Influence of nonionic surfactant on wool fiber dyeing thermodynamics and kinetics parameters

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The influence of nonionic surfactant and benzyl alcohol on low temperature dyeing of wool fiber with acid dye *C. I. Acid Orange 7* was studied. The thermodynamic properties of dyeing – standard affinity of dye, standard heat, standard entropy of dye sorption and the apparent diffusion coefficient and activation energy of dye sorption were determined. The results have shown distinct differences in the mechanisms of dye sorption into fiber in the system water-dye-auxiliary-wool fiber. Our studies have demonstrated that the favorable effects of nonionic surfactant on dyeing thermodynamics are related with the screening of hydrophobic sites available on the wool fiber surface, thus improving dye migration into fiber and its fixation.

Key words: wool fiber, acid dye sorption, thermodynamics

INTRODUCTION

In order to obtain satisfactory properties of shade development and fastness, complete penetration of dye into the fiber interior is essential. The rate at which this occurs is controlled by the rate of dye diffusion across the fiber surface and then throughout the whole interior [1–3]. Nonionic surface-active agents are useful in low temperature dyeing of wool [3–5]. Low temperature dyeing enables to get a good shade, minimize the damage of wool fiber during dyeing and consequently to avoid deterioration of its physical properties [4,6]. One of the current needs for improving the future of low temperature dyeing of wool is the knowledge of the action mechanism [7–10]. It is suggested that one of the action mechanisms of nonionic product incorporating ethoxylated alkylphenols is the modification of hydrophobic domains of cellular membrane complex (CMC) in wool fibers and the lipid disruption could favor dye diffusion into the fiber [7]. K. Joko and J. Kogo have shown that benzyl alcohol diffuses into the bulk phase (cuticle and cortical cells) [11]. Authors suggested that some temporary structural destruction and the loosening of the molecular structure in the bulk phase of the wool fibre take place. Therefore the addition of benzyl alcohol to the system enlarges the effective volume for the diffusion of dye and consequently results in an enhanced rate of diffusion of dyes in the bulk phase of wool fibres.

In the studies of wool dyeing in the presence of nonionic surface-active agents a supplementary tool to enlarge the possibilities to clear the mechanism of actions could be an attempt to refer to thermodynamic parameters of such systems. Therefore the purpose of this paper was to determine the effect of a nonylphenylethoxylate-based nonionic surfactant on wool fiber dyeing with *C. I. Acid Orange 7* kinetic and thermodynamic properties in comparison with those for dyeing in presence of benzyl alcohol.

EXPERIMENTAL

Material preparation. Standard wool fabric was treated according to *ISO 105/F–1985 (E)* standard conditions and was used in all experiments. The diameter of the merino fibre was 18.9 μm. The standard fabric was extracted with a chloroform/methanol (70:30) mixture in a Soxhlet extractor. The extraction lasted 10 overfills. The solvent-extracted fabric is below designated as purified wool.

Acid dye *C.I. Acid Orange 7* of 98% purity (Sigma) was used in dyeing.

The *Lanasan LT* (nonionic nonylphenylethoxylate) and benzyl alcohol were used as auxiliaries in dyeing solutions. Benzyl alcohol and other used chemicals were of reagent grade.

Dyeing conditions. All wool fabrics were immersed in a buffer solution, pH 4.2, for an hour before dyeing. The non-steady dyeing process at 30 °C and 60 °C was chosen for the study, because the effect

of benzyl alcohol and *Lanasan LT* is expected to be high at low temperatures. The dyeing process was carried out on standard fabric and purified fabric. The dyeing solution pH was 4.2 (0.05 M sodium acetate and acetic acid) and composed of 1% (w.w.) *C. I. Acid Orange 7* dye and auxiliary. The liquid ratio was 150:1.

Dye concentration measurement. The dye concentration in the dyebath was measured at the start and after 5, 10, 15, 20, 30, 45, 60, 75, 90, 105, 120, 135, 150, 180 and 210 min. The measurements were carried out at λ = 488 nm in a 10 mm cell using a *Spectronic Unicom Genesys TM 8* spectrophotometer. The sorption of the dye into wool fibre was calculated as a difference between the initial dye concentration in dyeing solution and that at the time *t*.

Determination of thermodynamic properties and kinetic parameters. Standard affinity, $\Delta\mu^o$ (J/mol), measured at 30 °C and 60 °C (303 and 333 K), was calculated using eqn. 1 [12, 13, 15]:

$$\Delta\mu^o = -RT \; ln \; [C]_f/V \; [C]_s, \qquad (1)$$

where $[C]_f$ is the concentration of dye in the fibre (mol kg^{-1}), $[C]_s$ is the concentration of dye in the bath (mol l^{-1}), V is the volume of internal phase of fibre, 0.31 for wool (mol kg^{-1}), R is the gas constant (8.317 J/mol), T is the absolute temperature (K).

The heat of sorption $\Delta H°$ (kJ/mol) was calculated in accordance with eqn. 2 [12]:

$$\Delta\mathrm{H}^O = \frac{T_2\Delta\mu_1^O - T_1\Delta\mu_2^O}{T_2 - T_1}, \qquad (2)$$

where T_1 and T_2 are the absolute temperatures 303 and 333 K and $\Delta\mu^o_1$ and $\Delta\mu^o_2$ (J/mol) are the standard affinities at T_1 and T_2.

The entropy of dyeing $\Delta S°$ (J/mol K) was calculated using eqn. 3.:

$$\Delta\mu° = \Delta H° - T\Delta S° \qquad (3)$$

Apparent activation energy E of diffusion was calculated using eqn. 4:

$$\log\left(t_{1/2}\right)_1 - \log\left(t_{1/2}\right)_2 = \frac{E}{2.3R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \qquad (4)$$

where T_1 and T_2 are the absolute temperatures 303 and 333 K, $(t_{1/2})_1$ and $(t_{1/2})_2$ are the time of half-dyeing at T_1 and T_2, E is the activation energy of diffusion (kJ/mol).

The kinetic constant K (10^{-5} mol/g min) was calculated from eqn. 5 [13]:

$$C_t = K \times t, \qquad (5)$$

C_t represent dye adsorbed on fiber at a time t of dyeing.

The apparent diffusion coefficient D (10^{-12} m^2/min) for the dye was calculated from Hill's relationship [13]:

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{D \cdot t}{\pi \times r^2}}, \qquad (6)$$

where C_∞ and C_t represent dye adsorbed on fiber at an infinite and shorter time *t* of dyeing, D is the diffusion coefficient, r is the radius of cylindrical fiber.

RESULTS AND DISCUSSION

The effects of nonionic surfactant and benzyl alcohol on acid dye sorption kinetics

The study was carried out on standard wool fabric and on that scoured with chloroform / methanol by Soxhlet extraction.

Figures 1 and 2 show the sorption kinetics of *C. I. Acid Orange 7* on wool fiber of standard fabrics in dyeings at 30 °C using surfactant or benzyl alcohol, while Figures 3 and 4 show the results of dye sorption on purified wool fiber. The slope of curves representing the dyeing liquors containing surfactant or benzyl alcohol at the start of dyeing are steeper than those of control (Fig. 1 and 2), and the equilibrium of the dye exhaustion value is about 2.5×10^{-5} mol/g. The effect of surfactant on dye sorption into purified wool (Fig. 2) is somewhat higher comparing with that for benzyl alcohol, while sorption into wool of standard fabric in presence of benzyl alcohol occurs significantly faster.
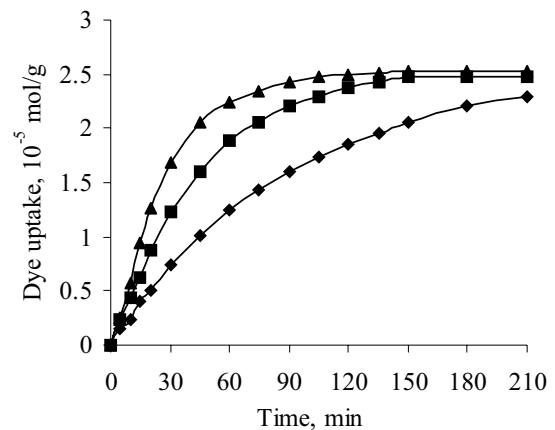

Fig. 1. Dyeing rate plots for original (standard) wool fabric at 30 °C in absence of auxiliary (♦), with *Lanasan LT* (■), with benzyl alcohol (▲)
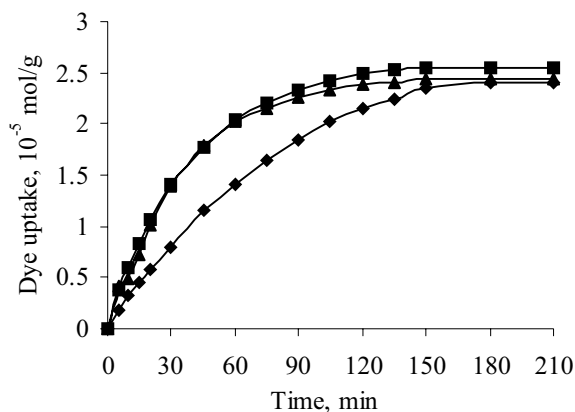
Fig. 2. Dyeing rate plots for purified wool fabric at 30 °C in absence of auxiliary (♦), with *Lanasan LT* (■), with benzyl alcohol (▲)

Fig. 4. Dyeing rate plots for purified wool fabric at 60 °C in absence of auxiliary (♦), with *Lanasan LT* (■), with benzyl alcohol (▲)

In Figures 3 and 4, the curves representing dyeing at 60 °C indicate the higher increase in dyeing rate when *Lanasan LT* is present in dyeing liquor. A significantly lower dyeing rate is for benzyl alcohol assisted dyeing and purified wool (Fig. 4) and somewhat lower for standard wool fabrics. Benzyl alcohol has a negative effect on the level of dye equilibrium concentration in wool fiber, while it has no influence on dye sorption equilibrium comparing with control dyeing using purified wool (Fig. 4).

It is generally agreed that when benzyl alcohol is assisted in dyeing of fibers containing ionic sites the dyeing rate is enhanced [13]. Although benzyl alcohol has a low affinity for wool, its uptake from the dyebath is very rapid. On the basis of this fact the conclusion was made that the sorption of benzyl alcohol on wool is associated mainly with its hydrophobic nature and that the process is one of the simple physical adsorption, with little intrinsic
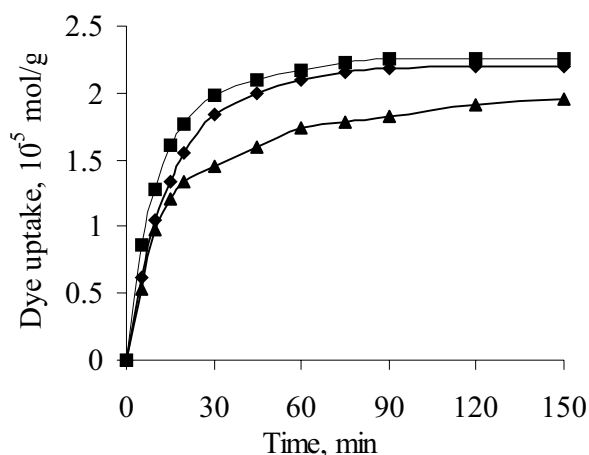
affinity arising from specific interactions. Thus the "solvent layer" concept of benzyl alcohol action in wool dyeing has been supported, *i.e.* the suggestion was made that dyeing takes place from a layer of solvent covering the fiber surface. Another concept, which could be applied to explain the enhanced rate of wool dyeing in presence of benzyl alcohol was proposed by Speakman et al. [14]. They found that the permanent changes of the physical properties of wool are caused by bond-breaking occurring due to action of aqueous solution of benzyl alcohol at low temperatures.

The hydrophobic intermolecular bonds in wool fiber seem to be important in dyeing with anionic dyes at 30 °C and pH 4.2 and less important at 60 °C. The results presented in Figs. 1 and 2 show a insignificant difference in dye equilibrium concentration in wool fibre for both *Lanasan LT* and benzyl alcohol, implying that the solution used for dyeing, which contained monosulfonated anionic dye *C. I. Acid Orange 7* (initial concentration in dyebath 1.8×10^{-4} mol/l), the nonionic surface-active agent *Lanasan LT* (0.15×10^{-3} mol/l, i.e. lower than critical micelle concentration) and 0.05 M of sodium acetate with an appropriate acetic acid was a correct molecular solution. The hydrophobicity of nonionic *Lanasan LT* is higher comparing with that of benzyl alcohol, and tends to be absorbed at hydrophobic sites on wool fiber surface. Thus, the sorption of a nonionic surface-active agent by wool fiber leads to a screening of hydrophobic sites on wool fiber surface, which usually are able to form hydrophobic bonds with hydrophobic parts of dye molecules. In turn, a decrease of the amount of hydrophobic sites able to form hydrophobic bonds with dye molecules occurs, and dye migration into the wool fiber is facilitated.

Table 1 shows, that the value of the dye diffusion coefficient for dyeing at 60 °C in the presence

Fig. 3. Dyeing rate plots for original (standard) wool fabric at 60 °C in absence of auxiliary (♦), with *Lanasan LT* (■), with benzyl alcohol (▲)
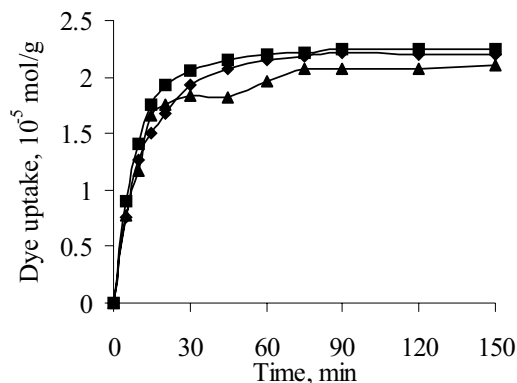
Table 1. **The kinetic constant (K) and the apparent diffusion coeficient (D) of *C. I. Acid Orange 7* in the presence of benzyl alcohol and *Lanasan LT***

Fabric and the auxiliary	Kinetic constant K, $\times 10^{-5}$ mol/g $\times$ $\times$ min, at		Diffusion coefficient D, $\times 10^{-12}$ m²/min, at	
	30 °C	60 °C	30 °C	60 °C
Standard:				
no auxiliary	0.021	0.099	0.231	1.593
Lanasan LT	0.041	0.141	0.584	2.191
benzyl alcohol	0.064	0.101	0.876	1.947
Purified:				
no auxiliary	0.024	0.139	0.663	2.191
Lanasan LT	0.048	0.172	0.663	2.696
benzyl alcohol	0.047	0.130	0.682	2.191

of benzyl alcohol was about the same as for control dyeing (in absence of benzyl alcohol). The suggestion could be made that the dye diffusion into fiber is facilitated when internal lipids of wool are extracted before dyeing, using solvents or heating during dyeing at a temperature exceeding the point of fusion of internal lipids (dyeing at 60 °C in the present study). That is why the effect of benzyl alcohol on the dye apparent diffusion coefficient value at 60 °C is markedly lower than that at 30 °C for the untreated standard wool fabric fiber, and there was no effect when purified wool fabric was dyed.

A different picture is obtained when *Lanasan LT* as a dyeing auxiliary is used. The effect of this agent on the apparent diffusion coefficient values is equally significant for both temperatures dyeing at 30 °C and 60 °C. This leads to the assumption that nonionic surface-active agent acts not only as a dispersing agent on internal lipids of wool fiber and thus helps to overcome the barrier for dye diffusion into fiber. The mechanism of *Lanasan LT* action seems to be different from the depicted above mechanism for benzyl alcohol action.

Our unpublished experimental data have shown that the diffusion of relatively highly hydrophobic nonionic surface-active *Lanasan LT* into wool fiber

from aqueous solution is very rapid and the formation of hydrophobic bonds surfactant–hydrophobic sites of fiber takes place during sorption. Since the solubility of the nonionic surfactant decreases as the temperature of solution increases, it is reasonable to believe that when dyeing occurs at a temperature of 60 °C, the screening effect of the nonionic surfactant on the hydrophobic sites of wool fiber is higher than at 30 °C.

2. Thermodynamics of dye sorption into wool fiber in presence of nonionic auxiliary

The results presented in Table 2 show that when benzyl alcohol assists, the standard affinity of acid dye *C. I. Acid Orange 7* to the wool fiber is lower, comparing with that when dyeing occurs in absence of an auxiliary or with a surfactant. The presence of benzyl alcohol in dyeing liquor is known to change the coefficient of dye partition [13]. This means that the dye is more soluble in water–benzyl alcohol mixture than in pure water (free of organic additives). Due to a very rapid uptake of benzyl alcohol by the wool fiber the dye sorption into fiber is also enhanced. However, the solution in the internal volume of fiber is composed from water–benzyl alcohol–dye, and the affinity of dye to the solution is higher than that for the dye–water system. Thus, when benzyl alcohol assists in dyeing, the activity of dye in dye–fiber interaction tends to be lower and this reflects on the lower value of standard affinity of dye (Table 2). Taking into consideration the affinity reduction of the dye due to presence of benzyl alcohol, the increase of the apparent dye diffusion coefficient is expected (Table 1).

The influence of *Lanasan LT* on *C. I. Acid Orange 7* dye affinity to the wool fiber is significant only at 30 °C (Table 2).

The mechanism of dyeing in presence of *Lanasan LT* is apparently not the same as for benzyl

Table 2. **Standard affinity ($\Delta\mu°$), heat of sorption ($\Delta\mu°$), standard entropy ($\Delta\mu°$), activation energy (E) of *C. I. Acid Orange 7* diffusion into wool fibre**

Fabric and the auxiliary	$\Delta\mu°$ (kJ/mol)		$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol × K)		Activation energy E, kJ/mol
	30 °C	60 °C		303 K	333 K	
Standard:						
no auxiliary	–17.349	–15.951	–31.469	–47	–47	47.41
Lanasan LT	–15.079	–15.941	–6.373	29	29	36.93
benzyl alcohol	–14.896	–15.212	–11.704	11	11	21.60
Purified:						
no auxiliary	–17.484	–16.023	–32.240	–49	–49	52.79
Lanasan LT	–15.538	–16.048	–10.387	17	17	39.17
benzyl alcohol	–15.001	–15.635	–8.600	21	21	32.61

alcohol. First, the effect of added *Lanasan LT* could not increase the solubility of the dye like benzyl alcohol, because the concentration in moles of a surface-active agent (*Lanasan LT*) is markedly lower than its critical micelle concentration or the molar concentration of dye in the solution. Thus, there is no evidence to suggest that the presence of surfactant in fact increases the concentration of dye in a true molecular solution. Second, the effect of increase in dyeing rate (diffusion coefficient value) for *Lanasan LT* (Table 1) seems to be not related to the change of dye concentration in true solution, since the surface-active agent does not change the amount of dye absorbed at equilibrium. Third, if the nonionic surface-active agent would form complexes with dye, the latter would be less soluble and less electronegative than dye alone. The less electronegative complexes in turn would be less sensitive (attractive) to wool fiber. Yet our results have shown that in presence of *Lanasan LT* the dye sorption is enhanced, therefore it can be concluded that the formation dye–surfactant complexes in the system do not take place. Figure 4 shows that the sorption of dye in the presence of nonionic surface-active agent is faster from the beginning up to the equilibrium. Thus the mechanism of *C. I. Acid Orange 7* dye sorption into the wool fiber in the presence of nonionic surface-active *Lanasan LT* could be suggested. It provides the way of preliminary sorption of the nonionic surface-active agent on the hydrophobic sites of wool fibre surface.

The results presented in Table 2 show the increase of standard dye affinity values in presence of both kinds of additives, surface-active *Lanasan LT* or benzyl alcohol, when the temperature of dyeing liquor is increased from 30 ° up to 60 °C. Such change could be due to an increase in the amount of accessible hydrophobic sites available in the non-ceratinous regions of wool fibre, namely those of cuticle or/and cellular membrane complex.

The heat of dyeing is considered as a measure of bonding force of the dye with the fibre [15]. In fact, $\Delta H° = Energy\ of\ broken\ bonds - Energy\ of\ formed\ bonds.$

If the bond energy is the heat which must be supplied to break a certain bond, the energy balance of a number of bonds involved per mole of dye will be the heat of dyeing.

Among the bonds that absorb heat and break could be the bonds among dye molecules or ionic bonds in these molecules. The breakages of the solvatation bonds or hydrogen bonds inside the fiber, or the breakage of the Van der Waals' forces could occur also. The greater the value of the energy of bonds formed between the fiber and dye, the more stable the dyeing will be. If this value is greater

than the energy of broken bonds, the heat of dyeing is negative [15].

The results presented in Table 2 show that the nonionic surface-active agent as well as benzyl alcohol significantly decrease the heat of dye sorption. This means that the heat of dye–fiber bond formation decreases and that the dye combines more easily with the fiber.

When the molecules of dye are absorbed by the fiber, they arrange themselves in the interior in an orderly manner and are oriented in a longitudinal sense to the fiber. They have less freedom of movement and the state of probability will be minor, therefore the entropy ($\Delta S°$) will be reduced [15]. Table 5 shows that when the wool fiber of standard fabric is dyed in presence of *Lanasan LT*, the sample has a higher $\Delta S°$ than when dyed without auxiliary or even that for benzyl alcohol. This indicates that the dye tends to become more confined to the fiber phase. Our unpublished results obtained in another study on colour fastness to washing or to boiling in water support the meaning of diference in $\Delta S°$ values for two systems: fiber–dye–water and fiber–dye–water–nonionic surface-active agent *Lanasan LT*. The colour difference Delta E after washing (*ISO 105/C06 A1S*) or after boiling in water during 5 min for samples of standard fabric dyed in presence of nonionic surfactant was significantly lower comparing with that of dyed with dye alone.

Apparent activation energy values have been calculated using equation 4 and are presented in Table 2. The E values are defined as the amount of energy that allows the dye to overcome the surface barrier of the fibre and to diffuse inside. A lower E value of dye diffusion activation energy means that the dye requires less energy before entering the fibre. As we have shown [4], the action of benzyl alcohol on the wool fiber is the consequence of unwanted changes in the physical properties of fibre – the reduction of strength and elongation at break. Such kind of deterioration of fibre was not observed for wool fibre dyed in the presence of the surfactant *Lanasan LT*. Thus, the interaction between *Lanasan LT* and wool fiber during dyeing with acid dye is favorable in the aspect of thermodynamics of dyeing and allows to avoid a significant deterioration of the physical properties of the wool fibre.

CONCLUSIONS

The presence of the nonionic surfactant (nonylphenylethoxylate) *Lanasan LT* in low temperature wool fiber dyeing with the anionic dye *C. I. Acid Orange 7* results in a decrease of dye standard affinity, standard heat and apparent activation energy of dye

sorption and an increase in the apparent coefficient of dye diffusion value.

Distinct differences in the mechanisms of low temperature dyeing of wool fiber for frequently applied chemicals – benzyl alcohol and nonionic surfactant have been noted. It is suggested that the favorable effect of *Lanasan LT* on wool dyeing thermodynamics is related to the screening of hydrophobic sites available on wool fiber surface, thus improving dye migration into the fiber and its fixation.

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NEJONINĖS PAVIRŠINIO AKTYVUMO MEDŽIAGOS ĮTAKA VILNOS DAŽYMO TERMODINAMIKAI

S a n t r a u k a

Darbe nagrinėjamas rūgštinio dažiklio *C. I. Acid Orange 7* migracijos vilnos pluošte intensyvumo padidėjimo, kai dažymo tirpale yra nejoninės paviršinio aktyvumo medžiagos ar benzilo alkoholio, mechanizmas. Tiriamoms sistemoms, kurias sudarant naudotos ar nenaudotos pagalbinės dažymo medžiagos, buvo apskaičiuotos difuzijos charakteristikų – kinetinės konstantos bei tariamojo difuzijos koeficiento vertės ir termodinaminių charakteristikų – standartinio dažiklio giminingumo pluoštui, dažiklio sorbcijos standartinės šilumos, standartinės entropijos bei tariamosios aktyvacijos energijos vertės.

Rezultatai parodė, kad nejoninė paviršinio aktyvumo medžiaga *Lanasan LT* sumažina dažiklio giminingumą, dažiklio sorbcijos šilumą bei aktyvacijos energiją ir padidina dažiklio tariamojo difuzijos koeficiento vertes. Pažymėti vilnai dažyti neaukštoje temperatūroje dviejų dažnai naudojamų cheminių medžiagų – nejoninės paviršinio aktyvumo medžiagos *Lanasan LT* ir benzilo alkoholio veikimo mechanizmų panašumai ir skirtumai. Pasiūlytas nejoninio alkilfeniletoksilato veikimo mechanizmas pagrįstas vilnos pluošto hidrofobinių centrų ekranavimo efektu. Padaryta išvada, kad toks ekranavimas gali turėti įtakos dažiklio migracijos ir jo fiksacijos vilnos pluošte reiškiniams.