ELSEVIER

Dyes and Pigments 40 (1999) 225–233

DYES AND PIGMENTS

Dye–fibre bond stabilities of some reactive dyes on cotton

Marija Gorenšek *

Department of Textiles, Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia

Received 20 May 1998; accepted 15 June 1998

Abstract

Cotton fabric dyed with commercial reactive dyes of the monochloro-s-triazine, bis(monochloro-s-triazine), and bis(monofluoro-s-triazine) type was treated in buffer solutions pH 10 and 12 at 60, 85 and 98°C. Hydrolysis has been investigated using spectrophotometrical measurements of hydrolysed dye at λ_{max}. The percent of hydrolysed dye was calculated. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrolysis; Monochloro-s-triazine reactive dye; Bis(monochloro-s-triazine) reactive dye; Bis(monofluoro-s-triazine) reactive dye; Cellulose fibre

1. Introduction

Several researchers have investigated the hydrolysis of reactive dyes in aqueous solutions of different pH values [1,2], the stability of the bond between the dye and the model compounds [1,3,6,7] and also dye–fibre bond stabilities [1,3,8–18]. Studies of the hydrolysis of several types of reactive dyes on cellulosic [1,3,8–18], wool [17] and silk [18] fibres have been published.

The kinetics of the hydrolysis reaction of trichloropyrimidyl amino compounds with water, alcohol and cellulose were investigated by Ackermann and Dussy and the reaction mechanisms were discussed [1]. It was also concluded that the rate of hydrolysis of reactive dyes containing the vinyl sulphone reactive group depends much more on the pH value compared with reactive dyes containing the acrylamide reactive group [5]. The influence of the temperature, pH value and the quantity of electrolyte on the rate of hydrolysis of cellulosic fibres dyed with vinyl sulphone dyes at 60°C [8], and the hydrolysis of dichlorotriazine and vinyl sulphone dyes on cellulosic fibres in acetic acid and alkaline medium was also investigated. A mechanism of the first reaction rate for the hydrolysis in acid and also for the first 30 min in alkaline medium was proposed [9]. Senn used model reactive dyes containing the same chromogen structure with different reactive groups on cellulosic fibres for hydrolysis tests in buffer solutions of the same ionic strength from pH 1 to pH 10. He concluded that because the hydrolysis reaction runs simultaneously with many partial reactions with different rates, the mechanism of the reaction is not comparable to the mechanism of first order reaction. Senn published his results of the hydrolysis of the dyes as percent of hydrolysed dye per hour (%/h), calculated on the value of the dye fixed on the cellulosic fibre. Results confirm the dye–fibre bond stability in neutral medium and an increased hydrolysis in acid and

---

* Fax: +386-61-125-31-75; e-mail: textiles@uni.lj.si

PII: S0143-7208(98)00052-7

alkaline medium [10]. By analogy to ester hydrolysis, fission of the bond of reactive dyes containing triazine or diazine reactive group to cellulose fibre was proposed. With respect to the concentration of hydroxyl ions, this mechanism agreed with a first order reaction [11,12].

The rate of hydrolysis of reactive dyes containing the phosphonium group on cellulosic fibres at pH values from 2.2 to 8.6 at 98°C has also been investigated. The maximum bond stability was found between pH 6 and 7, similar to that of monochlorotriazine reactive dyes. High wet fastness was found by dyeings with dyes containing the phosphonic group [13]. Comparison of the wet fastness of dyeings with dyes containing the phosphonic reactive group and those with a carboxylic reactive group in alkaline medium at pH 7–10 at 60°C, the higher stability of the first mentioned dyeings to alkaline hydrolysis was indicated [16]. A detailed study of the hydrolysis of monofluorotriazine reactive dyes and model compounds has also been made [14].

Comparison of the stability of the bond between cellulose and bifunctional monochlorotriazine and sulphatoethylsulphone dyes having a similar constituent composition with the same monofunctional reactive dyes in aqueous buffer solution pH 1.6–10 at 98°C showed higher stability of the bifunctional dyes. The fixation of those dyes to the fibres was evidently better [15]. The kinetics of hydrolysis was studied also on model compounds, i.e. methyl-α-D-glucoside and vinyl sulphone reactive dyes. It was established that, in the first stage, elimination took place [6]. When methyl-α-D-glucoside and a vinylsulphone dye was treated in an aqueous solution of dioxan, it was observed that only the C_6 and C_4 hydroxyl groups are involved in the hydrolysis reaction. The influence of some substituents on the aromatic ring to the reactivity of vinyl sulphone reactive groups, and also to the kinetics of the alkaline hydrolysis, was evident [7]. Using HPLC analysis, the hydrolysis of C.I. Reactive Red 194 and model compounds, such as C.I. Reactive Red 3 in aqueous solutions pH 9–12 at 50°C was studied. For both types of dyes, rate constants were calculated and also a reaction scheme for the pseudo first order reaction was proposed, neglecting the hydrolysis of the imino bonding groups, which is unusually small [4]. Using HPLC, the kinetics of the hydrolysis of monochloro-s-triazine and bis(monochloro-s-triazine) reactive dyes at pH 11 by 80°C have been determined [2].

For reactive dyes, during the dyeing process which takes place usually in alkaline conditions, two types of reactions are possible i.e. covalent bonding with the fibres and an unfavourable alkaline hydrolysis. Because of the selectivity of the dyes, fixation with the fibres is preferable, while only a smaller part of the dye hydrolyses. This dye is lost for the dyeing process, and at the end phase can result in ecological problems. The synthesis of bifunctional reactive dyes with high substantivity, has been reported, and this allows them to achieve excellent exhaustion in batchwise dyeing, achieving fixation values of about 70–80% [19]. However, a considerable possibility of dye hydrolysis in the dyebath and on the fibres still occurs, particular with heavy shades. Hydrolysis of reactive dyes occurs not only in dyeing, but also in normal every day washing of reactively dyed cellulosic material.

2. Experimental

2.1. Materials

2.1.1. Fabric

Bleached unmercerized cotton fabric was used throughout the work, produced by Aqua Sava, Kranj.

2.1.2. Dyes

All dyes used were of commercial grade. They are listed in Table 1.

2.1.3. Chemicals

All reagents for the dyeing process were of general purpose grade. Chemicals used for hydrolysis were buffer $pH_{20^\circ C} = 10$, containing boric acid (Kemika, Zagreb), potassium chloride (Kemika, Zagreb) and sodium hydroxide solution (Zorka, Šabac).

Buffer $pH_{20^\circ C} = 12$ contained disodium hydrogen phosphate (Kemika, Zagreb) and sodium hydroxide solution (Zorka, Šabac). All chemicals

Table 1
Dyes used in this study

Commercial name	Dye no.	Reactive group
Procion Scarlet H-2G	**1**	monochloro-s-triazine
Procion Blue H-4R	**2**	monochloro-s-triazine
Procion Red H-E7B	**3**	bis(monochloro-s-triazine)
Procion Blue H-ERD	**4**	bis(monochloro-s-triazine)
Cibacron Scarlet LS-2G	**5**	bis(monofluoro-s-triazine)
Cibacron Blue LS-3R	**6**	bis(monofluoro-s-triazine)

used for hydrolysis were p.a. grade. Buffer solutions used are shown in Table 2; pH values of the buffer solutions were checked using a pH-meter Iskra MA 5740.

2.1.4. Dyeing procedures

Dyeing was carried at a liquor ratio 1:20 by the all-in procedure using 1% of commercial dye. The all-in procedure used for Procion H and H-E dyes has already been discussed by us [20]. For the Cibacron LS (Ciba) dyes, the all-in procedure was also used. Comparing the all-in and migration method proposed by Ciba [21], 3% abs. better fixation of the dye was found by the all-in procedure. The dyeing bath contained: 1% Cibacron LS, 15 g/litre anh. Na_2SO_4, 10 g/litre Na_2CO_3.

Comparing dyeings with Procion HE dyes, only 1/3 of the electrolyte is used. Washing and soaping of dyed fabrics was carried out in accordance with the manufacturer's instructions [21]. For the determination of the stability of the covalent bond between the reactive dye and cellulosic fibre, stripping of unfixed dye from the dyed cotton fabric is important. This procedure has been discussed in detail [20]. From spectrophotometrical values, the percentage fixation F (%) of dyes on cellulosic fibre was then calculated [20]. It was calculated as the amount of dye added originally to the dyebath which is fixed on the cotton, following the equation:

$$F(\%) = \left(1 - \frac{C_a + C_{1w} + C_{2w} + C_s + C_{\mathrm{TMU}}}{C_b}\right) \times 100$$

where:

C_b,	concentration of the dye before the dyeing process (g/litre)
C_a,	concentration of the dye after the dyeing process (g/litre)
C_{1w},	concentration of the dye in the first washing bath (g/litre)
C_{2w},	concentration of the dye in the second washing bath (g/litre)
C_s,	concentration of the dye in the soaping bath (g/litre)
C_{TMU},	concentration of the dye in TMU solution (g/litre).

For 1% dyeings of cellulosic fabric by the all-in procedure in a 1:20 liquor ratio, the percentage fixation values F (%) are listed in Table 3.

2.2. Hydrolysis

2.2.1. Hydrolysis procedure

Three grams of dyed aftertreated cotton fabric [20] was treated in 300 ml of buffer solution pH 10 and pH 12 at 98, 85 and 60°C. For hydrolysis at 85 and 60°C thermostated baths were used. After appropriate time intervals (10 min) 7–10 ml of hydrolysed solution was removed. The solution was cooled to room temperature and the visible spectrum was measured. The cooled hydrolysed sample was quickly returned to the solution before

Table 2
Buffer solutions used for hydrolysis tests

Buffer solution	pH Value at 20°C
3.092 g/litre H_3BO_3 3.728 g/litre KCl 1.759 g/litre NaOH	10
4.450 g/l $Na_2HPO_4 \times 2H_2O$ 0.892 g/l NaOH	12

Table 3
F (%) for dyes used in this study

Dye no.	F (%)
1	57.8
2	16.4
3	72.1
4	72.6
5	80.3
6	67.7

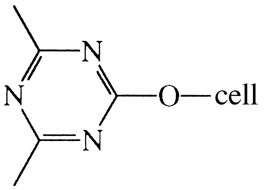
the next measurement. The concentration of the dye in solution was also determined by comparing the absorbance value at the absorption maximum with that of a known concentration in the same buffer solution. For measurement of absorbances, an Opton H4Q III-DMR 21 spectrophotometer was used. The hydrolysis was being monitored over 420 min. Results are the average values of four measurements of hydrolysis.

3. Results and discussion

The stability of the covalent bond between a reactive dye and cellulosic fibre can be determined by spectrophotometrical detection of the concentration of hydrolysed dye after a fixed time at λ_{max} of hydrolysed dye. For some reactive dyes the split on the imino bond can run out, but from literature data this can be neglected [4]. It has been found that, from the stability of the bond towards hydrolysis of a certain dyeing, the type of reactive system used can be determined [22–24].

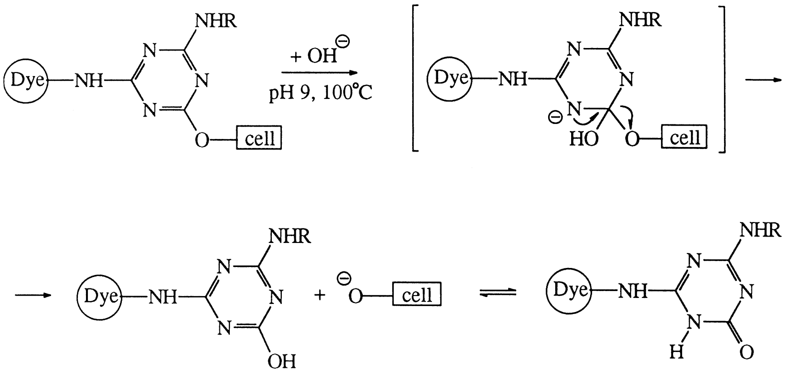
Interpretation of the hydrolysis of the bond between the reactive dye and cellulosic fibre is possible when the chemical structure of the reactive group is known [12,16]. When monochloro-s-triazine, bis(monochloro-s-triazine) or bis(monofluoro-s-triazine) reactive groups are bound on the reactive dye, a chlorine or fluorine atom is exchanged by a high molecular weight alkoxy group after reaction with cellulose fibre. In stronger alkaline medium, nucleophilic substitution takes place on this dye–fibre bond, as shown in Scheme 1 [25].

The covalent bond between dye and cellulose fibre in the form of



is evidently similar to an ester, and the mechanism of alkaline hydrolysis is similar to fission of the ester [12].

Most published results of the hydrolysis of reactive dyes are based on investigations of the influence of different pH media on fibre–dye bond stability, using reactive dyes of equal chromogen structure [10,13,15,16]. Several authors have studied the hydrolysis of reactive dyes and established maximal stability of reactive dyes on cellulosic fibres between pH 6 and 7 [10,12,13,15,16]. The amount of hydrolysed dye increases at higher and lower pH values. The results of hydrolysis in solution at pH 10 show that there is a great difference in the quantity of hydrolysed dye between dichloro-s-triazine dyes bound only by one bond to the cellulose fibre and those bounded completely [12]. After one hour treatment of dyed cellulosic material at the boil, the split-off of the first mentioned dye was more than three times greater than those linked with



Scheme 1. The mechanism of alkaline hydrolysis of a triazine reactive dye.

two bonds to cellulose fibre. Normally both dyes retain the same chromogen structure. The influence of different temperatures of the treating baths on the fission of the bond was not investigated in this work.

The influence of temperature at using solutions of pH 10 and 12 on the hydrolysis of the bond between some monochloro-s-triazine, bis(monochloro-s-triazine) and bis(monofluoro-s-triazine) reactive dyes and cellulosic fibres is described in this present investigation.

From Fig. 1 there is an evident very good stability of the bond between the monochloro-s-triazine Procion Scarlet H-2G and cellulosic fibre at 60°C.

The percentage of hydrolysed monofunctional scarlet dye at 60°C after 1 h treatment in solutions pH 10 and 12 is equally small. After 7 h in solution pH 12 at 60°C, the hydrolysis is almost 3 times greater than in the solution of pH 10. Using higher temperatures, i.e. 85 and 98C, the influence of higher pH value on the split off of the bond is apparent. After one hour treatment, 9 or 7 times more dye hydrolyses at pH 12.

Similar relations are apparent in Fig. 2 for dyeings with 1% Procion Blue H-4R. The dye–fibre bond is less stable when a solution of pH 12 was used. Higher temperatures and pH value of the solution cause a more rapid interruption of the ester bond. Treatment of dyed cotton in a solution of pH 12 at 98°C shows 21.1% of hydrolysed dye after 1 h and in a solution of pH 10 6.4% of hydrolysed dye. This blue monofunctional dye is very unstable when boiling temperatures are used.

Red and blue bis(monochloro-s-triazine) dyes are especially stable to alkali treatment at 60°C and also over 1 h at 85°C. No hydrolysis was detected when cotton dyed with 1% Procion Blue H-ERD was treated at 60°C in solution of pH 10, and therefore there is no curve shown in Fig. 4 for this temperature.

The hydrolysis of Procion Red H-E7B and of Procion Blue H-ERD at the boil in a solution of pH 12 is about 2.9%/h. From the results of some previous researchers evaluating the hydrolysis of some reactive dyes, this value implies that such dyes are technically very usable [10]. Those bifunctional dyeings exhibit high wet fastness at 60°C and our conclusion is that they possess high wet fastness also at 85°C using alkaline media up to pH 12.

The bis(monofluoro-s-triazine) dye Cibacron Scarlet LS-2G possesses high stability at pH 10

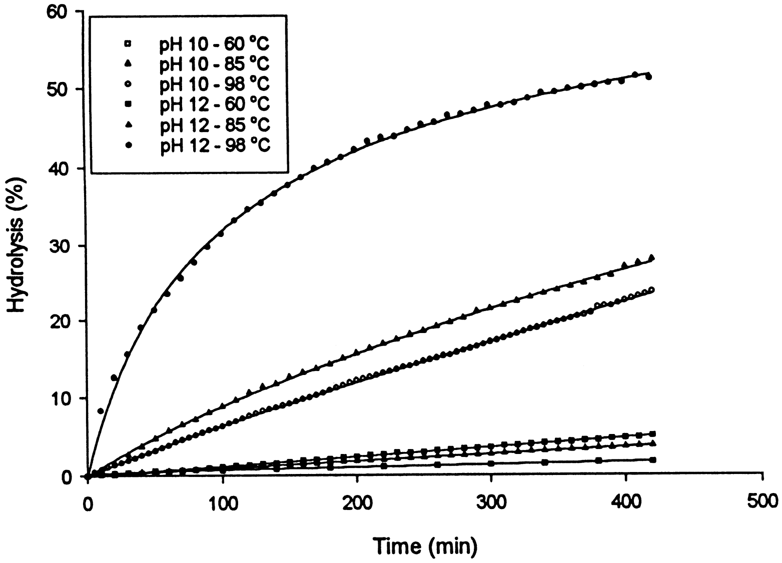


Fig. 1. Effect of temperature and pH on percent of hydrolysis of cotton dyed with 1% Procion Scarlet H-2G.

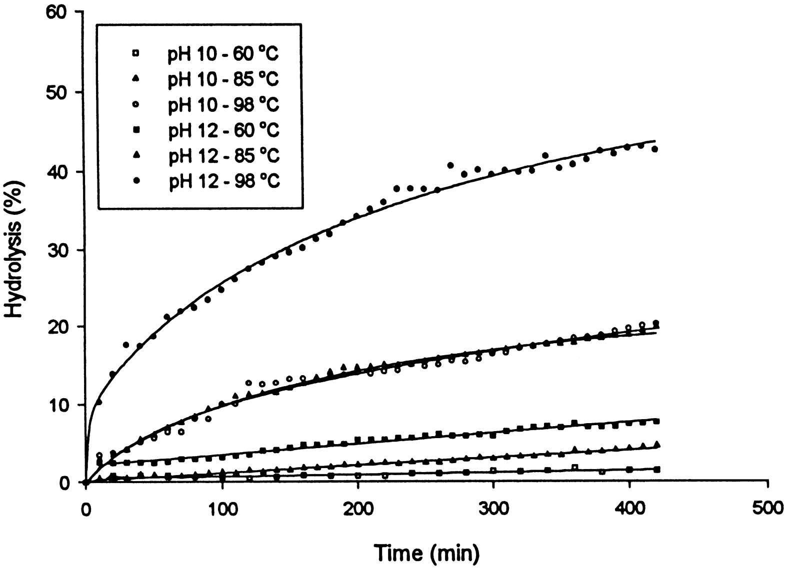


Fig. 2. Effect of temperature and pH on percent of hydrolysis of cotton dyed with 1% Procion Blue H-4R.

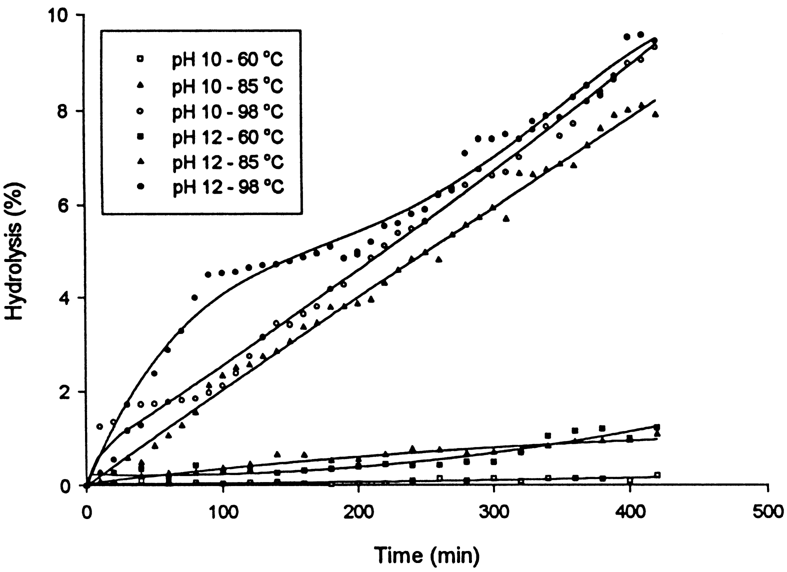


Fig. 3. Effect of temperature and pH on percent of hydrolysis of cotton dyed with 1% Procion Red H-E7B.

and 12 at 60°C and also at 85°C. One-hour-boiling of the dyeings at pH 10 also does not result in cleavage of the covalent bond. Longer treatment under these conditions leads to 4.6% of the hydrolysed form.

Boiling the dyeings at pH 12 causes more hydrolysis and from Fig. 5, it is evident that after 1 h treatment, the quantity of hydrolysed dye is 2.12%.

When the dyeings are treated 7 h in solutions of pH 10 at 98°C, 4.59% of hydrolysed dye is

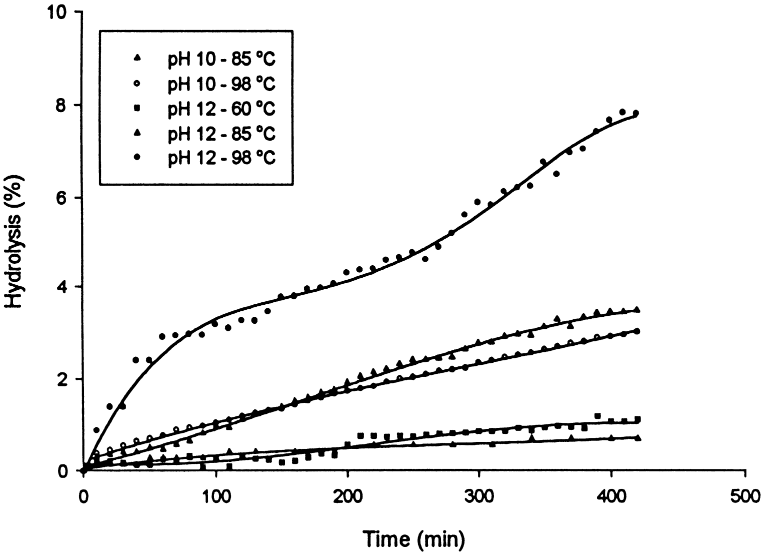


Fig. 4. Effect of temperature and pH on percent of hydrolysis of cotton dyed with 1% Procion Blue H-ERD.

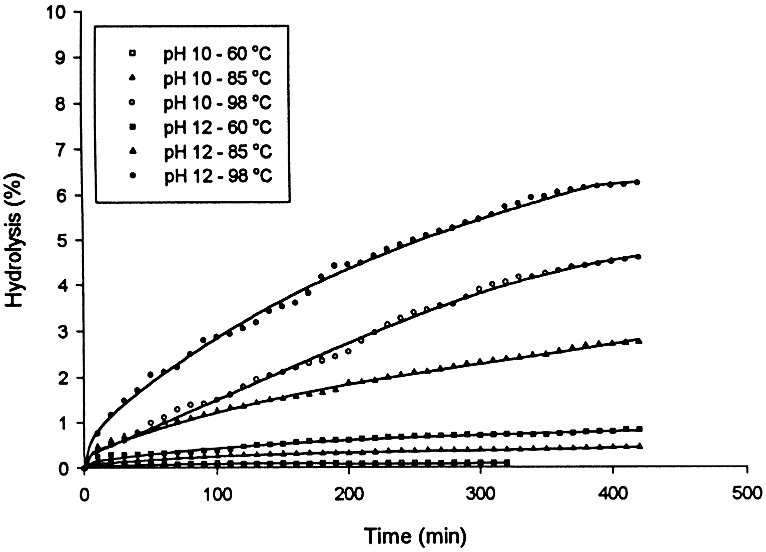


Fig. 5. Effect of temperature and pH on percent of hydrolysis of cotton dyed with 1% Cibacron Scarlet LS-2G.

formed. 6.26% of hydrolysed dye is formed after 7 h treatment at 98°C at pH 12.

The covalent bond formed between Cibacron Blue LS-3R and cellulose fibre posses high stability in solutions pH 10 at all temperatures, including boiling. Also, higher alkaline media pH 12 does not result in fission of the bond at 60°C and 85°C. At boiling temperature in solution at pH 12, the bond is also highly stable when treatment of the dyeing is no longer than one hour. After seven hours treating of the dyeings at pH 12, only 3.86% dye hydrolyses. These influences on cotton dyed with 1% Cibacron Blue LS-3R are represented in Fig. 6.

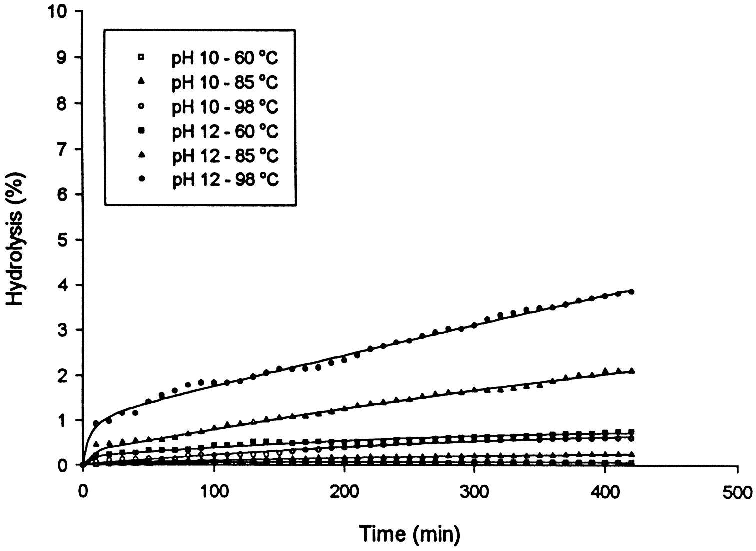


Fig. 6. Effect of temperature and pH on percent of hydrolysis of cotton dyed with 1% Cibacron Blue LS-3R.

4. Conclusions

The purpose of the work was an investigation of the influence of two pH media and three temperatures on the stability of the bond between reactive dyes and cellulosic fibre. Monochloro-s-triazine, bis(monochloro-s-triazine) and bis(monofluoro-s-triazine) dyes are widely used in textile dyehouses. Hydrolysis tests have been carried out on cotton dyeings from the same chromogen structure. Results of the investigation are:

1. The covalent bond of the investigated red and blue monochloro-s-triazine dyes is most stable at 60°C in solution of pH 10. In the same solution at 85°C the dyeings are stable for one hour. Low wet fastness at 98°C are shown for cotton dyed with monochloro-s-triazine dyes, especially in solution of pH 12.
2. The stability of the bond on cotton dyed with bis(monochloro-s-triazine) dyes is excellent at 60°C in solutions of pH 10 and 12. They possess equal stability after treating for 1 h at 85°C. Bis(monochloro-s-triazine) dyes on the cellulosic fibre are quite stable at 98°C at pH 10, while the influence of pH 12 solution on the cleavage of the bonds is marked.
3. Dyeings using bis(monofluoro-s-triazine) dyes on cellulosic fibre are highly stable in solutions of pH 10 and 12 at 60 and at 85°C. Conditions of 98°C and pH 10 also do not disturb the stability of the bond, but at pH 12 and 98°C, greater hydrolysis occurs after a longer treatment time.

For reactive dyes, good stability to washing at 60°C is prescribed. With both the bifunctional types of dyes used in our research, the wash process could run out at 85°C in solutions of pH 10 and 12. Every day washing processes are limited from an economical viewpoint to be no longer than 1 h. It is known that when we use for the wash test ECE Colour Fastness Test Detergent 77 (Henkel) in a concentration of 10 g/litre, the solution has pH 10.3 at 20°C. Solutions of detergents obtained from the market possess pH values from pH 10 to 12. This was also one of the reasons why we tried to investigate the influence of these two alkaline media at different temperatures on the stability of dyeings with selected dye types.

Acknowledgements

The author expresses gratitude to D. Sc. F. Sluga (Faculty of Natural Sciences and Engineering) for his useful suggestions as well as to the colleagues from the Department of Chemical Textile Technology. This work was supported by the Ministry of Science and Technology of Slovenia.

References

[1] Ackermann H, Dussy P. Melliand Textilberichte 1961;42:1167.
[2] Klančnik M, Gorenšek M. Dyes and Pigments 1997;33:337.
[3] Wen J, Zhenghua Z, Kongchang C. Dyes and Pigments 1989;10:217.
[4] Morita Z, Yamada A, Shigehara K, Motomura H. Dyes and Pigments 1996;30:151.
[5] Baumgarte U, Feichtmayr F. Melliand Textilberichte 1963;3:267.
[6] Zheng-Hua Z, Jian-Mei X, Kong-Chang C. Dyes and Pigments 1991;17:217.
[7] Zheng-Hua Z, Zhu Wei-Ping Z. Dyes and Pigments 1994;25:87.
[8] Bohnert E, Weingarten R. Melliand Textilberichte 1959;40:1036.
[9] Elöd E, Nakahara Y. Melliand Textilberichte 1960;41:567.
[10] Senn RCh, Stamm OA, Zollinger H. Melliand Textilberichte 1963;44:261.
[11] Hine BJ. Physical organic chemistry. New York 1956:167.
[12] Senn RCh, Zollinger H. Helvetica Chimica Acta 1963;46:781,789.
[13] Gisler M, Zollinger H. Textile Research Journal 1980; September:519.
[14] Luttringer JP, Dussy P. Melliand Textilberichte 1981;1:84.
[15] Matsui M, Meyer U, Zollinger H. Journal of the Society of Dyers and Colourists 1988;104:425.
[16] Nkeonye PO. Textile Dyer and Printer 1988;August:20.
[17] Rouette HK, Wilshire JFK, Yamase J, Zollinger H. Textile Research Journal 1971;6:518.
[18] Meyer U, Wang J, Xia Y, Yang J, Zollinger H. Journal of the Society of Dyers and Colourists 1986;102:6.
[19] Shore J. Cellulosics Dyeing. Bradford, UK: Society of Dyers and Colourists, 1995:204.
[20] Gorenšek M, Gaber V, Peternelj N, Vrhunc V. Journal of the Society of Dyers and Colourists 1995;111:19.
[21] Technical documentation, Cibacron LS, Ciba.
[22] Bode A. Melliand Textilberichte 1960;41:34.
[23] Jordison F, Lockwood R. Journal of the Society of Dyers and Colourists 1962;78:122.
[24] Jordison F, Lockwood R. Journal of the Society of Dyers and Colourists 1964;80:202.
[25] Venkataraman K. The chemistry of synthetic dyes, Vol. VI, Reactive dyes. New York: Academic Press, 1972.