposited nonionic surfactant layer on the increase of dye affinity for cotton.
Key words: *non-ionic surfactant, cotton, wetting, direct and reactive dye*

1. Introduction

Several classes of dyes are used for dyeing cotton, but in recent years, as the most important, stand out classes of reactive, direct and vat dyes, with a share of over 80 % in the consumption of cotton dyes [1]. Water soluble direct and reactive dyes have the advantage over non soluble vat dyes as they are more environmentally friendly and managing of technological dyeing procedure is simpler, therefore dyeing systems with these dyes are often studied in terms of the technological process improvements. Solutions of these dyes are poly disperse systems, representing an intermediate condition between real and colloid solutions. The state of dye in solution, fiber surface characteristics, addition of auxiliary chemicals and electrolytes are deciding parameters affecting dye yield from technological solution on a cotton substrate. Low affinity of direct and reactive dyes and repulsive forces on interface fiber surface/solution, require addition of large amounts of electrolyte that after dyeing arrives, together with non fixed dye, into waterways causing disruption of delicate biochemistry of aquatic organisms.

The purpose of physical and chemical modification processes is to increase the degree of exhaustion and fixation of dyes. The treatment with nonionic surfactants to improve dyeability of cotton has not been studied, although they are products of high biodegradability, which can be adsorbed on cotton and establish interactions with anionic dyes. By studying isothermal adsorption of a number of nonionic surfactants on cotton, high levels of adsorption, sufficient to create a dense monolayer on cotton, are observed [2]. In a number of published papers studied were interactions between dyes and nonionic surfactants [3-11]. The intensity and character of the interaction between dye and nonionic surfactant depends on surfactant concentration and surfactant and dye hydrophility. Interactions between dye ions and nonionic surfactant at surfactant concentrations below the critical micelle concentration (CMC) are less pronounced and can be interpreted by ionic interaction between the sulfo group and oxonium ion of nonionic surfactants. At high surfactant concentrations (> CMC) hydrophobic interactions occur between hydrophobic alkyl chains of surfactant and hydrophobic parts of dye [12]. Oxonium ion in nonionic surfactant appears when a water molecule binds on ether oxygen atom producing a partial cationic character of these products in the form of polyoxonium bases [13]. The presence of these types of ions is practically confirmed by measuring the viscosity of an aqueous solution of a mixture of cationic and nonionic surfactants. In this binary system, a progressive viscosity decrease of an aqueous solution with increase of cationic surfactant mole fraction was observed, due to repulsive forces of cationic surfactant hydrophilic group and oxonium ion species of nonionic surfactant [14].

In this paper, cotton fabric was treated with non-ionic surfactants to enhance dyeing capabilities using direct and reactive dyes. Identification of nonionic agent on samples of cotton fabric was performed by scanning electron microscopy and by measuring wettability. The ability of surfactant to interact with dyes was determined by measuring surfactant cloud point. The aim of this study was to determine the possibility of increased utilization of direct and reactive dyes on cotton fabrics by treatment with non-ionic surfactants.

2. Experimental

2.1. Materials

In this study, bleached cotton fabric having surface mass of 204,5 g/m^2 was used. Sample pretreatment was carried out using FN-10 nonionic agent (nonylphenol ethylenoxide) (Merima, Krusevac). Direct dyes C.I. Direct yellow 95 (Cuprophenil yellow 3GL200 %) and C.I. Direct Red 80 (Solophenil rot 3BL140 %) (Ciba-Geygi, Switzerland), and monochlorotriazine reactive dyes C.I. Reactive Red 45:1 (Ostazin red H-3B) and C. I. Reactive Blue 5 (Ostazin Blue H-BR) (Chemapol, Czech Republic) were used for dyeing. The dyes were commercial quality.

2.2. The treatment of cotton fabric with nonionic surfactant

The cotton fabric was treated in the FN-10 solution with concentration of 1 g/dm^3, using exhaustion method at 50 °C, and bath ratio 1:30. Treatment time was different and was at 10 minutes, 20 minutes and 30 minutes. The treated samples were washed with cold distilled water three times, and dried at room temperature. Tab.1 shows the labels of samples, and treatment parameters.

2.3. Analysis of the samples by scanning electron microscopy

For the characterization of surface morphology changes a scanning electron microscope JEOL JCM 5300 (Jeol-Japan) was used. The samples were prepared for scanning using standard preparative technique of sputter coating of gold which creates a conductive surface, on a cathode gold sputter for 5 minutes.

2.4. Wettability measurement

To assess the wettability of fabric, water drop test method according to AATCC standard was used [15]. According to AATCC test method 39-1980 the wetting time was determined by placing a drop of water on stretched fabric sample from a burette from a distance of 1 cm from the fabric. Time necessary for water mirror to disappear on the sample surface (i.e. the time it takes for water drop to lose its reflection of light) is recorded as the wetting time (in seconds). The results are the average of at least 5 measurements.

2.5. The dyeing of samples

Dyeing of 4 g samples were performed in a laboratory apparatus Ahiba type G7B (Ahiba, Switzerland) with a vertical movement of material with a bath ratio of 1:45. In all tests, the dye concentration was 1 % of material mass. Dyeing with direct dyes was performed at 98 °C for 60 minutes, and the temperature was reached in 30 minutes, starting from room temperature. The dyeing was carried out both without the addition of electrolytes and with the addition of 20 % of $Na_2 SO_4$ based on material. After dyeing, the samples were washed with hot distilled water and with cold distilled water and dried at room temperature.

Dyeing with reactive dyes was performed by all-in method at 80 °C for 2 h, and temperature was reached in 20 minutes, starting from room temperature. The concentration Na_2CO_3 was 20 g/dm^3, while the concentration of Na_2SO_4 was 10 and 50 g/dm^3. After dyeing the samples were washed five times with cold distilled water and divided into two portions. One portion of the samples was treated in a 2 g/dm^3 solution of anionic washing agent Jugopon 50 (Chromos, Croatia) at 95 °C for 10 minutes. After hot and cold rinsing and drying at room temperature, measurements of color were carried out on both sides of samples on Spectraflash SF600X reflectance spectrophotometer (Datacolor, USA) for determination the color intensity (K/S), fixation degree F and percentage of color intensity increase (I).

Color intensities (K/S) were determined at wavelengths of maximum absorption for used dyes (C.I. Direct Yellow 95, λ = 400 nm, C.I. Direct Red 80, λ = 550 nm, C.I. Reactive Red 45:1, λ = 550 nm; C.I. Reactive Blue 5, λ = 630 nm) using Kubelka-Munk equation (1):

Tab.1 Designation of samples and treatment parameters

Mark	Treatment
NT	Untreated cotton fabric
A	Treatment with solution FN-10 c = 1 g/dm^3, 10 min
B	Treatment with solution FN-10 c = 1 g/dm^3, 20 min
C	Treatment with solution FN-10 c = 1 g/dm^3, 30 min

$$\frac{K}{S}=\frac{(1-R)^2}{2R} \qquad (1)$$

where: K – absorption coefficient, S – scattering coefficient, R – reflection of D65/10 light.
Fixation degree was calculated from equation (2):

$$F=\frac{\left(\frac{K}{S}\right)_T}{\left(\frac{K}{S}\right)_0}\cdot 100 \qquad (2)$$

where subscript T refers to the fabric treated in the solution of washing agent and subscript 0 to non treated fabric.
The percentage of color intensity increase (I) on surfactant treated sample compared to non treated sample was calculated from the following equation:

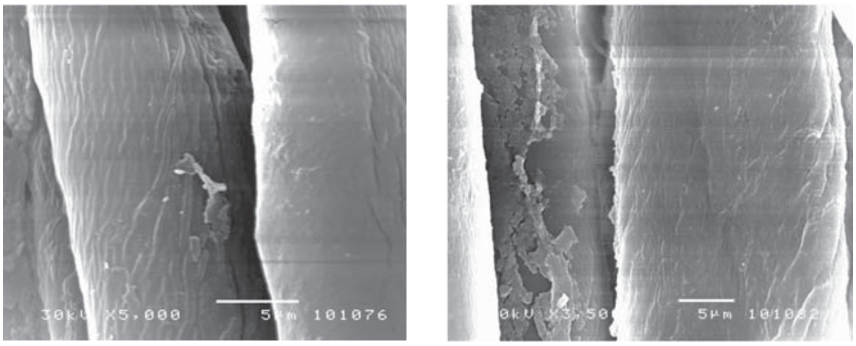
$$\text{I}=\frac{(K/S)_t-(K/S)_o}{(K/S)_o}\cdot 100\ [\%] \qquad (3)$$

where subscript t refers to treated fabric samples and subscript o to non treated fabric samples.

3. Results and discussion

3.1. Surface morphology

The surface structure of cotton fiber was tested using scanning electron microscope to assess the effect of non ionic surfactant treatment on surface morphology on a micro scale. Fig.1a) shows a micrograph of the surface of non treated cotton fiber displaying a system of shallow parallel groves. Fig.1b) is a micrograph of the surface of treated fibers. Based on the micrographs of modified fibers it can be concluded that there are no major changes in surface morphology, although the fiber surface, compared to untreated cotton fiber, is slightly coarser due to depositions of nonionic surfactant. Regardless of the increased surface roughness of modified cotton fibers, it can be said that the treatment with nonionic agents did not affected the physical structure of fibers so that the hand of samples tested remained unchanged, which is an advantage of this process compared to polymer treatment which often causes a certain stiffening of fabrics.



a) b)

Fig.1 Micrograph of: a) untreated cotton and b) cotton treated with FN-10 1g/dm3 solution

3.2. Wettability of fabrics

Wetting and absorption of liquids are essential in industrial processes such as dyeing and finishing, but also for functional and exploitation properties of textile products. Wetting, transport and retention of liquids in porous textile materials are complex phenomena that depend on the fiber surface morphology and geometry of pores in fabric. Attractive forces on fiber-liquid contact surface cause wetting fibers and changes in chemical composition and surface morphology of the fiber and fabric pore structure can modify hydrophilic properties of the fabric.

Fig.2 shows the results of absorption of water drops for untreated samples and samples treated with non-ionic surfactant. Time of absorption of water droplets was significantly lower on the treated samples compared to untreated samples. On treated samples the wetting time had approximate values and it can be said that treatment duration was not significant for changing hydrophilic properties of modified samples. Rapid wettability increase of treated samples can be attributed to nonionic surfactant layer deposited on fabric surface, which additionally enhances attractiveness of water drops due to hydrogen interactions. By increasing the wettability of fabrics, the speed and degree of swelling increase, which is favorable for dye penetration into the internal zone of fibers.

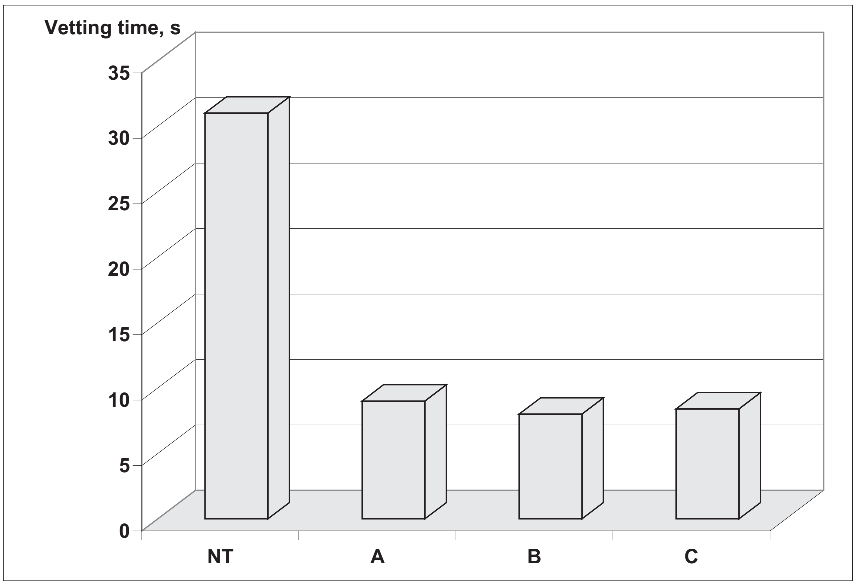


Fig.2 The wettability of cotton fabric after treatment with non-ionic surfactant

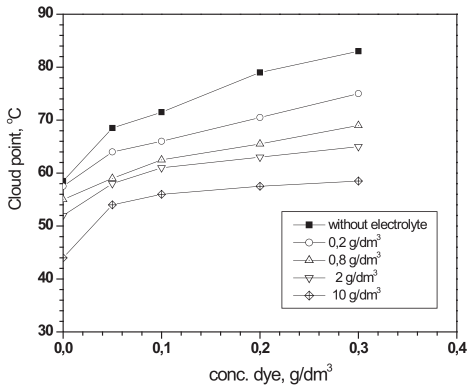


Fig.3 The effect of C.I. Direct Yellow 95 dye concentration on cloud point of FN-10 at various concentrations of Na_2SO_4

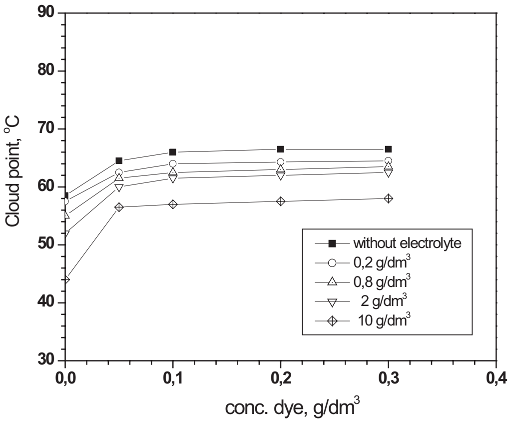


Fig.4 The effect of C.I. Direct Red 80 dye concentration on cloud point of FN-10 at various concentrations of Na_2SO_4

3.3. Dye/surfactant interactions

Fig.3-6 show diagrams of cloud point vs. dye concentration for different concentrations of electrolytes. Cloud point can be considered as a criterion of dye/surfactant interaction, i.e. the higher the cloud point the more intense interaction. With direct dyes studied, the addition of dye in the absence of electrolyte contributes to the increase of cloud point. With C.I. Direct Yellow 95, the cloud point value uniformly increases with the increase of dye concentration and with C.I. Direct Red 80, after registered increase at minimum dye concentration, further increase of dye amount produces no significant change in the value of cloud point. It is obvious that C.I. Direct yellow 95 gives a stronger interaction with the non-ionic surfactants, probably as a result of dye chemical structure.

With reactive dyes too, the addition of dye in the absence of electrolyte increases the cloud point due to the interaction of surfactants and dye. Progressively, with increasing amounts of reactive dyes, the non-ionic surfactant cloud point increases

Tab.2 Dyeing results of cotton fabrics with direct dyes after treatment with non-ionic surfactant

Dye	Fabric	Without electrolyte			20 % Na_2SO_4		
		K/S	I [%]	Washing fastness	K/S	I [%]	Washing fastness
C.I. Direct Yellow 95	NT	1,54	-	3-4	5,92	-	3-4
	A	1,60	3,89	3-4	6,02	1,68	3-4
	B	1,77	14,90	3-4	6,03	1,85	3-4
	C	1,87	21,40	3-4	6,07	2,53	3-4
C.I. Direct Red 80	NT	1,16	-	3-4	6,37	-	3-4
	A	1,23	6,12	3-4	6,44	1,15	3-4
	B	1,29	11,20	3-4	6,56	2,96	3-4
	C	1,28	10,86	3-4	6,52	2,35	3-4

Tab.3 Dyeing results of cotton fabrics with reactive dyes after treatment with non-ionic surfactant

Dye	Fabric	10 g/dm³ Na_2SO_4				50 g/dm³ Na_2SO_4			
		K/S	I [%]	F [%]	Washing fastness	K/S	I [%]	F [%]	Washing fastness
C.I. Reactive Red 45:1	NT	0,63	-	0,81	4	1,48	-	0,78	4
	A	0,68	7,93	0,82	3-4	1,51	2,05	0,77	4
	B	0,91	45,03	0,81	3-4	1,59	7,43	0,78	4
	C	0,92	46,05	0,80	4	1,58	6,88	0,77	4
C.I. Reactive Blue 5	NT	0,78	-	0,80	4	1,47	-	0,80	3-4
	A	0,84	7,79	0,79	4	1,54	4,76	0,81	3-4
	B	0,90	15,68	0,78	4	1,56	6,12	0,80	4
	C	0,88	13,56	0,83	4	1,56	6,04	0,78	4

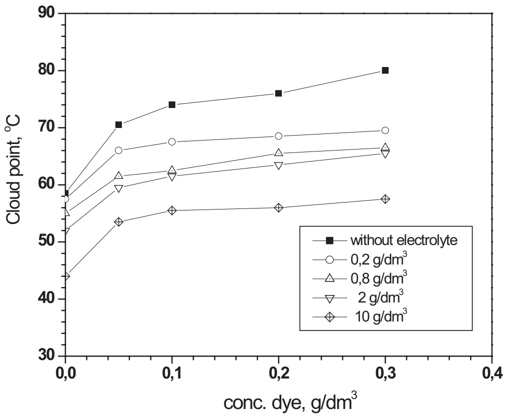


Fig.5 The effect of C.I. Reactive Red 45:1 dye concentration on cloud point of FN-10 at various concentrations of Na_2SO_4

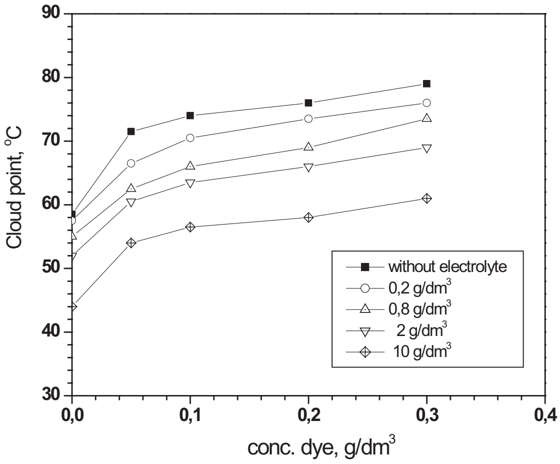


Fig.6 The effect of C.I. Reactive Blue 5 dye concentration on cloud point of FN-10 at various concentrations of Na_2SO_4

in the range of tested concentrations.

The increase of nonionic surfactant cloud point in the presence of direct and reactive dyes is the result of dye/surfactant interactions and also, creation of associates in which dye hydrophobic part is oriented towards surfactant micelle, while the hydrophilic part is directed towards the aqueous phase contributing to increased hydration of nonionic surfactant, which is manifested as an increase in cloud point of nonionic surfactants.

The addition of electrolyte reduces cloud point already at the lowest concentration of electrolyte (0,2 g/dm³) and by increasing electrolyte concentration the cloud point drops to values lower than those of surfactant solutions without additives. Reducing of cloud point suggests a reduced hydration of surfactant micelles due to the adsorption of electrolyte cation and neutralization of dye/surfactant associates, wherefore the enlarging of micelles and their final phase separation is enhanced at lower temperatures.

3.4. Dyeing results

Tab.2 and 3 show the dyeing results of cotton fabric with direct and reactive dyes in the presence of various amounts of salt after treatment with non-ionic surfactant FN-10. In the presence or absence of salt, untreated samples dyed with direct dyes have the lowest value of color intensity K/S (Tab.2). Untreated samples dyed in a bath containing 20 % Na_2SO_4 display significantly higher value of color intensity compared to samples dyed in a bath without salt, indicating the importance of using salt in conventional direct dyeing of cotton. The samples treated in FN-10 solution had higher color intensity and the percentage of color intensity increase for dye *I* which is higher on samples dyed in technological solution without salt. With C.I. Direct Yellow 95 higher increases in intensity of color were obtained. It can be said that the surface depositions of nonionic surfactant on cotton fabric contributed to higher absorption of direct dyes, due to possible dye/surfactant interactions. Regardless of the attraction of surfactants and dye, the presence of salt continues to play a major role in dye transfer to cotton, and it can be said that the surfactant layer cooperatively contributes to an increased yield of direct dyes. Surfactant treatment had not a negative impact on the stability of direct dyes, because similar values were obtained on all samples.

On fabrics too, dyed with reactive dyes, a positive effect of the treatment conducted with nonionic surfactant solution on the exhaustion and fixation of reactive dyes was observed (Tab.3). With reactive dyes also, intensity increase was higher on samples dyed in the presence of minimal amounts of salt (10 g/dm³). Greater percentage increase in the intensity of the color is obtained by using C.I. Reactive Red 45:1, which was found to generate stronger interaction with non-ionic surfactant.

It can be said that the attractive hydrophobic and hydrophilic interactions between direct and reactive dyes and nonionic surfactant deposits on cotton fibers, illustrated in Fig.7, contribute to the increased utilization of dye, and they are more important in systems without or only a with a minimum amount of salt.

With standard salt concentrations, the contribution of deposited nonionic surfactant is 2-7 % of the increase in color intensity, and in this respect dyeing characteristics of treated fabrics are the result of combined action of salt, which increases the chemical potential of dye in the solution and reduces fiber and surfactant zeta potential on the surface of fibers enhancing dye adsorption.

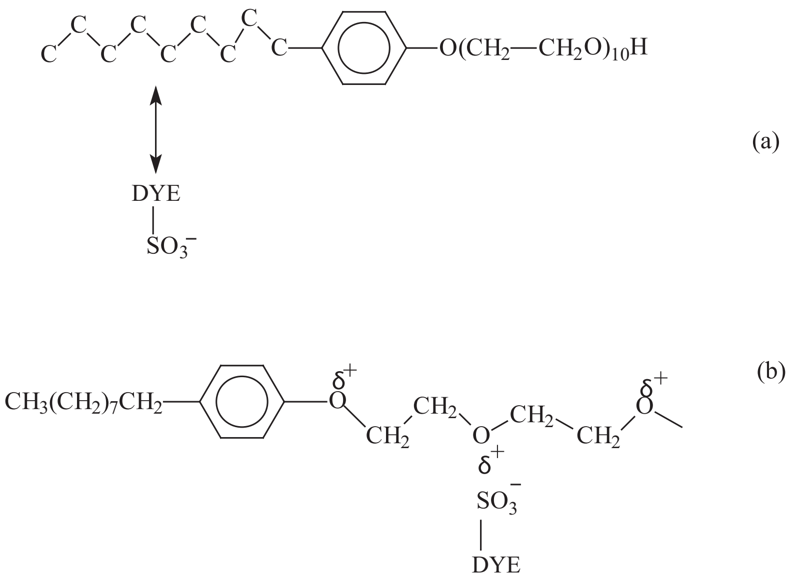


Fig.7 Attractive hydrophobic (a) and hydrophilic (b) interactions of FN-10/anionic dye

The degree of fixation and fastness have values similar those for untreated sample, which indicates the importance of surfactant layers for the adsorption of reactive dyes on fiber surface, with diffusion and fixation of dyes on cotton the same as in the conventional dyeing.

4. Conclusion

The main purpose of this paper is to investigate the increase of utilization of direct and reactive dyes by pretreatment of cotton fabric with nonionic surfactants capable of attractive interactions with dyes, which was confirmed by measuring the cloud point of surfactants. Surfactant layers deposited on the surface of cotton fibers, which were identified by scanning electron microscope, increase the wettability of cotton fabrics, facilitating the transport of technological solution through the fabric structure and diffusion of dye in the fiber. The dyeing of samples treated with salt produces higher color intensities compared to samples dyed in the presence of standard amounts of salt. With reactive dyes the same trend is observed, i.e. percentage increase in the color intensity is higher in the samples that were dyed with the addition of reduced salt concentration (10 g/dm^3). Based on these results it can be concluded that the attractive effects are more prominent in systems with lower affinity and can be regarded as complementary to the action of salt on dye exhaustion staining in dyeing systems having the same charge. This is confirmed by the fact that a larger percentage increase in the intensity is obtained on samples dyed with reactive dyes, which have a lower affinity for cotton compared with direct dyes.

In the presence of standard amounts of salt dye affinity is increased and more intense dyeings are produced. On samples treated with surfactants, recorded increase in the intensity of color can be considered as the contribution of cooperative action of nonionic surfactants and salts on dye adsorption. On all samples, standard dye fastness levels and approximate values of fixation degrees were recorded for reactive dyes suggesting that non-ionic surfactant has an importance for dye adsorption and diffusion and fixation of dyes takes place as in standard dyeing.

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