

EFFECT OF NONIONIC SURFACTANTS ON THE DYEING PROCESS OF CELLULOSE FIBRES WITH C.I. REACTIVE BLUE 217

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Abstract:

This investigation addressed the role of nonionic surfactants on the sorption of C.I. Reactive Blue 217 by cellulose fibres, focusing on the influence of the surfactant concentration and type on the spectroscopic properties of this dye. It was found that surfactants in dyeing baths change the spectroscopic properties of dye solutions, resulting in the decomposition of aggregates and agglomerates to form a surfactant-dye complex. The surfactants in baths counteract the aggregating action of sodium chloride. The performed studies concerned the sorption kinetics of dye from dyeing baths containing various surfactants and their influence on the exhaustion coefficients of the dye. Changes in the electrokinetic potential of the dyeing bath were also examined. It was found that nonionic surfactants retard the sorption processes of dye from the dyeing bath, improving dyeing quality.

Key words:

Anionic reactive dye - nonionic surfactant interaction, effect of surfactants on dyeing processes, sorption kinetics of C.I. Reactive Blue 217, nonionic surfactants, electrokinetic potential of dyeing bath

Introduction

Surfactants are commonly used in textile dyeing processes. Their use improves the quality of final dyeing. Interactions between dyes and surfactants in aqueous solutions have been described in many papers [1-12].

In dyeing polyester fibres and their blends with cellulose fibres, nonionic surfactants are mainly used. Polyester/cotton blends are dyed in a single-bath, one-stage process with mixtures of reactive dyes, Kayacelon React dyes and disperse dyes. The dyeing bath contains a dye, electrolytes, a buffer and surfactants [13-14].

It has been considered important to study the phenomena taking place in a dyeing bath containing a reactive dye of the Kayacelon React type, surfactants and electrolytes, focusing on the effect of surfactants on the spectrophotometric properties of the dye solution, changes in the electrokinetic potential of dyeing bath and dyeing yield.

Experimental

Subject of research

Dye

C.I. Reactive Blue 217 (Figure 1) has been selected and synthesised for these studies.

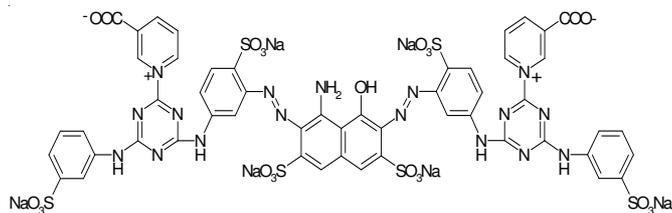


Figure 1. Structure of C.I. Reactive Blue 217.

The sodium chloride content, as determined by the potentiometric method, was 36.5%. C.I. Reactive Blue 217 is characterised by an absorption band in water with $\lambda_{\max} = 605$ nm.

Surfactants

Surfactants with various structures and properties were used for the study. They constitute ethoxylated fatty alcohols. The chemical constitutions and properties of nonionic surfactants used are given in Table 1. The properties of 0.1% (1 g/dm³) aqueous solutions of these surfactants are listed in Table 2.

Table 1. Chemical constitutions and properties of surfactants.

Surfactant symbol	Molecular weight [g/mol]	Chemical constitution: ethoxylated fatty alcohols: RO-(CH ₂ CH ₂ O) _n H	HLB*
S-1	530	R = C12-C15 n = ~ 7	ca. 12
S-2	430	R=C9-11, n = ~ 6	12.5
S-3	500	R = C12-14, n = ~7	12.9
S-4	640	R = C12-14, n = ~ 10	14.1
S-5	1060	R= C18, n = ~18	16.3
S-6	4600	R= C18 n = ~100	18.8

* Values provided by producer: PCC Rokita

Electrokinetic potential measurements were carried out using a particle charge detector (PCD O3 pH from Mutek Analytik GmbH, Germany).

Table 2. Properties of aqueous solutions of surfactants at 1 g/dm³ concentration at 40°C.

Symbol	pH	CMT * [°C]	Surface tension [mN/m]	Electrokinetic potential of surfactant solutions [mV]	
				No dye	Dye with a concentration of 1.72 * 10 ⁻⁵ [mol/dm ³]
S - 1	4.73	53	27.74	-336	-278
S - 2	3.65	50	29.81	-400	-316
S - 3	4.33	54	28.6	-323	-250
S - 4	5.22	89	30.47	-335	-247
S - 5	4.23	100	42.66	-372	-296
S - 6	5.28	>100	53.54	-336	-298
H ₂ O	-	-	72.88**	-683	-625

*Critical micelles temperature,

**Surface tension of water using for dyeing.

Buffer

In application tests, a phosphate buffer (pH = 7.0) was used, which was prepared by mixing 1/15 M solution of KH₂PO₄ with 1/15 M solution of Na₂HPO₄ in volumetric proportion 2:3.

Spectrophotometric measurements

Spectrophotometric measurements were taken for the dye solutions with a concentration of 1.72 x 10⁻⁵ mol/dm³ and surfactant concentration of: 0, 0.02, 0.04, 0.06, 0.1, 0.2, 0.4, 0.7, 1.0, 2.0 or 5.0 g/dm³. Prior to the measurements, the dye and surfactant mixed solutions were stabilised at 40°C for 60 min. The spectral characteristics of the absorbances of aqueous dye solutions containing various quantities of surfactant S-4 are shown in Figure 2.

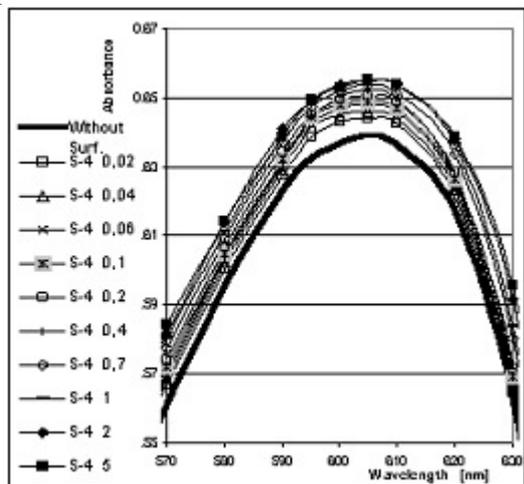


Figure 2. Spectral characteristics of peaks of the absorbance of aqueous solutions of C.I. Reactive Blue 217 containing 0-5 g/dm³ of surfactant S-4.

The effect of selected surfactants on the maximum absorbance value of C.I. Reactive Blue 217 is shown in Figure 3.

The spectral characteristics of the absorbances of aqueous dye solutions with the addition of various surfactants at 1 g/dm³ concentration are shown in Figure 4.

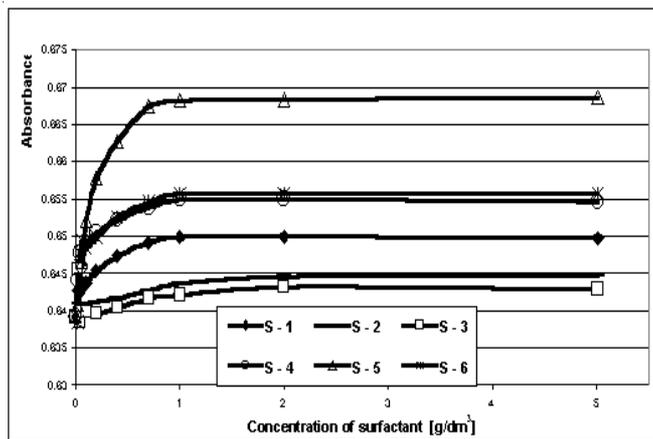


Figure 3. Relationship between the concentration of the selected surfactant in solution and the maximum absorbance of C.I. Reactive Blue 217 [13].

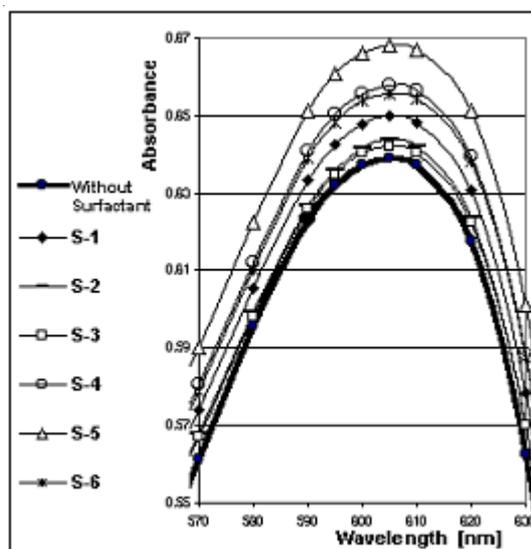


Figure 4. Spectral characteristics of peaks of absorbance of C.I. Reactive Blue 217 aqueous solutions containing various surfactants at 1 g/dm³ concentration.

Because the dyeing processes with reactive dyes are carried out in dyeing baths containing 20 to 60 g/dm³ of sodium chloride, it was reasonable to perform spectrophotometric measurements of the dye in 40 g/dm³ aqueous solutions of sodium chloride containing various surfactants at 1 g/dm³ concentration. The results obtained are shown in Figure 5.

Dyeing tests

Dyeing tests were carried out with a bleached woven fabric, type Noris 1/150 STB. Under standard conditions, the fabric was dyed isothermally at 40°C, using an initial dye concentration of 0.1%, liquor ratio of 1:40, time 2 h, with various variants of additives: phosphate buffer, phosphate buffer + surfactant (1 g/dm³) and phosphate buffer + sodium chloride (40 g/dm³) + surfactant (1 g/dm³). At 40°C, the dye practically did not form covalent bonds with cellulose fibre. After 1 h of dyeing, the bath was alkalisied with sodium carbonate (15 g/dm³). The dyeing course was monitored by spectrophotometric measurements of the dye concentration in the bath. The sorption curves obtained are shown in Figure 6.

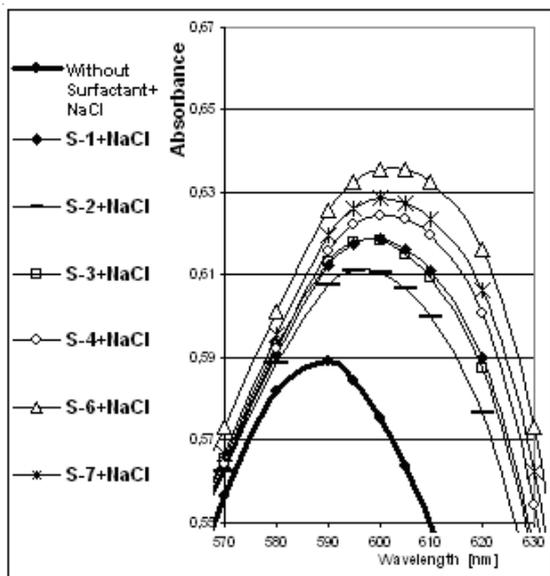


Figure 5. Spectral characteristics of the absorbances of C.I. Reactive Blue 217 in 40 g/dm³ NaCl solution containing various surfactants with a concentration of 1 g/dm³.

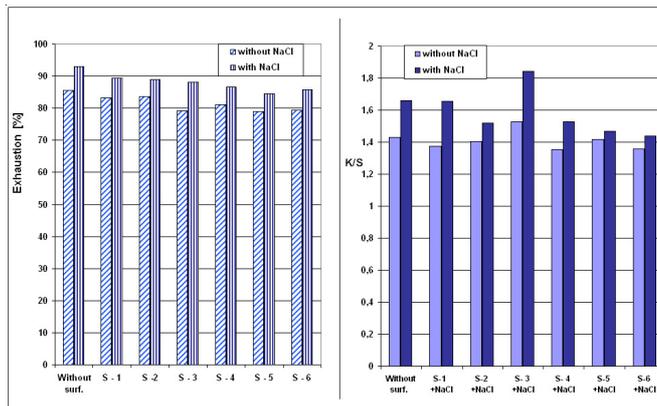


Figure 7. Effect of nonionic surfactants on the exhaustion coefficients at 40°C and relative dyeing strengths.

was continued for another hour. The bath was then cooled to 40°C.

Method B* Cotton fabric was pretreated in a solution of specified surfactant at 40°C and then the buffer and dye solution was added to perform the dyeing process as above (Method A*).

One half of the dyed fabric was washed in a bath containing 1 g/dm³ of nonionic surfactant, Marlipal O13/120 (HLB 14.5), at 90°C for 15 min, using a liquor ratio of 1:40. Then, the fabric was successively rinsed with warm and cold water. The dyed and washed fabrics, after drying, were subjected to the spectrophotometric assessment of dyeing intensity by measuring the relative dyeing strength. The obtained results are shown in Figure 8.

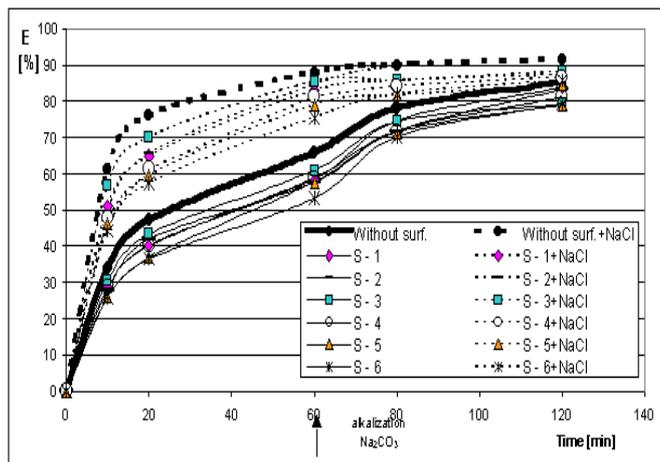


Figure 6. Sorption curves of Reactive Blue 217 at 40°C in surfactant solution at 1 g/dm³ concentration [13].

The performed dyeing tests allowed the determination of the dye exhaustion coefficients. After dyeing, the fabrics were squeezed out onto a filter paper. While drying at room temperature they were subjected to spectrophotometric measurements to determine the relative dyeing strength in accordance with Kubelka Munk's equation:

$$K/S = (1 - R) / 2R \quad (1)$$

where R is the remission coefficient, K is the absorption coefficient and S is the reflection coefficient. The obtained results of the exhaustion coefficients and relative dyeing strengths are shown in Figure 7.

One percent dyeing tests were carried out at 90°C for 2 h, with a liquor ratio of 1:10 and the same variants as above.

Method A* A cotton fabric sample was placed in the dyeing bath containing buffer, dye, surfactants and electrolytes as necessary. The dyeing process was carried out for 1 h at 90°C, then sodium carbonate (Na_2CO_3) (15 g/dm³) and the dyeing

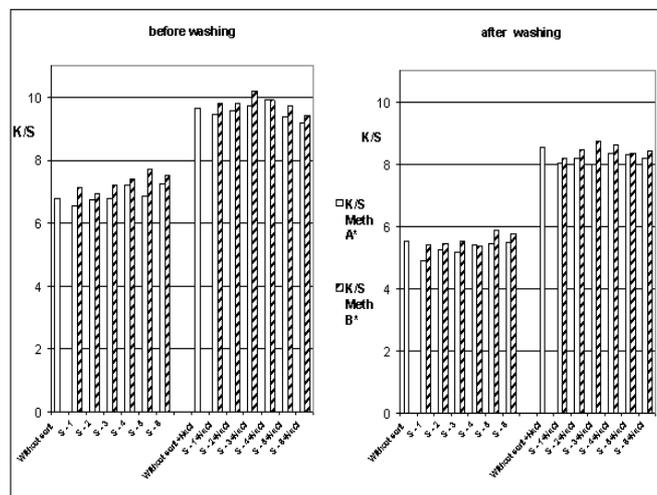


Figure 8. Influence of the nonionic surfactants used in dyeing processes on dyeing intensity [13].

Measurements of the electrokinetic potential of dyeing baths

Changes in the electrokinetic potential of dyeing baths, containing Reactive Blue 217 (1.72×10^{-5} mole/dm³) and various surfactants in different quantities, were measured by a particle charge detector PCD 03 pH. The obtained results are shown in Figure 9.

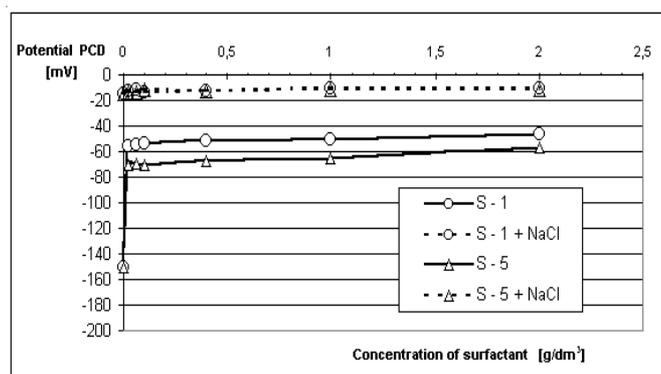


Figure 9. Electrokinetic potential of C.I. Reactive Blue 217 solutions at 40°C as a function of surfactant concentration in solution.

Discussion

As shown by the performed tests, nonionic surfactants influence the dyeing of cellulose fibres with C.I. Reactive Blue 217 containing two 3-carboxypyridine triazine systems in its molecule. It has been shown that the addition of a nonionic surfactant to a solution of dye changes its spectroscopic properties by increasing its specific absorbance with no changes in the λ_{\max} position. The addition of sodium chloride to an aqueous dye solution results in the displacement of λ_{\max} towards shorter waves and a reduction in the specific absorbance of the solution at the same time. The sodium chloride present in the solution changes its physicochemical properties by increasing the dye aggregation and agglomeration in solution. The simultaneous addition of sodium chloride and a surfactant to the dye solution also causes bathochromic and hyperchromic effects (Fig. 5). Such an action of a surfactant indicates the decomposition of aggregates and agglomerates. The action of a surfactant is opposite to that of sodium chloride. The values of λ_{\max} and Abs $_{\max}$ are intermediate between those of an aqueous dye solution and a dye solution containing sodium chloride.

It has been observed that surfactants act differently depending on their chemical constitutions. Surfactants with lower HLB values affect the spectroscopic properties of dye to a lesser extent. An exception is surfactant S-6 (HLB 18.8), which is characterised by lower solubilising properties than surfactant S-5 (HLB 16.3). In an aqueous medium, surfactants and dyes form surfactant-dye complexes. It was experimentally found that the changes in the spectroscopic properties of the aqueous dye solution take place with the increase in surfactant concentration in solution from 0 to 1 g/dm³. The further increase in the surfactant concentration in solution does not change the values of λ_{\max} and Abs $_{\max}$. The electrokinetic potential of the dye solution in a surfactant solution assumes higher values than those of an aqueous dye and an aqueous surfactant solution (Table 2).

The exhaustion rate of the dye from the dyeing bath and the final equilibrium states depend on the electrolyte concentration in the bath (including phosphates and sodium carbonate). In the presence of an electrolyte, the dye exhaustion rate increases simultaneously with the increase in the dye exhaustion coefficients. An important role is also played by surfactants. All of the tested surfactants decrease the dye exhaustion rate and dye exhaustion coefficients at the same time. Surfactant S-1 in a bath without salt decreases the dye exhaustion coefficients by 2.2 %, but by 4.5% in a bath with salt. Surfactant S-5 in a bath containing the buffer and in a bath

with sodium chloride decreases these coefficients by 7.7% and 9.2%, respectively. The other surfactants also decrease the dye exhaustion coefficients whose values range between those of surfactant S-1 and S-5.

The addition of a surfactant at a quantity of 0.02 g/dm³ to the dye solution significantly increases the value of electrokinetic potential, which also indicates the formation of dye-surfactant complexes. The further increase in the surfactant concentration in solution changes the electrokinetic potential of the dyeing bath only to a small extent (Figure 9). The dye is exhausted more quickly from baths containing sodium chloride (Figure 6). However, the addition of a surfactant to the dyeing bath decreases the dye exhaustion rate despite the increased electrokinetic potential of the bath. The problem might be more complex and the dye exhaustion rate might, for instance, depend on the size and stability of the dye-surfactant complex or the stability of the dye aggregates in water.

Although surfactants decrease the dye exhaustion coefficient, the dyeing intensity expressed by the relative dyeing strength K/S is not decreased and, in many cases, it is slightly increased (Figure 8). This takes place mainly in the case of variant B*, which consisted of dyeing cellulose fabric after its pretreatment with a surfactant solution.

Thus, surfactants act also inside fibres preventing dye aggregation in fibres. The highest values of K/S for dyeings without sodium chloride at 90°C were shown by the fabric dyed with the addition of the S-5 surfactant and by the fabric dyed in a bath containing the S-3 surfactant and sodium chloride.

Conclusion

Nonionic surfactants in dyeing baths affect the physical and chemical properties of dye solutions, inducing the decomposition of aggregates and agglomerates and thereby resulting in the formation of surfactant-dye complexes. This phenomenon changes the kinetics of dye absorption by cellulose fibres. As a result, the process of dye exhaustion slows and the dyeing effects become bright as the dye is absorbed by fibres in the monomolecular form. The lower dye exhaustion rate makes it possible to obtain more uniform dyeing effects. Surfactants also prevent the aggregation of C.I. Reactive Blue 217 on cellulose fibres, causing, in many cases, an increase in the relative dyeing strength despite a lower dye concentration on fibres. The addition of surfactants to a dyeing bath improves the quality of dyeing cellulose fibres with C.I. Reactive Blue 217.

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