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The Influence of a Surfactant's Structure and the Mode of its Action During Reactive Wool Dyeing

Vpliv strukture tenzidov in načina njihovega delovanja na barvanje volne z reaktivnim barvilom

Abstract

The modes of actions of different surfactants during reactive wool dyeing using C.I. Reactive Red 120 was investigated at pH 3 and temperatures between 50 and 90℃. The studied surfactants included the following: the anionic surfactant sodium dodecylsulphate (SDS); the cationic surfactant n-dodecyltrimethylammonium bromide (DTAB); the nonionic surfactants Brij C10, Brij S10, Brij L23, Brij 58, Brij S20 and Brij S100; and the commercially available amphoteric product Albegal B. Compared with surfactant-free dyeing, SDS and Brij S100 slightly decreased the dye exhaustion after 360 minutes of dyeing, whereas the other studied surfactants significantly increased the dye exhaustion. The enhanced dye uptake was attributed to the adsorptions of the surfactants to the wool fibres, which increased the cationic characteristics and the hydrophilicity of the fibre surface. The surfactants facilitate dye fixation up to a dyeing temperature of 80℃ and decrease it at 90℃. The surfactants increased the *K/S* values and changed the CIELAB values of the dyeing. Albegal B exhibited the strongest effect.
Keywords: wool, reactive dye, surfactant, dye exhaustion, dye fixation

Izvleček

V raziskavi je bil proučevan način delovanja različnih tenzidov pri barvanju volne z reaktivnim barvilom C.I. Reactive Red 120 pri pH 3 in temperaturah od 50 do 90 °C. Uporabljeni so bili naslednji tenzidi: anionski tenzid natrijev dodecilsulfat (SDS); kationski tenzid n-dodeciltrimetilamonijev bromid (DTAB); neionski tenzidi Brij C10, Brij S10, Brij L23, Brij 58, Brij S20 in Brij S100; in tržno dostopen amfoterni proizvod Albegal B. V primerjavi z barvanjem brez tenzidov, sta SDS in Brij S100 nekoliko zmanjšala izčrpanje barvila pri 360 minutah barvanja, medtem ko so ostali proučevani tenzidi bistveno povečali izčrpanje barvila. Povečano navzemanje barvila smo pripisali adsorpciji tenzidov na volnena vlakna, zaradi povečanja kationskega karakterja in hidrofilnosti površine vlakna. Tenzidi so pospešili fiksiranje barvila pri temperaturah barvanja do 80 °C in zmanjšali fiksiranje pri 90 °C. Tenzidi so povečali vrednosti K/S in spremenili CIELAB vrednosti obarvanj. Albegal B je pokazal najmočnejši učinek.
Ključne besede: volna, reaktivno barvilo, tenzid, izčrpanje barvila, fiksiranje barvila

1 Introduction

The mechanisms of surfactants working as levelling agents during reactive wool dyeing have received much attention over recent years due to skittery dyeing [1], which represents a serious technological problem. Surface active agents (surfactants) used as levelling agents during reactive wool dyeing can be dye- or fibre-substantive regarding their ionic activities. Non-ionic surfactants are usually dye-substantive and form water-soluble dye-surfactant complexes in the dyebath, whereas ionic agents are

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either dye- or fibre-substantive. If the surfactant is fibre-substantive, the surfactant and the dye compete for the fibre. In contrast, a dye-substantive surfactant can form complex with the dye and therefore does not compete with the dye for the fibre [2]. Within wool fibres, the differences in dyeabilities can be noticed as a consequence of their chemical and morphological heterogeneities [3, 4]. Wool fibres consist of a complex mixture of different polypeptides, which cause local hydrophobicity in the fibre molecules. Furthermore, the cuticles' hydrophobicity form a water-repellent barrier that prevents the dyeing bath from penetrating into the fibres. Uneven dyeing is also caused by the differences between the relatively hydrophobic roots and the weathered hydrophilic tips of the fibres. Therefore hydrophilic reactive dyes preferentially adsorb on the tips of the wool fibres and covalently bind to the wool reactive groups before level dyeing is achieved [1]. To avoid unevenness within the fibre during reactive wool dyeing, special complex amphoteric and weakly cationic levelling agents have been developed simultaneously with the synthesis of the reactive dyes. These special surfactants, which have an affinity to both dye and fibres [2], should enhance dye exhaustion and fixation, promote dye migration, act as retarding agents and prevent tippy wool dyeing [1]. It is assumed that the surfactant complexes with the dye in the dyebath at low temperatures permit a more even and extensive dye exhaustion on the surface of the wool fibre. As the dyebath temperature is increased, the dye-surfactant complex breaks down, which allows the dye to penetrate and react with the fibre functional groups [1]. Many publications [5–16] address wool dyeing with acid and reactive dyes in the presence of levelling agents. These studies have intensively investigated the influences of different parameters, such as the dye and the surfactant chemical structure, pre-treatment of wool fibres and dyebath pH and temperature, on the dyeing properties. For wool dyeing with the reactive dyes, the more effective levelling agents, including amphoteric surfactants [7, 11, 12, 16], are ethoxylated aliphatic amines [1]. This special class of surfactants is thought to overcome tip/root fibre unevenness by forming a hydrophobic complex with the dye that has an affinity for the hydrophobic root of the wool fibre. The differing degrees of adsorption to the tips and roots balance the dye distribution on the fibre surface and the penetration into

the wool fibres, which leads to greater dye migration [8]. In the literature [8, 16], three possible mechanisms have been proposed for explaining the actions of amphoteric surfactants during reactive wool dyeing and their influences on tip/root levelling: the dye complex mechanism, fibre mechanism, and surface mechanism. The dye complex mechanism states that the formation of dye-surfactant complexes increases their affinity for the more hydrophobic root of the wool fibre. The fibre mechanism states that the presence of the surfactant increases the mobility of the dye inside the fibre by causing swelling of the fibre, thereby changing the charge density or competing for binding sites. The surface mechanism states that the surfactant accumulates at tips and roots to different extents, thereby improving the dye distribution between these two parts of the wool fibre. The prevalence of one mechanism over the other two depends on the fabric's pre-treatment and dyebath pH, and the temperature [16].

In the presented paper, the influences of a series of surfactants that differ amongst each other in structure and ionic activity on the dye adsorption during the reactive wool dyeing was investigated with the aim of elucidating their modes of action within the dye-surfactant-fibre system. The study also exposes which mechanism prevails from among the studied surfactants and is responsible for the rise or reduction of the adsorption of a very hydrophilic bis(aminochlorotriazine) dye, CI Reactive Red 120, to wool fabric. In the research model cationic, anionic and non-ionic surfactants were used. For comparison, the commercially available amphoteric auxiliary product Albegal B was used, which has been introduced for Lanasol dyes by Ciba-Geigy. It was assumed that the structure of the surfactant and its ionic activity would affect the dye exhaustion and fixation and that the dye adsorption would also be influenced by the dyeing time and temperature.

2 Materials and methods

2.1 Materials

Voltaire wool fine natural, already prepared for dyeing, was kindly supplied by Whaleys (Bradford) Ltd. The homobifunctional bis(aminochlorotriazine) reactive dye C.I. Reactive Red 120 (RR120), the anionic surfactant sodium dodecylsulphate (SDS), the
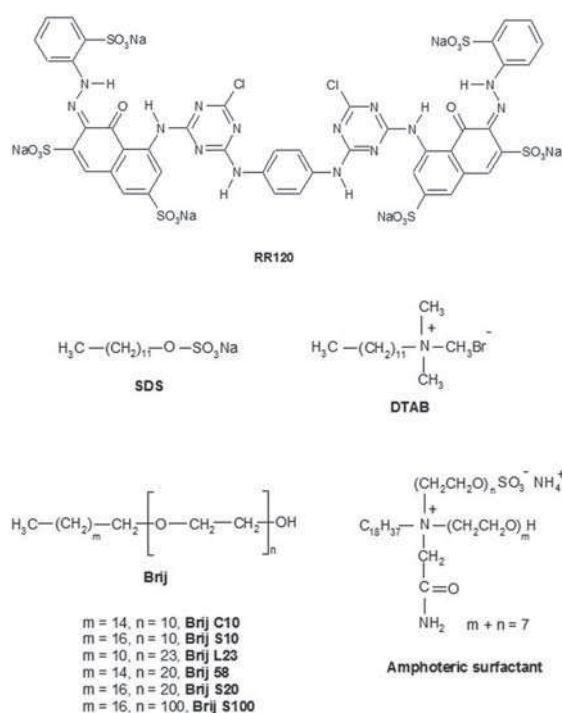
Figure 1: Chemical structures of the dye and surfactants used in the research

cationic surfactant n-dodecyltrimethylammonium bromide (DTAB) and the non-ionic surfactants polyoxyethylene (10) cetyl ether (Brij C10), polyoxyethylene (10) stearyl ether (Brij S10), polyoxyethylene (23) lauryl ether (Brij L23), polyoxyethylene (20) cetyl ether (Brij 58), polyoxyethylene (20) stearyl ether (Brij S20) and polyoxyethylene (100) stearyl ether (Brij S100) were commercial products

from the Sigma-Aldrich Chemical Company. A commercial amphoteric levelling agent, Albegal B, was kindly provided by Huntsman. The surfactants and the dye were not purified prior to use. A citric acid/disodium hydrogen phosphate buffer, the McIlvaine buffer system, was used to control the dyebath pH [17]. The structural formulas of the dye and surfactants are presented in Figure 1; note that the typical structure of the amphoteric surfactants is presented rather than the real structure of Albegal B [1].

2.2 Dying procedure

Time dependence studies

All dyeings were performed in a Labomat laboratory dyeing machine (Mathis, Switzerland) with stainless steel beakers. A wool fabric sample (2 g) was dyed with 2% omf RR120 at 50°C using a 150:1 liquor ratio (LR). The pH was adjusted to 3 using the McIlvaine buffer and monitored using an Iskra MA 5740 pH metre with a WTWSenTix 81 electrode. The dye solutions were prepared with and without ionic (DTAB, SDS), non-ionic (Brij C10, Brij S10, Brij L23, Brij 58, Brij S20, Brij S100) and amphoteric (Albegal B) surfactants using deionised water. The surfactant concentrations were 5.0×10^{-3} mol/L for non-ionic surfactants (above the critical micelle concentration, c.m.c.), 1.0×10^{-4} mol/L for ionic surfactants (below the c.m.c.) and 1% omf for Albegal B. The c.m.c., cloud point and HLB values of surfactants used in this research are collated in Table 1.

Table 1: Critical micelle concentration (c.m.c.), cloud point and HLB values of surfactants used in the research

Surfactant	c.m.c.[a] [mol/L]	Cloud point[b] [°C]	HLB[c]
DTAB	1.6×10^{-2}	/	/
SDS	8.2×10^{-3}	/	/
Brij C10	2.0×10^{-6}	74	12.9
Brij S10	3.0×10^{-6}	68	12.4
Brij L23	6.0×10^{-5}	> 100	16.9
Brij 58	7.0×10^{-6}	> 100	15.7
Brij S20	5.7×10^{-6}	> 70	15.3
Brij S100	2.0×10^{-5}	~ 100	18.8

[a] Values of c.m.c. in aqueous solution at 298 K were obtained from References 18 and 19.

[b] Values of Cloud point were obtained from References 20 and 21.

[c] Values of HLB were obtained from Reference 19.

Each dyeing was performed in two sets, and the average values were taken to minimise the random error. The dyeing method is presented in Figure 2. At the end of the dyeing, the samples were removed and allowed to dry in the open air.
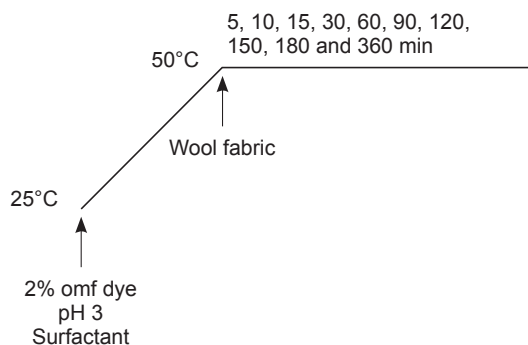

Figure 2: Dyeing method for the time dependence studies

Temperature dependence studies

Dyeings with RR120 (2% omf) and with and without DTAB, Brij S10 and Albegal B were performed in a Labomat dyeing machine with stainless steel beakers at four dyeing temperatures (60, 70, 80 and 90°C) for 120 min at pH 3 using a 150:1 liquor ratio. The fabric sample masses and surfactant concentrations were the same as those used in the time dependence studies. The dyeing method is shown in Figure 3. At the end of the dyeing, the samples were removed and allowed to dry in the open air.
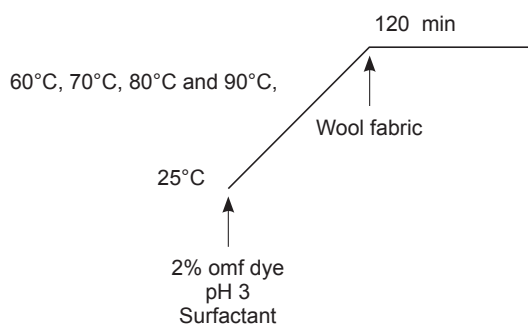

Figure 3: Dyeing method for the temperature dependence studies

Measurements of dye exhaustion and fixation

The extent of the RR120 exhaustion (*%E*), which is a function of the dyeing time and temperature, was calculated using the following equation:

$$\%E = \left(\frac{A_0 - A_f}{A_0} \right) \times 100 \tag{1},$$

where A_0 and A_f are the absorbances at the λ_{max} of the dye in the dyebath before and after dyeing, respectively. The absorbance was determined at room temperature using a Varian Cary 1E UV-Visible Spectrophotometer with 1-cm cells except for the dye-baths containing Brij S10 or Brij C10, for which the absorbance was measured at 50°C because of the low surfactant solubility at room temperature.

The extent of RR120 fixation (*%F*) to the wool fibres was determined by stripping the unfixed dye from the dyed material using a 20% aqueous pyridine solution. This stripping treatment was performed repeatedly using fresh aqueous pyridine solution until no further dye was removed. After stripping, the samples were rinsed with water and allowed to dry in air. The value of *%F* was calculated as follows:

$$\%F = \frac{(K/S)_2}{(K/S)_1} \times 100 \tag{2}$$

In Eq. 2, the indices 1 and 2 denote the colour strength (*K/S*) of the dyeing determined before and after stripping, respectively. The *K/S* value was determined from the reflectance (*R*) measurements of the dyed samples at the λ_{max} of the dye (550 nm for RR120) using a Datacolor Spectraflash SF 600 Plus-CT spectrophotometer under D65 standard illumination and a 10° standard observer, with the specular component included. A 30-mm aperture was used. The samples were conditioned according to ISO 139 before measurements. Ten measurements of *R* were obtained for each sample using four layers of the sample, and the average value was determined. *K/S* was calculated using the following equation:

$$K/S = (K/S)_d - (K/S)_u = \left(\frac{(1-R)^2}{2R} \right)_d - \left(\frac{(1-R)^2}{2R} \right)_u \tag{3},$$

where *K* represents the absorption coefficient, *S* is the scattering coefficient for the colorant and the indices *d* and *u* denote the *K/S* values of the dyed and undyed wool fabric, respectively.

The overall fixation efficiency (*%T*), which describes the amount of exhausted dye (*%E*) that has been fixed (*%F*), was calculated using the following equation:

$$\%T = \frac{\%E \times \%F}{100} \tag{4},$$

Measurements of colour coordinates

The CIELAB values were determined at 10 points on the individual dyed sample using a Datacolor Spectraflash SF 600 Plus-CT spectrophotometer under the same conditions used for the K/S determination, except that a 9-mm aperture was used. From the a^* and b^* values, chroma (C^*_{ab}) and hue (h_{ab}) were calculated.

Absorption spectra of the dye-surfactant mixtures

The visible absorption spectra of RR120 in the presence of SDS, DTAB, Albegal B, Brij C10, Brij S10, Brij L23, Brij58, Brij S20 and Brij S100 were recorded at 50°C on a Varian Cary 1E UV-Visible spectrophotometer using 1-cm cells. All solutions were prepared in buffer solution of pH3. The RR120 concentration was 0.0667 g/L. The surfactant concentrations were as follows: SDS and DTAB, 1.0×10^{-4} mol/L; Brij C10, Brij S10, Brij L23, Brij 58, Brij S20, Brij S100, 5.0×10^{-3} mol/L; and Albegal B, 0.0667 g/L. For non-ionic surfactants, additional spectra were recorded for surfactant concentrations of 5.0×10^{-5} and 5.0×10^{-4} mol/L.

3 Results and discussion

3.1 The influences of surfactants on dye exhaustion

In order to study the influence of the surfactant structure and its ionic activity on the dye exhaustion (*%E*), a series of dyeings of wool fabric with 2% omf of dye RR120 was performed at pH 3 and 50°C with and without the surfactants (Figure 4).

A 50°C dyeing temperature was chosen because it is the typical starting temperature for reactive wool

dyeing, at which point the levelling action of the surfactant is of great importance. In the study, a model dye RR120 of a known structure was used. RR120 is a typical representative of homo bi-functional mono-chlorotriazine (MCT) dyes, originally produced for high temperature exhaust dyeing of cellulosic fibres. Even though the dye is not suitable for wool dyeing in practice, several reliable scientific studies have been conducted on the basis of this dye [11, 12, 22]. Dyeing of untreated wool is usually performed in a slightly acidic dye-bath. The pH is determined by the depth of the dyeing required, therefore full depths are dyed at pH 5–5.5 and paler depths at pH 5.5–6.0. [1]. According to our preliminary thermodynamic study about the influence of pH on the extent of exhaustion of RR120 onto the wool fabric at 50°C, the highest value of the extent of dye exhaustion was achieved at pH 3. Thus this pH was used in the research. At pH 3, the wool fibres acquire an overall positive potential. The basic residues, such as arginine, lysine, histidine and N-terminal amino groups, are largely protonated, whilst acidic residues, such as aspartic acid, glutamic acid and C-terminal carboxylated groups, are undissociated [11]. Therefore, sulphonated dyes, including RR120, can be adsorbed to the protonated amino groups by electrostatic interactions. Sulphonate residues present in RR120 enable dye to behave like acid dyes when applied to wool fibre under acidic conditions [11, 23]. As RR120 contains 6 sulphonate groups in its structure, it is very hydrophilic and would thus have a very low affinity to wool [12]. The dye RR120 could, due to its relatively large molecular size (Mw = 1469.98 g/mol), also have difficulty in penetrating the wool fibre at low temperatures, as the fibre surface barrier and consequently ring-dyeing can be produced. The latter was established by Cho
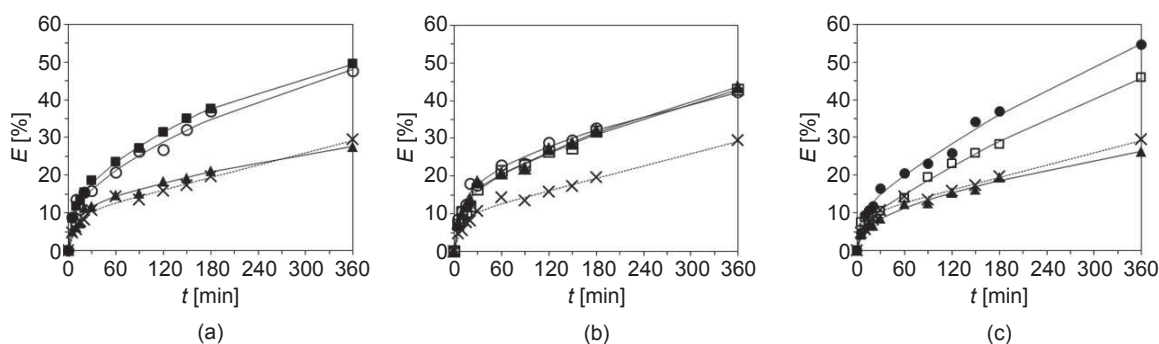

Figure 4: Extent of exhaustion (%E) of RR120 with and without surfactants at pH 3 and 50°C: (a) × No surfactant, ▲ SDS, ○ DTAB, ■ Albegal B, (b) × No surfactant, ○ Brij L23, ▲ Brij 58, □ Brij S20, (c) × No surfactant, □ Brij C10, ● Brij S10, ▲ Brij S100

and Lewis [12] with the cross-sections of wool fibre dyed with RR120 at pH 5 and 100°C, where the skitteriness of the dyeings was assessed by determining the brightness of the images using computer software. Lewis also elucidated in one of his articles that the migration ability of anionic dyes decreases with the increase of the number of sulphonic groups within a dye molecule [24]. By taking into account the findings, the hexa-sulphonated RR120 could migrate with great difficulty as a consequence of electrostatic repulsive forces between adsorbed dye molecules. The reason for the low exhaustion of RR120, obtained even after 300 minutes of dyeing at pH 3 and 50°C (Figure 4), could be the rise of electrostatic repulsion between the dye in the fibre and the dye in the dye-bath due to the negative charge build-up from the sulphonate groups on the dye molecule [12]. Therefore, it is very difficult to achieve complete diffusion and exhaustion, due to the repulsive forces which can restrict further diffusion and movement of the dye from the dye-bath into the fibre [12]. This can explain why the exhaustion process continued even after 360 minutes of dyeing at 50°C and that equilibrium was still not reached at that time. The adsorption of the RR120 anion (D^-) to the positively-charged wool fabric (W^+) can be expressed by the following equation:

$$D^- + W^+ \rightleftharpoons WD \tag{I},$$

where WD represents the dye adsorbed to the wool. Furthermore, it has to be emphasised that the adsorption of RR120 onto wool is mainly governed by attractive electrostatic forces at such low pH. Nevertheless, once the physical adsorption occurs, then covalent fixation takes place, which is irreversible at reactive wool dyeing and inhibits the migration and diffusion process [12]. Hence, it has to be stressed that when the fixation occurred, Equation I could not be treated as the equilibrium equation anymore. In addition to the dye exhaustion in the presence of the surfactant, the interactions between the dye and the surfactant in the dye-bath were investigated spectrophotometrically. Figure 5 shows that the visible absorption spectrum of 0.0667 g/L RR120 exhibits two absorption maxima in buffered solution (pH 3) at 50°C: 513 and 534 nm. In general, the formation of the dye-surfactant complexes affects both the intensity and the maximum absorption wavelength of the electronic absorption spectra.

Figure 4 shows that, similar to the commercially available amphoteric surfactant Albegal B, the cationic surfactant DTAB and the non-ionic surfactants Brij L23, Brij 58, Brij S20, Brij C10 and Brij S10 significantly increased the RR120 exhaustion for all time intervals, whereas the anionic surfactant SDS and non-ionic surfactant Brij S100 negligibly influenced the dyeing process. These results clearly indicate that at least two different dyeing regimes occurred in the studied dye-surfactant-fibre systems, which is discussed in more detail below.

According to the main mechanisms by which the levelling agents operate, SDS, which is anionic, is a fibre-substantive levelling agent. Therefore, it was assumed that it competes with anionic RR120 for free positive sites on wool fabric. Because the SDS anions are smaller than the RR120 molecules, they can be adsorbed by the fibre more quickly than the dye anions. This adsorption slowed the dye exhaustion and enabled more level dyeing. However, once the SDS anions are adsorbed onto the fibre, they can be displaced by the more substantive dye anions. From Figure 4a, it can be seen that the displacement of SDS by RR120 did not significantly decrease the concentration of exhausted dye after 360 minutes of dyeing. Our assumption is not completely in accordance with the obtained results, which show that the addition of SDS into the dye-bath causes an insignificant increase of exhaustion of RR120, obtained even after 180 minutes of dyeing. It seems that the "competition effect" is unobserved within 210 minutes of dyeing, but expressed only after 300 minutes of dyeing, where lower exhaustion was noticed compared to the surfactant-free dyeing. One of the possible explanations could be that SDS due to its adsorption onto the wool surface governed by electrostatic interactions, which occurred between negatively-charged sulphate groups of SDS molecules and positively-charged amino groups of wool, negligibly accelerates adsorption of RR120 anions by hydrophobic interactions. Nevertheless, the affinity of RR120 to adsorb onto the SDS molecules which are already adsorbed on the wool surface is very low due to the negative charge-charge repulsions of the sulphonate groups of the dye's chemical structure. This is in agreement with the results obtained by Cestari et al. [25], where the adsorption of some reactive dyes onto aminopropyl-silica at pH 4 in the presence of SDS was studied at temperatures ranging from 25 to 55°C. As SDS and RR120 carry the same charge, they do not form complexes in the
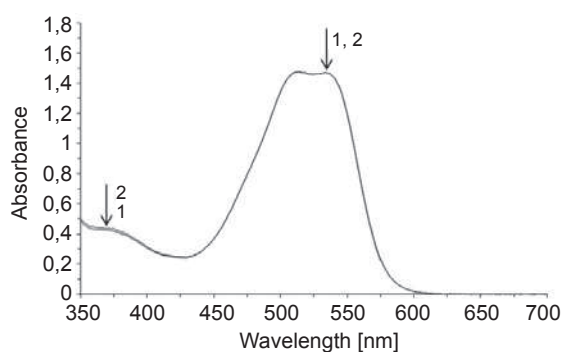
Figure 5: Visible absorption spectra of RR120 ($c_{RR120} =$ 0.0667 g/kg) with and without SDS ($c_{SDS} = 5.0 \times 10^{-3}$ mol/kg) at pH 3 and 50°C
Legend: (1) RR120; (2) RR120 + SDS

dye-bath. The absence of attractive electrostatic interactions between RR120 and SDS was confirmed from the absorption spectrum of RR120 in the presence of SDS, in which no spectral changes were observed (Figure 5). The reactions that occurred during the dyeing process in the presence of SDS can be represented by the following equations:

$$S^- + W^+ \rightleftharpoons WS \qquad (II),$$
$$WS + D^- \rightleftharpoons WD + S^- \qquad (III),$$
$$WS + D^- \rightleftharpoons WSD \qquad (IV),$$

where S^- represents the SDS anion, WS represents the SDS anion bound to the wool cationic functional group and WSD represents the dye anion bound to the surfactant which is already adsorbed on the cationic wool functional group.

In contrast to SDS, Brij S100 acted as a dye-substantive levelling agent at concentrations above c.m.c. and therefore formed complexes with RR120 in the dye-bath (Figure 6).

The presence of complexes between RR120 and the Brij S100 micelles was proven by the bathochromic shift (from 513 to 515 nm at first λ_{max} and from 534 to 541 nm at second λ_{max}) accompanied by the hyper-chromic shift (from A = 1.476 to A = 1.666 at first λ_{max} and from A = 1.471 to A = 1.719 at second λ_{max}) of the RR120 absorption spectrum. The same results were also obtained for the other non-ionic surfactants. Furthermore, the two isosbestic points observed in the RR120-Brij 58 (at 502 and 575 nm) and RR120-Brij S20 (at 505 and 580 nm) systems (Figure 7) indicated a 1:1 complex formation between the dye and non-ionic micelles.
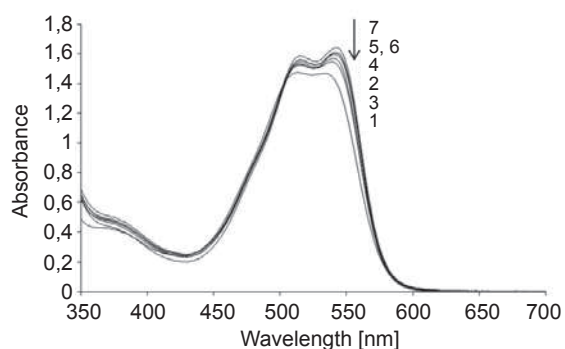

Figure 6: The visible absorption spectra of RR120 ($c_{RR120} = 0.0667$ g/kg) with and without different non-ionic surfactants ($c_N = 5.0 \times 10^{-3}$ mol/kg), obtained at pH 3 and 50°C
Legend: (1) RR120; (2) RR120 + Brij C10; (3) RR120 + Brij S10; (4) RR120 + Brij L23; (5) RR120 + Brij 58; (6) RR120 + Brij S20; (7) RR120 + Brij S100
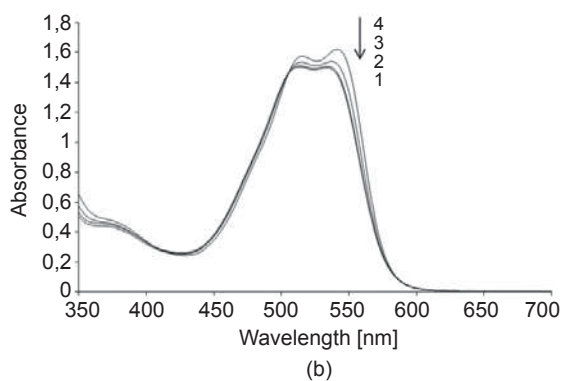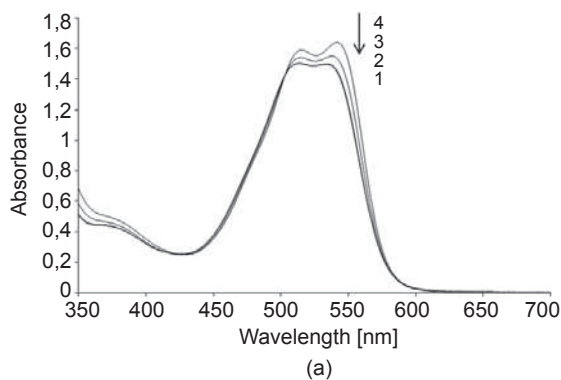

(a)

(b)

Figure 7: The visible absorption spectra of RR120 ($c_{RR120} = 0.0667$ g/kg) at various concentrations of Brij 58 (a) and Brij S20 (b), obtained at 50°C
Legend: (1) 0.0 mol/kg, (2) 5.0×10^{-5} mol/kg, (3) 5.0×10^{-4} mol/kg, (4) 5.0×10^{-3} mol/kg

Because the dyeing process was performed at pH 3, the interactions between RR120 and the non-ionic surfactant micelles could be attributed to the attractive electrostatic interactions between the anionic sulphonic groups of the dye and the positively-charged oxonium groups of the non-ionic surfactant [26] and hydrophobic interactions. The results presented in Figure 4c indicate that the RR120-Brij S100 interactions decreased the rate and extent of dye exhaustion by creating two competitive reactions during the dyeing process: the dye-surfactant and the dye-fibre interactions. This competition resulted in a lower value of *%E* even after 360 minutes of dyeing. The proposed levelling mechanism can be expressed by the following equations:

$$nN \rightleftharpoons M \qquad \text{(V)},$$
$$D^- + M \rightleftharpoons MD^- \qquad \text{(VI)},$$
$$D^- + W^+ \rightleftharpoons WD \qquad \text{(VII)},$$

where *N* represents a molecule of the non-ionic surfactant, *M* is the micelle of the non-ionic surfactant and *MD⁻* is the complex between the dye and the non-ionic surfactant micelle.

The results for the mode of action of SDS (Equations II and III) and Brij S100 (Equations VI and VII) clearly indicate that the competition between the surfactant and the dye for the fibre (in the case of SDS) or the surfactant and the fibre for the dye (in the case of Brij S100) did not result in increased dye exhaustion. Instead, this competition creates a

counterbalance against dye-fibre attractive forces, thereby restricting the dye uptake by wool fibres in equilibrium. The enhanced dye exhaustion would only be possible if the adsorption of the non-ionic surfactant onto wool fibres occurred in the surfactant solution, which would increase the adhesion properties and dyeability of the wool. Although Albegal B, DTAB, Brij L23, Brij 58, Brij S20, Brij C10 and Brij S10 formed dye-surfactant complexes in the dye-bath (Figures 6 to 9), these surfactants should also be fibre-substantive levelling agents, which was proven by an FTIR analysis of the untreated and treated wool (Figure 10).
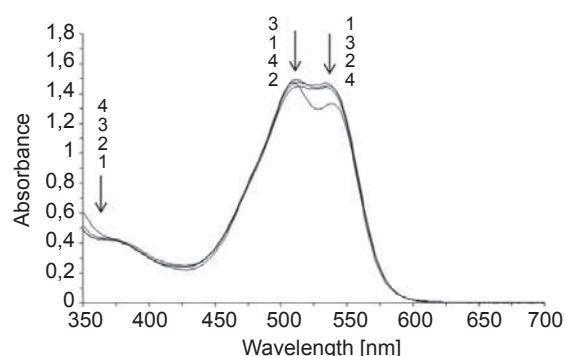

Figure 9: The visible absorption spectra of RR120 (c_{RR120} = 0.0667 g/kg) with and without DTAB (c_{DTAB} = 5.0 x 10⁻³ mol/kg) at pH 3, obtained at 50°C Legend: (1) RR120; (2) RR120 + DTAB; (3) RR120 obtained at 25°C; (4) RR120 + DTAB obtained at 25°C
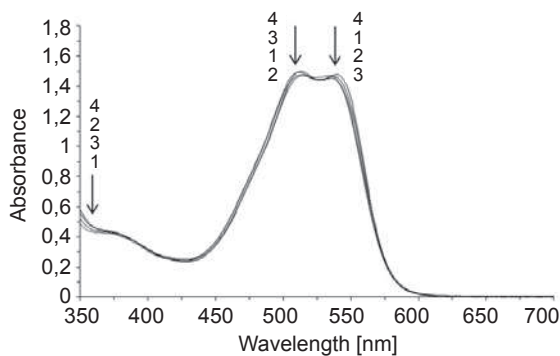

Figure 8: Absorption spectra of RR120 (c_{RR120} = 0.0667 g/kg) with and without Albegal B ($c_{Albegal\ B}$ = 0.0667 g/kg) at pH 3, obtained at 50°C Legend: (1) RR120; (2) RR120 + Albegal B; (3) RR120 obtained at 25°C; (4) RR120 + Albegal B obtained at 25°C
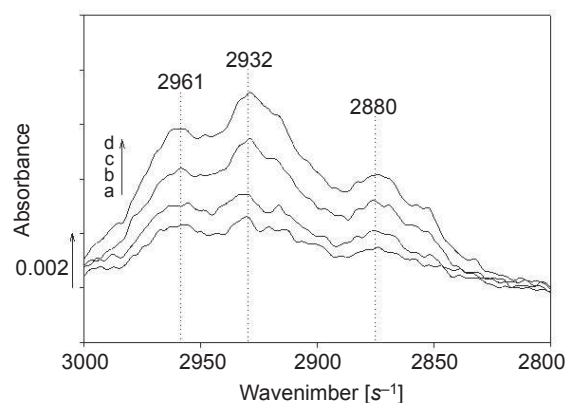

Figure 10: IR ATR spectra of the untreated wool sample (a) and samples treated with DTAB (b), Albegal B (c) and Brij S10 (d)

In this case, the levelling behaviour was not related to the main mechanism of the fibre-substantive levelling agents, which compete with dyes for the sorption sites in the wool fibres. Rather, the adsorbed surfactants creating a more hydrophilic fibre surface [16, 27] such that the adsorption of RR120 increased. For the FTIR analysis, the wool samples were treated for 120 minutes in buffered (pH 3) surfactant solution at 50°C. The concentrations of surfactants (DTAB, Albegal B and Brij S10) were the same as those used for dyeing. After the treatment, the samples were allowed to dry in the open air at room temperature before the FTIR spectra were taken.

The spectra in Figures 8 and 9 reveal that the formation of the RR120-Albegal B complexes was accompanied by small bathochromic (25°C: from 511 nm to 513 nm at the first λ_{max} and from 536 nm to 539 nm at the second λ_{max}; 50°C: from 534 to 537 nm at the second λ_{max}), hyperchromic (25°C: from A = 1.492 to A = 1.499 at the first λ_{max} and from A = 1.452 to A = 1.477 at the second λ_{max}) and hypochromic shifts (50°C: from A = 1.471 to A = 1.466 at the second λ_{max}) (Figure 8), whereas the formation of the RR120-DTAB complexes (Figure 9) resulted in a significant hypochromic shift of the dye absorption maximum at 536 nm (25°C) and at 534 nm (50°C), respectively. In both dye-surfactant systems, the complex formation in the dye-bath is assumed to be governed by attractive electrostatic and hydrophobic interactions. Figures 8 and 9 also show that the shapes of the spectra changed when the temperature increased from 25 to 50°C. This finding indicates that the stability of the complexes was temperature dependent. At higher temperatures, the complexes broke down, and the dye-free anions were released. These results confirm that the dye-surfactant complex formation in the dye-bath is not critical for the exhaustion of RR120 in the presence of DTAB and Albegal B at initial dyeing temperatures of 50°C or above.

Figure 10 reveals that the presence of each surfactant altered the IR spectrum of the wool fibres between 3,000 and 2,800 s^{-1} where typical bands of those alkyl groups characteristic of surfactants are located. The bands at 2,917 and 2,845 cm^{-1} in the spectra of the wool treated with DTAB, Brij S10 and Albegal B are attributed to the asymmetric and symmetric stretching vibrations of the C–H bonds (ν_a(CH$_2$), ν_s(CH$_2$) and ν(CH$_3$)) of the aliphatic alkyl groups [28], which confirms that the studied

surfactants are fibre-substantive and were adsorbed by the wool fibres [8, 16].

The surfactant-fibre interactions were clearly responsible for the enhanced RR120 exhaustion. As the untreated wool used in our study was hydrophobic, the adsorption of Albegal B, DTAB, Brij L23, Brij 58, Brij S20, Brij C10 and Brij S10 to wool likely occurred via hydrophobic interactions. These surfactants were probably oriented with their alkyl chains towards the wool fibre surface and the polar ionic and non-ionic groups away from the fibre surface. It should be noted that in the case of non-ionic surfactants, only free surfactant molecules and not micelles could be adsorbed by the fibres. This property increased the concentration of the cationic sorption sites in the case of DTAB and concentration of the non-ionic polar polyoxyethylene groups on the fibre surface in the case of Brijs. Accordingly, the increased cationic character and wool hydrophilicity significantly increased the RR120 uptake by the fibres. As Albegal B includes positively-charged nitrogen and non-ionic hydrophilic polyoxyethylene groups, it had a dual effect. At pH 3, the anionic functional group of Albegal B was not exposed. The increased dye exhaustion as a result of the previous adsorption of the DTAB cation to the wool fibres can be expressed by the following equations:

$$S^+ + W^+ \rightleftharpoons S^+W^+ \tag{VIII},$$
$$2D^- + S^+W^+ \rightleftharpoons WDSD \tag{IX},$$

where S^+ represents the DTAB cation in the dye-bath, W^+S^+ is the wool fibre including adsorbed DTAB and $WDSD$ represents the RR120 anions adsorbed by the fibre, on which DTAB can be adsorbed.

Although it is reasonable to speculate that the adsorptions of the surfactants to the wool fibres occurs via hydrophobic interactions, the results in Figure 4b show that the time dependence of the *%E* value for RR120 was similar in the presence of Brij L23, Brij 58 and Brij S20 despite their differing alkyl chain lengths, i.e., dodecyl groups in Brij L23, hexadecyl groups in Brij 58 and octadecyl groups in Brij S20. These results suggest that the length of the hydrophobic group is not crucial for surfactant adsorption by the wool fibres and the subsequent enhancement of the dye exhaustion. This hypothesis is supported by the results for Brij S100; although it had an octadecyl group, it decreased the RR120 uptake by the wool. Therefore, the hydrophilic-lipophilic balance (HLB)

of the non-ionic surfactants is more responsible for the surfactant-fibre interactions than the hydrophobicity alone. This finding holds for extreme cases: Brij S10 had the lowest HLB (12.4) but most strongly increased the RR120 exhaustion, whereas Brij S100 had the highest HLB (18.8) but decreased the dye exhaustion (Figure 4c). These findings may be explained by the high hydrophilicity of Brij S100, which primarily acts in polar aqueous media to form dye-surfactant micelle complexes and has no tendency to adsorb on the hydrophobic wool fibres. In contrast, the surfactants with low HLB values that include long alkyl and short polyoxyethylene chains tend to adsorb on the hydrophobic wool fibres, thus increasing their hydrophilic characteristics. However, it should be stressed that the cloud point (Table 1) of all the used non-ionic surfactants lay above the studied dyeing temperature, i.e. 50°C and thus corresponded to the requirements for non-ionic surfactants used as levelling agents [29]. However, if the dyeing proceeds at 100°C, only those non-ionic surfactants will be appropriate, the cloud point of which is above 100°C.

3.2 The influence of dyeing temperature on dye exhaustion, fixation and colour strength

In order to study the influence of the dyeing temperature on the RR120 exhaustion, only the surfactants that greatly increased the %E at 50°C and pH 3 were used. The dye exhaustion was determined after 120 min of dyeing at pH 3 and 60, 70, 80 or 90°C, as presented in Table 2.

Table 2 shows that increases in the dyeing temperature strongly increased the dye exhaustion up to 80°C, at which the maximum dye exhaustion with and without surfactants was obtained. At 80°C, the %E value of RR120 reached almost 100 with and without DTAB and Albegal B, whereas Brij S10 slightly decreased the dye exhaustion; this effect was not enhanced by the further temperature increase to 90°C. Therefore, the influence of the dyeing temperature and the surfactant on the %E value was more pronounced at lower temperatures.

The results of the covalent fixation, %F, and the overall fixation efficiency, %T, of RR120 are presented in Table 2, and they show that in all dyeing systems, the

Table 2: Extent of exhaustion (%E), covalent fixation (%F), overall fixation efficiency (%T) and colour strength (K/S) before and after stripping of wool samples dyed with RR120 in absence and presence of DTAB, Brij S10 and Albegal B, obtained after 120 min of dyeing at 60, 70, 80 or 90°C and pH 3

Surfactant	T [°C]	E [%]	F [%]	T [%]	K/S	
					before stripping	after stripping
No surfactant	60	34.0	49.5	16.8	8.3	4.1
	70	72.6	69.1	50.2	16.1	11.1
	80	99.9	76.6	76.5	23.6	18.1
	90	99.9	72.8	72.7	26.7	19.4
DTAB	60	64.7	54.1	35.0	15.8	8.6
	70	95.3	76.2	74.3	23.2	18.1
	80	99.9	77.9	76.1	26.4	20.1
	90	99.8	73.0	72.9	27.9	20.3
Brij S10	60	51.5	54.2	27.9	17.6	9.5
	70	97.1	75.1	72.9	26.5	19.9
	80	98.5	75.8	74.7	31.6	23.9
	90	98.3	68.1	66.9	35.7	24.3
Albegal B	60	60.4	61.5	37.1	15.8	9.7
	70	98.1	75.9	74.5	28.3	21.5
	80	99.7	77.9	77.6	31.7	24.7
	90	99.8	72.6	72.5	34.8	25.2

values for *%F* and *%T* increased with temperature from 60 to 80°C, peaked at 80°C and decreased at 90°C. Thus, the fixation of RR120, including two MCT groups, occurs with the nucleophilic substitution reaction of the halotriazine group with the fibre under acidic dyeing conditions [11]. The values of *%F* also show that the dye fixation by covalent bonding on reactive wool sites was activated by the change in the dyeing temperature from 60 to 90°C. The results obtained for *%T* were in good agreement with those for *%F*. The presence of each surfactant increased *%F* and *%T* for RR120 at 60 and 70°C in comparison with the dye-only system. In contrast, DTAB and Albegal B, which behaved similarly to each other, also slightly enhanced the dye fixation at 80°C. These results clearly indicate that with respect to the *%E*, *%F* and *%T* of RR120, a dyeing temperature of 80°C is the most effective and that an increase to 90°C has no effect.

Although the results for the dye exhaustion and fixation were expected to reflect the colour strength of the dyed wool fabric samples, a reasonable relationship among these quantities was not obtained. The same phenomenon has already been obtained in the dyeing of wool with acid dyes in the presence of fatty acid ethoxylates [30]. The *K/S* values presented in Table 2 unexpectedly increased with increasing dyeing temperature up to 90°C for all dyeing systems, even though the maximal *%E* was obtained at 80°C (Table 2). Moreover, the presence of each surfactant significantly increased the *K/S* values of the dyed wool samples compared with the surfactant-free samples. This phenomenon was more obvious for Albegal B and Brij S10 than for DTAB. Despite the decreased dye exhaustion in the presence of Brij S10 at 80 and 90°C, the surfactant increased the *K/S* value of the dyed wool samples from approximately 24 to 32 at 80°C and 27 to 36 at 90°C (Table 2) compared with the DTAB sample. However, at the same *%E* value of 100 at 80°C, the *K/S* values of the dyed samples with and without DTAB and Albegal B varied from 24 to 32 (Table 2), which is difficult to explain. Two possible interpretations are as follows: Brij S10 and Albegal B treatment resulted in a greater concentration of RR120 on the wool fibre surface or influenced the change in the colour coordinates of the adsorbed RR120. The same pattern was observed after the extraction of the unfixed dye from the dyed samples using a 20% aqueous pyridine solution (Table 2).

In order to determine the influence of the surfactant on the colour of the dyed wool samples, the CIE-LAB values of the dyed fabrics were also considered.

Table 3: CIELAB values, chroma, $C^\star_{ab}$ and hue, h_{ab}, of wool fabric dyed with RR120 with and without different surfactants at pH 3 after 120 min at four temperatures, T: 60, 70, 80 and 90°C

Surfactant	*T* [°C]	*L**	*a**	*b**	*C**$_{ab}$	*h*$_{ab}$ [°]
No surfactant	60	47.65	52.74	5.84	53.07	6.32
	70	41.34	55.86	10.78	56.89	10.92
	80	37.54	56.49	15.20	58.50	15.06
	90	36.74	57.18	17.22	59.72	16.76
DTAB	60	41.63	56.88	10.66	57.88	10.61
	70	38.21	57.17	14.27	58.93	14.01
	80	37.11	57.10	16.25	59.37	15.88
	90	36.82	57.35	17.29	59.90	16.78
Brij S10	60	41.51	57.15	10.90	58.19	10.79
	70	36.80	57.46	16.36	59.75	15.89
	80	35.91	57.81	18.52	60.71	17.76
	90	35.52	58.26	20.39	61.72	19.29
Albegal B	60	41.70	57.17	10.58	58.14	10.48
	70	36.50	57.38	16.45	59.69	15.99
	80	36.09	58.10	18.54	60.98	17.70
	90	35.53	58.48	21.46	62.30	20.15

The data in Table 3 show that at all dyeing temperatures, the surfactants decreased the lightness (L^*) and increased the chroma (C^*_{ab}) and hue (h_{ab}) of the dyed wool; that is, the wool became darker, redder and less blue than the surfactant-free dyed wool. Among the studied surfactants, Albegal B had the strongest effect on L^*, a^* and b^*. The studied surfactants enhanced the colour strength, which affected the change in the CIELAB values during the dyeings. According to the obtained results of %E, %F, %T and $K/S_{after\ stripping}$, Albegal B was the most effective levelling agent among the studied surfactants.

4 Conclusion

This study confirmed that the extent of RR120 exhaustion in the hydrophobic wool fibres is strongly influenced by the chemical structure of the surfactant present in the dye-bath. The main mechanisms by which the levelling agents operate could not explain the increase of the dye uptake by the wool fibre in the presence of the studied cationic, amphoteric and non-ionic surfactants. The dye exhaustion was not increased by surfactants that were fibre-substantive only, i.e., that competed with RR120 for free positive sites on the wool fabric, or dye-substantive only, i.e., that formed complexes with RR120 in the dye-bath. The dye exhaustion occurred in the presence of the surfactants that are simultaneously fibre and dye-substantive. These surfactants could be adsorbed by the wool fibres via hydrophobic interactions, which significantly increased the number of positive charges available and the hydrophilicity of the fibres and therefore enhanced the adhesion properties and ability of the wool to be dyed. The dye uptake and the surfactant adsorption increased the K/S value of the dyed wool samples compared with the surfactant-free dyed wool samples, which resulted in a decrease in lightness (L^*) and an increase in both chroma (C^*_{ab}) and hue (h_{ab}).

References

1. *Wool Dyeing*. Edited by David M. Lewis. Bradford : Society of Dyers and Colourists, 1992, 372.
2. *Colorants and auxiliaries: Organic chemistry and application properties, Volume 2- Auxiliaries.* Edited by John Shore. Bradford : Society of Dyers and Colourists, 1990, 372.
3. ASPLAND, J. Richard. *Textile Dyeing and Coloration.* New York : American Association of Textile Chemists and Colorists, 1997, 410.
4. BURKINSHAW, Stephen M. Application of Dyes. V *The Chemistry and Application of Dyes*. Edited by D. R. Waring and G. Hallas. New York : Plenum press, 1990, 244–277.
5. BÜHLER, A., CASTY, R. Hochechte Reactivfarbstoffe für Wolle. *Melliand Textilber*, 1976, **6**, 693–696.
6. CEGARRA, J., RIVA, A., AIZPURUA, L. The action of Albegal B on the dyeing of wool with α-Bromoacrylamide reactive des. *Journal of the Society of Dyers and Colourists*, 1978, **94**(9), 394–401, doi: 10.1111/j.1478-4408.1978.tb03425.x.
7. LEWIS, D. M. The Dyeing of wool with reactive dyes. *Journal of the Society of Dyers and Colourists*, 1982, **98**(5–6), 165–175, doi: 10.1111/j.1478-4408.1982.tb03631.x.
8. HANNEMANN, Klaus. Mechanistic investigations on the action of levelling agents in reactive wool dyeing. *Journal of the Society of Dyers and Colourists,* 1992, **108**(4), 200–202, doi: 10.1111/j.1478-4408.1992.tb01440.x.
9. JOCIĆ, Dragan, JULIA, M. R., ERRA, P. Application of chitosan/nonionic surfactant mixture to wool assessed by dyeing with a reactive dye. *Journal of the Society of Dyers and Colourists,* 1997, **113**(1), 25–31, doi: 10.1111/j.1478-4408.1997.tb01842.x.
10. YEN, Ming-Shien. Application of chitosan/nonionic surfactant mixture in reactive dyes for dyeing wool fabrics. *Journal of Applied Polymer Science*, 2001, **80**(14), 2859–2864, doi: 10.1002/app.1403.
11. CHO, Ho Jung, LEWIS, David M. Reactive dyeing systems for wool fibres based on hetero-bifunctional reactive dyes. Part 1: Application of commercial reactive dyes. *Coloration Technology*, 2002, **118**(4), 198–204, doi: 10.1111/j.1478-4408.2002.tb00100.x.

12. CHO, Ho Jung, LEWIS, David M. Reactive dyeing systems for wool fibres based on hetero-bifunctional reactive dyes. Part 2: Investigation of dyeing properties during the dyeing cycle. *Coloration Technology*, 2002, **118**(5), 220–225, doi: 10.1111/j.1478-4408.2002.tb00103.x.

13. RIVA, A., CEGARRA, J. The influence of amphoteric products on the affinity of wool for acid dyes. *Journal of the Society of Dyers and Colourists*, 1987, **103**(1), 32–37, doi: 10.1111/j.1478-4408.1987.tb01083.x.

14. RIVA, A., CEGARRA, J., PRIETO, R. Sorption of nonionic auxiliary products by wool and its influence on dyeing with acid dyes. *Journal of the Society of Dyers and Colourists*, 1996, **112**(4), 114–116, doi: 10.1111/j.1478-4408.1996.tb01797.x.

15. BROOKS, John H. The mode of action of levelling agents in the dyeing of wool. *Journal of the Society of Dyers and Colourists*, 1974, **90**(5), 158–163, doi: 10.1111/j.1478-4408.1974.tb03195.x.

16. NAEBE, Maryam, COOKSON, Peter G., RIPPON, John A., WANG, Xungai G. Effects of leveling agent on the uptake of reactive dyes by untreated and plasma-treated wool. *Textile Research Journal*, 2010, **80**(7), 612–622, doi: 10.1177/0040517509340603.

17. McILVAINE, C. A buffer solution for colorimetric comparison. *Journal of Biological Chemistry*, 1921, **49**(1), 183–186.

18. ROSEN, Milton J. *Surfactants and interfacial phenomena*. 1. ed. New York : John Wiley & Sons, 1989, 122–125.

19. HAIT, S. M., MOULIK, S. P. Determination of critical micelle concentration (CMC) of nonionic surfactants by donor-acceptor interaction with iodine and correlation of CMC with hydrophile-lipophile balance and other parameters of the surfactants. *Journal of Surfactants and Detergents*, 2001, **4**(3), 303–309, doi: 10.1007/s11743-001-0184-2.

20. SCOTT, Hans. Hydrophile-lipophile balance and cloud points of nonionic surfactants. *Journal of Pharmaceutical Sciences*, 1969, **58**(12), 1443–1449, doi: 10.1002/jps.2600581203.

21. Sigma Aldrich technical data [dostopno na daljavo]. Dostopno na svetovnem spletu: http://www.sigmaaldrich.com.

22. RUSZNÁK, I., FRANKL, J., GOMBKÖTŐ, J. Photoreactivity of wool dyed with reactive dyes. *Journal of the Society of Dyers and Colourists*, 1985, **101**(4), 130–136, doi: 10.1111/j.1478-4408.1985.tb01015.x.

23. CHO, H. J., LEWIS, David M., JIA, B. H. Improved reactive dyeing of wool with novel trifunctional reactive dyes. *Coloration Technology*, 2007, **123**(2), 86–95, doi: 10.1111/j.1478-4408.2007.00067.x.

24. LEWIS, David M. Dyestuff-fibre interactions. *Review of Progress in Coloration and Related Topics*, 1998, **28**(1), 12–17, doi: 10.1111/j.1478-4408.1998.tb00114.x.

25. CESTARI, Antonio R., VIEIRA, Eunice F. S., VIEIRA, Gláucia S., ALMEIDA, Luis E. The removal of anionic dyes from aqueous solutions in the presence of anionic surfactant using aminopropylsilica−A kinetic study. *Journal of Hazardous Materials*, 2006, **138**(1), 133–141, doi: 10.1016/j.jhazmat.2006.05.046.

26. DATYNER, Arved. *Surfactants in Textile processing*. New York : Marcel Dekker Inc., 1983, 85–105.

27. BRAC, N., LAMB, R., PHAM, D., TURNER, P. Nonionic surfactants and the wool fibre surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1999, **146**(1−3), 405–415, doi: 10.1016/S0927-7757(98)00863-2.

28. SOCRATES, George. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*. 3. ed. Chichester : John Wiley & Sons, 2004, 347.

29. DATYNER, Arved. Interactions between auxiliaries and dyes in the dyebath. *Review of Progress in Coloration and Related Topics*, 1993, **23**(1), 40–50, doi: 10.1111/j.1478-4408.1993.tb00095.x.

30. MUSNICKAS, J., SKULKINA, O., TREIGIENE, R., RAGELIENE, L. Effect of the interaction between acid dye and nonionic surfactants on the adsorption of dye in wool fibre. *Fibres & Textiles in Eastern Europe*, 2008, **16**(5), 117–121.