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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Use of Cationic Agents for Fixing Coloration of Textile Materials

O. I. Odintsova, M. N. Krotova, and B. N. Mel'nikov

Ivanovo State University of Chemical Technology, Ivanovo, Russia

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Abstract—Ways to increase the degree of utilization of active dyes, enhance the economic and environmental efficiency of coloration, and improve the quality parameters of fabric coloration and tints are considered. The theoretical and applied aspects of fixing coloration of textile materials colored with active dyes by using new alkylamine derivatives in the form of cationic polyelectrolytes and surfactants are studied.

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Active dyes, along with pigments, are still the most widely used in the textile industry. However, along with indubitable advantages, application of active dyes gives rise to environmental problems associated with the presence of a certain amount of the unfixed dye in the discharged wash waters. Furthermore, the economic efficiency of the process is impaired by low degree of fixation of such dyes on textile materials (usually 60–80%). The presence of the hydrolyzed form of an active dye significantly affects the fastness characteristics of colored and especially printed fabrics and deteriorates the aesthetic characteristics of the textile coloration [1, 2].

To solve the existing problems and enhance the resistance of fabric coloration to physicochemical actions, two groups of substances can be used: substances that efficiently remove the hydrolyzed dye from the fabric (dye transfer inhibitors) and substances strongly fixing the hydrolyzed dye in the fiber (coloration fixers) [3, 4].

The use of fixing agents is more promising from the viewpoint of attaining high quality of textile materials and making the fabric dyeing and printing environmentally clean and economically feasible [5–7].

In this study we examined the interaction of a wide range of alkylamine derivatives with hydrolyzed active dyes of various chemical structures.

EXPERIMENTAL

The hydrolyzed form of the dye was prepared by adding 30% acetic acid (to pH 6–7) to a solution of the following composition (g l^{-1}): active dye 20, NaOH 10; liquor ratio 20.

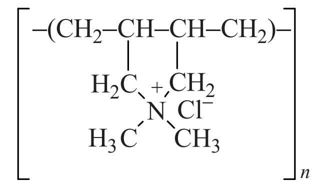
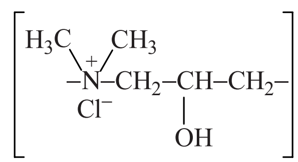
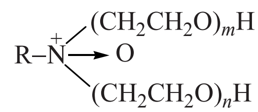
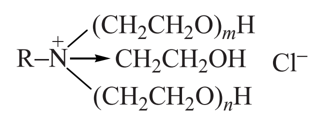
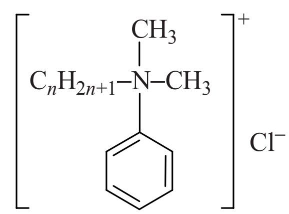
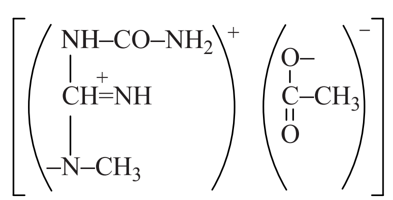
A preliminarily weighed specimen of cotton fabric (type of merchandise 262) was placed in the solution prepared, and the textile material was impregnated for 20 s. The specimen was squeezed on a laboratory padding machine, dried in air, and treated with solutions of various cationic compounds: product of the initial condensation of dicyandiamide with formaldehyde (DTsU), polydiallyldimethylammonium chloride (VPK-402), poly(epichlorohydrin–dimethylamine) (Kaustamin-15), alkyldimethylbenzylammonium chlorides (Katapav etc.), for various times at various temperatures [8]. After that, the amounts of the dye desorbed to the solution and retained on the textile material after the treatment were evaluated. The characteristics of the main cationic agents used in this study are given in Table 1.

The performance of fixing agents was evaluated by the degree of dye desorption, degree of its fixation on the fiber, and color characteristics of the treated specimens.

The dyeing solutions were analyzed for the presence of the active and hydrolyzed forms of the dye by paper chromatography. The dye forms were separated on chromatographic paper (grade S) in ascending solvent flow for 24 h. The dimethylformamide–butanol–water system (3 : 11 : 11) was used as eluent.

From the solution of the dye (hydrolyzed and nonhydrolyzed), we took samples with a micropipet and placed them on the start line of chromatographic

Table 1. Main characteristics of the agents used

Cationic agent	Structural formula
VPK-402 cationic polyelectrolyte [TU (Technical Specification) 2227-184-00203312–98]: molecular weight 3×10^5; colorless to yellow liquid of uniform consistence; weight fraction of the main substance no less than 25%	
Kaustamin-15 (TU 2227-222-00203312–2002): quaternary polyamine, polymer derived from epichlorohydrin and dimethylamine; molecular weight 10^4–10^6; aqueous solution is a viscous pale yellow liquid	
Oksamin oxide KM-7: laboratory sample, pale brown liquid	 $n + m = 7$
Kvatamin KM-10: laboratory sample, pale brown liquid	 $n + m = 10$
Katapav (TU 2482-008-04706205–2004): alkylbenzyldimethylammonium chloride; pale yellow liquid; weight fraction of the main substance 48–52%	 $n = 10$–16
Alkapav (TU 2482-004-04706205–2005): alkyltrimethylammonium chloride; pale yellow liquid; weight fraction of the main substance 25–30%	$[C_nH_{2n+1}-N^+(CH_3)_3]Cl^-$ $n = 10$–16
DTsU [GOST (State Standard) 6858–54]: mixture of acetates of products obtained by hydroxymethylation of dicyandiamide and hexamethylenetetramine with formaldehyde; yellow to pale brown syrupy liquid	

paper in the form of round spots at a distance of 2.5 cm from the sheet edge. After drying of the spots, the paper was immersed in an eluent solution in a chromatographic column for 24 h. Then the paper was withdrawn and dried in air.

The areas of the active and hydrolyzed forms on the chromatographic paper were cut, and the dye was washed out with dimethylformamide. The dimethylformamide solutions were subjected to colorimetric measurements, and the content of various forms of the dye was calculated as the ratio of the given form to the total amount of the dye.

Data on the content of hydrolyzed and active forms in the commercial and prehydrolyzed samples of the dyes are given in Table 2.

The degree of hydrolysis of the commercial forms of active dyes, irrespective of their chemical structure, is significant and ranges from 5 to 36%, and in prehydrolyzed dye samples the content of the active form is minimal.

As the object of our study is the hydrolyzed form of the active dye, we developed a procedure for estimating the effect of various chemical compounds on the degree of its binding. The procedure we suggest involves treatment of textile materials with the applied prehydrolyzed active dye in a medium of new cationic surfactants and polymeric electrolytes of various chemical structures. In this study we evaluated changes occurring in solution and on the fabric after the treatment.

Figure 1 shows how the examined substances affect the degree of desorption of the hydrolyzed form of Active Red-Violet 2KT from a cellulose substrate into solution.

We found that, when samples dyes with hydrolyzed Active Red-Violet 2KT are treated with ampholytic Oksamin oxide KM-7 and cationic oxyethylated alkylamine Kvatamin KM-10, and also with VPK-402 cationic polyelectrolyte, the amount of the bound hydrolyzed dye on the fiber is not increased significantly. On treatment with these agents, the dye is washed out from the cellulose material to 60–80%.

Good results were obtained with cationic agents derived from alkylamines (Alkapav and Katapav 1016S50) and with Kaustamin-15 polyelectrolyte.

The best results were obtained on adding to the fixing solution cationic agents of a new generation: Kvarteks and Katapav, which have a relatively long carbon chain (C_{10}–C_{16}). In this case, the degree of desorption is minimal (6.3%), i.e., the major fraction of the hydrolyzed dye remains on the textile material.

Thus, it can be assumed that treatment of the fabric involves interaction of an anionic dye with a cationic surfactant.

The composition of the compound formed on adding Katapav to an aqueous solution of the dye was determined by the method of molar ratios, consisting in measuring the optical densities of solutions with the varied concentration of one of the components [9]. To this end, we plotted the optical density vs. concentration ratio of the components in solution (Fig. 2).

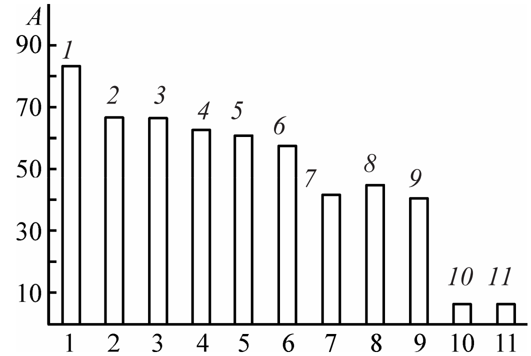


Fig. 1. Influence of the kind of the fixing agent on the degree of desorption *A* of hydrolyzed Active Red-Violet 2KT into solution. (*1*) Sulfoxide 61, (*2*) Oksamin oxide KM-7, (*3*) VPK-402, (*4*) Kvatamin KM-10, (*5*) water, (*6*) Alkapav 16S50, (*7*) Kaustamin-15, (*8*) Alkapav, (*9*)Katapav 1016S50, (*10*) Katapav, and (*11*) Kvatreks.

Figure 2 shows that the curve has a minimum corresponding to the composition of the compound formed. In the system under consideration, the 1 : 1 complex is formed predominantly:

Table 2. Content of hydrolyzed and active forms of active dyes of various chemical structures

Dye	Content, %	
	active form	hydrolyzed form
Commercial form		
Red-Violet 2KT	95.0	5.0
Bright Red 5SKh	63.7	36.3
Red-Brown 2KT	66.1	33.9
Bright Blue KKh	68.5	31.5
Turquoise 2ZT	74.9	25.1
Hydrolyzed dye		
Red-Violet 2KT	14.2	85.8
Bright Red 5SKh	5.8	94.2
Red-Brown 2KT	12.7	87.3
Bright Blue KKh	7.8	92.2
Turquoise 2ZT	10.1	89.9

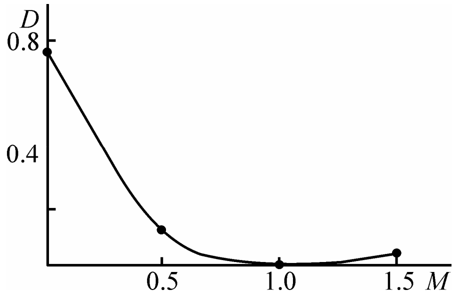
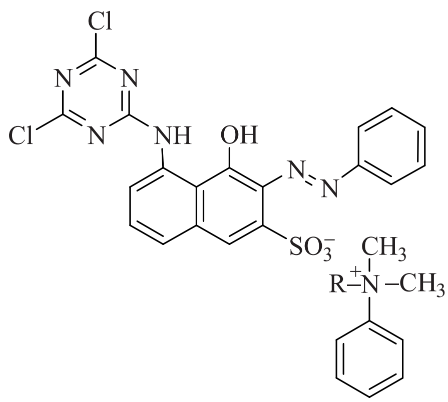


Fig. 2. Determination of the component ratio in the complex by the method of molar ratios *M*. (*D*) Optical density.



$R = C_{10}–C_{16}$.

However, most likely, the solution contains a mixture of compounds of various chemical structures, with 1 : 2 complexes present along with the major 1 : 1 complexes.

The effect of the concentrations of the cationic agents on the degree of fixation of the hydrolyzed dye and on the color parameters of textile materials is illustrated by Table 3. It can be seen that the traditionally used formaldehyde fixing agent DTsU in a concentration of 5 g l^{-1} does not noticeably bind the hydrolyzed active dye on the fiber. With this agent, the amount of the bound dye is as low as 19.5%.

The cationic surfactant (Katapav) and cationic polymeric electrolyte derived from epichlorohydrin (Kaustamin-15) firmly retain the hydrolyzed active dye on the fiber. The degree of binding of the hydrolyzed dye after treatment of the dyed textile material with a 2 g l^{-1} Katapav solution is 61%, and after treatment with a 5 g l^{-1} Kaustamin solution, 88.6 %. However, the minimal loss of the active dye was attained only with the fixing solution that contained the cationic polyelectrolyte (Kaustamin-15) and the cationic surfactant (Katapav) simultaneously.

Data on the amount of the bound hydrolyzed dye are well consistent with the color characteristics of the treated samples. The minimal lightness of the textile material is also attained with Kaustamin and Katapav. Table 4 characterizes the efficiency of the interaction of the agents under consideration with hydrolyzed active dyes of various chemical structures on the fiber and in solution.

Table 4 shows that the fixing action of the Kaustamin–Katapav system is efficient and universal in binding of vinyl sulfone (Turquoise 2ZT, Yellow 2KT), dichlorotriazine (Bright Red 5SKh, Orange KKh), and monochlorotriazine (Violet 4K, Green 2Zh) dyes.

The use of the developed fixing formulation in dyeing of textile materials with active dyes makes it possible to increase the degree of dye utilization, with attainment of high resistance of the coloration to physicochemical actions, and to reduce the material and power consumption for the dyeing.

Table 3. Effect of cationic agents on the degree of binding of the hydrolyzed dye and on the color characteristics of dyed textile materials

Fixing agent	Concentration, g l^{-1}	Lightness *L*, %	Deepness *C*, %	Color tint *H*, deg	Degree of dye binding *F*, %
DTsU	5	68.9	40.9	43.2	19.5
Alkapav	5	65.6	41.5	43.8	41.0
Katapav	2	55.0	42.2	44.7	61.0
Kaustamin-15	5	53.1	42.1	44.6	88.6
Katapav Kaustamin-15	2 5	50.6	42.6	36.6	97.9

Table 4. Efficiency of interaction of the composite fixing agent with hydrolyzed active dyes of various chemical structures

Dye	Lightness *L*, %	Deepness *C*, %	Color tint *H*, deg	Degree of dye binding *F*, %
Turquoise 2Zt	55.6	41.6	36.6	97.9
Yellow 2KT	51.9	59.4	61.9	89.73
Bright Red 5SKh	43.8	57.4	8.8	70.7
Orange KKh	64.9	73.1	58.0	71.5
Green 2Zh	44.1	30.1	–31.3	99.3
Violet 4K	27.9	29.7	–41.8	70.5

CONCLUSIONS

(1) A procedure was developed for evaluating the extent of interaction of a hydrolyzed active dye with various fixing agents.

(2) The composition of the compound formed by the active dye with alkyldimethylbenzylammonium chloride was determined.

(3) A composite agent consisting of a cationic surfactant (Katapav) and a synthetic polyelectrolyte (Kaustamin-15) was suggested. It allows the degree of binding of the inactive form of a dye to be increased to 70–99% depending on the chemical structure of the dye.

(4) The developed formulation is recommended for use in dye fixation on textile materials, to save the expensive active dyes.

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