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Kinetics of Hydrolysis of Monofunctional and Bifunctional Monochloro-*s*-triazine Reactive Dyes

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ABSTRACT

*The kinetics of hydrolysis of one monochloro-*s*-triazine and one bis(monochloro-*s*-triazine) reactive dye were investigated at dyeing conditions of pH 11 and temperature 80°C, and, for the monofunctional dye, also at the lower temperature of 20°C. The alkaline hydrolysis was monitored by high performance liquid chromatography. The pseudo-first-order rate constants of the monochloro-*s*-triazine dye, the bis(monochloro-*s*-triazine) form and the monochloromonohydroxybis-*s*-triazine form of the bifunctional dye were determined and compared. © 1997 Elsevier Science Ltd*

Keywords: Hydrolysis of reactive dyes, monocholorotriazine reactive dye, bis(monochlorotriazine) reactive dye, HPLC.

INTRODUCTION

The hydrolysis of reactive dyes represents an unfavourable reaction in an alkaline dyebath leading to a lower quantity of covalently bonded dyes on cellulosic fibres. The mechanism of the alkaline hydrolysis is the same as that of the formation of covalent bonds between dyes and fibres. Therefore the rate of hydrolysis of a reactive dye is also an indirect measure of the reactivity of the dye to cellulose at a given temperature and pH value.[1]

The hydrolysis reaction of reactive dyes in an aqueous alkaline solution depends on several factors: the dye structure (the nature of the reactive system,[2-5] of the chromogen[1-3,6-11] and of the bridging link),[12-15] the temperature,[2,3,7,9,11,14,15] the pH value of the medium[1-20] and the physical state of the dye in the solution.[14,21]

The alkaline hydrolysis of one monofunctional and one bifunctional monochloro-*s*-triazine reactive azo dye was studied. The kinetics of hydrolysis were investigated under conditions of fixation to cellulose: pH 11 and temperature 80 °C, and for the monofunctional dye also at a temperature of 20 °C.

The advantages of the bis(monochloro-*s*-triazine) reactive dye compared with simpler chloro-*s*-triazine derivatives are higher substantivity and the presence of two reactive groups. If one reactive group hydrolyses during the dyeing process, the other monochlorotriazine group can still chemically react with the hydroxyl groups of cellulose, leading to a higher fixation value. Therefore we were interested in the comparison of the reactivity of the bis(monochloro-*s*-triazine) and the monochloromonohydroxybis-*s*-trazine forms of the bifunctional dye.

EXPERIMENTAL

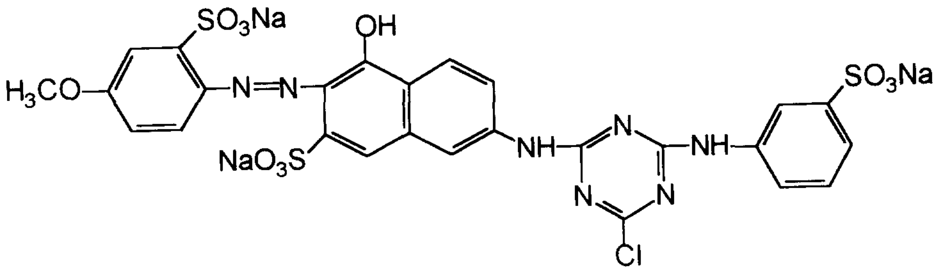
Materials

The dyes used were commercial samples of the monofunctional monochloro-*s*-triazine reactive dye C.I. Reactive Red 43 (**I**) and of the bis(monochloro-*s*-triazine) reactive dye C.I. Reactive Red 141 (**II**),[22] where D incorporates an azo-based chromogen moiety.

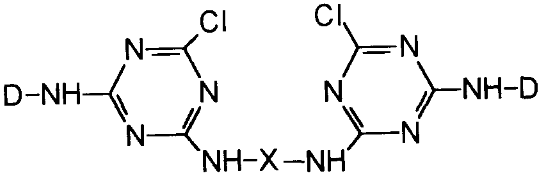
Chemicals used were buffer $pH_{20\,°C} = 11$, containing boric acid, potassium chloride and sodium hydroxide solution (produced by Riedel-de Haën AG), hydrochloric acid HCl p.a. (KT Podnart) and acetonitrile CH_3CN p.a. (Carlo Erba), tetrabutyl ammonium bromide $C_{16}H_{36}NBr$ p.a. (Fluka Chemie AG), ammonium dihydrogen phosphate $(NH_4)H_2PO_4$ p.a. (Kemika) and deionised water. All of them were filtered through 0.2 μm nylon filter.

Hydrolysis at 80 °C ±0.2 °C

The solutions of mono- and bifunctional reactive dyes were prepared by dissolving 0.3 g of the dye in 300 ml of buffer solution $pH_{20\,°C} = 11$ preheated to 80 °C. The dye solution was constantly stirred as it was heated to 80 °C. This temperature was then thermostatically controlled to maintain the solution at a constant temperature of 80 °C. Once at a thermal equilibrium, measurements were started: 10 ml aliquots were withdrawn from the dye solution at 20 min intervals and immediately cooled and neutralised with equivalent amounts of dilute HCl ($pH = 7 \pm 0.05$) to prevent further hydrolysis reactions.



(I)



(II)

Hydrolysis at 20 °C ± 0.2 °C

The solution of monofunctional reactive dye was prepared by dissolving 0.3 g of the dye in 300 ml of buffer solution $pH_{20\,°C} = 11$ precooled to 20 °C. The dye solution was constantly stirred and its temperature was thermostatically controlled and maintained at 20 °C. At 1 h intervals 10 ml aliquots were withdrawn from the dye solution. All aliquots were immediately neutralised by the addition of dilute HCl to $pH = 7 \pm 0.05$. After 8 h at a constant temperature of 20 °C the dye solution was held for 2 days at room temperature (25 ± 1 °C).

HPLC analysis

The neutralised samples were analysed at room temperature by using a high performance liquid chromatograph (made by Thermo Separation Products)

TABLE 1
Linear Gradient System for C.I. Reactive Red 43

Time (min)	*Solvent A*	*Solvent B*
0	30	70
5	50	50
7	30	70

TABLE 2
Linear Gradient System for C.I. Reactive Red 141

Time (min)	*Solvent A*	*Solvent B*
0	30	70
5	50	50
10	30	70

using the following ion-pair reversed-phase system: as the stationary phase, octadecylsilane (Hypersil ODS 3 μm) in a column of 250 mm × 4 mm i.d., and as the mobile phase, a mixture of solvents A and B.[23] Solvent A was 100% acetonitrile containing 0.025 M tetrabutylammonium bromide as ion pairing agent. Solvent B was a 30/70 mixture of acetonitrile containing 0.025 M tetrabutylammonium bromide and deionised water containing 0.05 M ammonium dihydrogen phosphate. The gradient systems shown in Tables 1 and 2 were used; flow rate 1.5 ml/min. Injected volume of analysed samples was 20 μl.

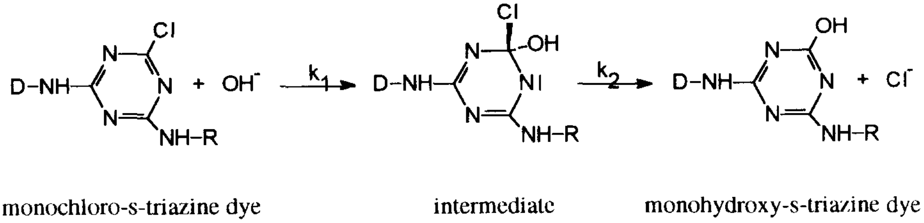
Solutions of the monofunctional dye, C.I. Reactive Red 43, were detected at a wavelength of 500 nm, and solutions of the bifunctional dye, C.I. Reactive Red 141, were detected at 550 nm using a Spectra Focus Forward Optical Scanning detector (Thermo Separation Products).

RESULTS AND DISCUSSION

Hydrolysis of C.I. Reactive Red 43

Monochloro-*s*-triazine reactive dyes react with hydroxide ions by the nucleophilic bimolecular (heteroaromatic) substitution mechanism shown in Scheme 1.

Considering that the addition of hydroxide ion to the electrophilic carbon of the triazine group is the rate-determining step of the hydrolysis reaction, and that the hydroxide ion concentration is kept constant (by the use of a



Scheme 1. Hydrolysis of monochloro-*s*-triazine dye.

buffer), the rate of concentration decrease of the monochloro-*s*-triazine dye form in the alkaline solution can be expressed by the equation:[24]

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_{\mathrm{psl}}[\mathrm{A}] \tag{1}$$

in which [A] is the concentration of the active, monochloro-*s*-triazine dye at hydrolysis time t, and k_{psl} is the pseudo-first-order rate constant of hydrolysis.

The chromatograms of the monofunctional monochloro-*s*-triazine dye, C.I. Reactive Red 43, recorded at different times of hydrolysis at 80 °C show the expected decrease in the amount of the monochloro-*s*-triazine dye and increase in the amount of the hydrolysed form of the dye (Fig. 1).

The values of the peak areas of the components determined from the chromatograms are linearly related to their amounts. By integrating eqn (1) and replacing the concentrations of the monochloro-*s*-triazine dye with its peak areas we obtain:

$$\ln\left(\frac{A_0}{A}\right) = k_{\mathrm{psl}}t \tag{2}$$

where A_0 and A are values of peak areas of the active monochloro-*s*-triazine dye at the time $t=0$ and at a later time t.

The plot of $\ln(A_0/A)$ against time t shown in Fig. 2 yields a straight line passing through the origin. According to eqn (2) the expected pseudo-first-order kinetics is confirmed and the slope of the plot is the rate constant k_{psl}.

The average value of pseudo-first-order rate constants of monochloro-*s*-triazine dye at 80 °C and pH 11 (k_{psl}) is 0.0144 (±0.0003) min^{-1}. It is calculated within a time of 240 min, when all hydrolysis measurements still show linear dependence of $\ln(A_0/A)$ on hydrolysis time and the average square of the correlation coefficient in the linear regression (R^2) is still 0.999.

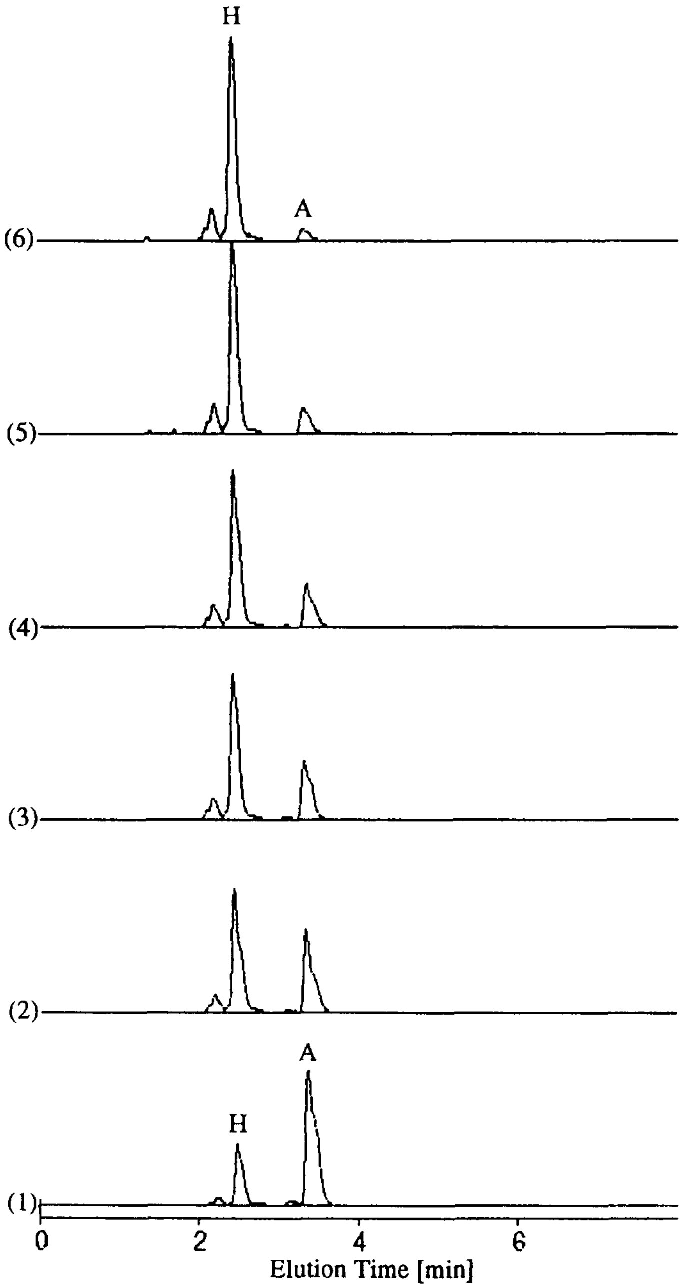


Fig. 1. Chromatograms of the commercial monochloro-*s*-triazine reactive dye in buffer of pH 11 recorded after various times of hydrolysis at 80 °C: (1) 0 min, (2) 40 min, (3) 60 min, (4) 80 min, (5) 120 min, (6) 180 min; where components A and H represent monochloro-*s*-triazine and monohydroxy-*s*-triazine forms.

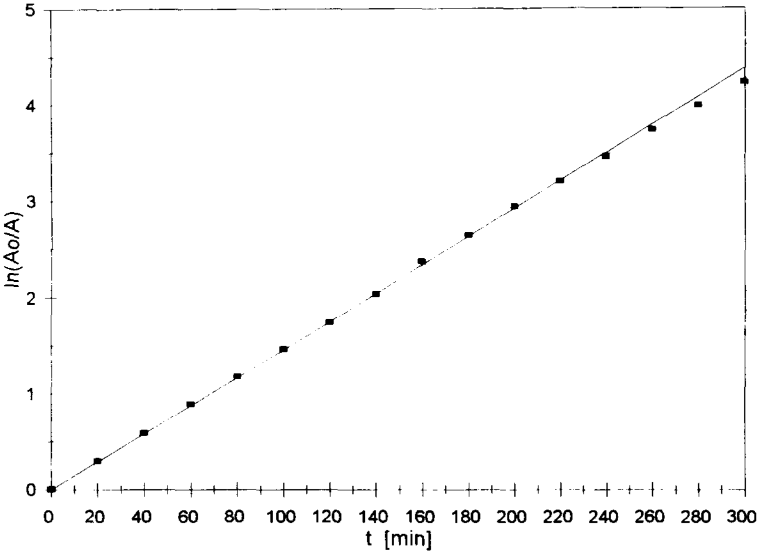


Fig. 2. Plot of $\ln(A_0/A)$ vs time of hydrolysis t at 80 °C in buffer of pH 11 for the monochloro-*s*-triazine reactive dye.

The chromatograms of the monofunctional dye recorded at different times of hydrolysis at temperature 20 °C show a relatively unchanged amount of the monochloro-*s*-triazine dye (Fig. 3).

The average pseudo-first-order rate constant of hydrolysis of the monochloro-*s*-triazine dye (k_{ps}) at 20 °C and pH 11, determined also by a graphical solution of eqn (2) (Fig. 4), is 5.4×10^{-6} ($\pm 0.5 \times 10^{-6}$) min^{-1} and the average square of the correlation coefficient (R^2) is 0.948.

The rate constant of hydrolysis of monochloro-*s*-triazine dye at 80 °C is about 2700 times higher than at 20 °C. After 8 h of hydrolysis at 20 °C the concentration of the monochloro-*s*-triazine form of the dye decreases by less than 0.3%. At room temperature (25 °C) for 1 day the concentration decrease is 1.3%, and after 2 days 2.5%.

Hydrolysis of C.I. Reactive Red 141

Bis(monochloro-*s*-triazine) reactive dyes such as C.I. Reactive Red 141 hydrolyse into two products, the monochloromonohydroxybis-*s*-triazine (B) and the bis(monohydroxy-*s*-triazine) (H), and their hydrolysis reaction can be presented in simplified form as in Scheme 2.

The chromatograms of the bifunctional dye recorded at different times of hydrolysis at 80 °C and pH 11 are shown in Fig. 5. Only the area of three peaks corresponding to the bis(monochloro-*s*-triazine) (A), the

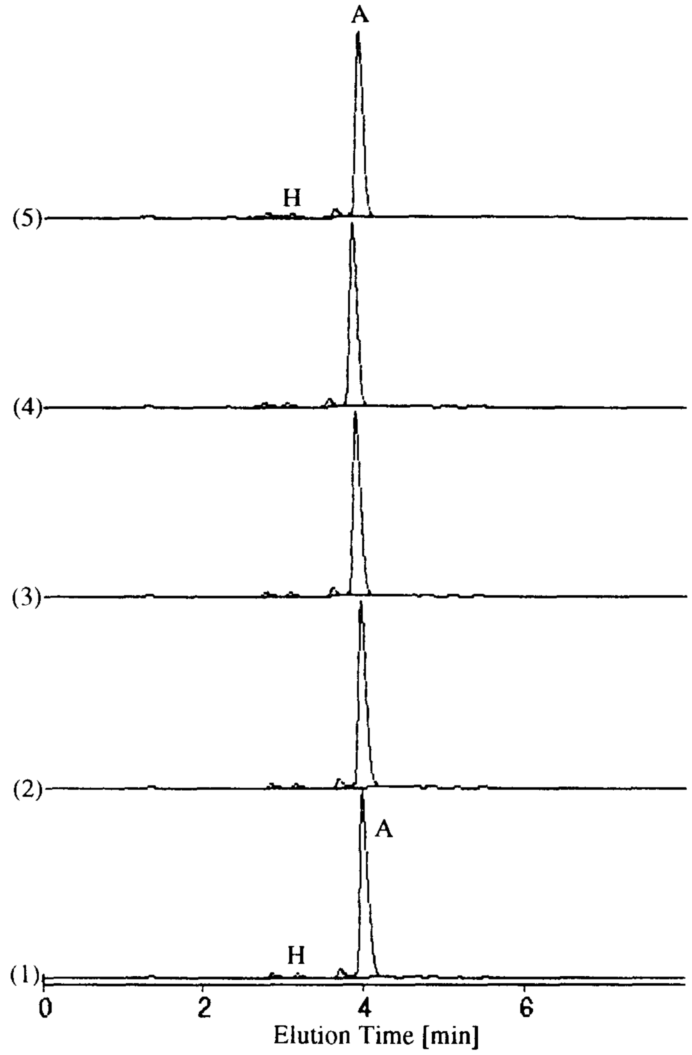


Fig. 3. Chromatograms of the commercial monochloro-*s*-triazine reactive dye in buffer of pH 11 recorded after various times of hydrolysis at 20 °C: (1) 0 min, (2) 120 min, (3) 240 min, (4) 360 min, (5) 480 min; where components A and H represent monochloro-*s*-triazine and monohydroxy-*s*-triazine forms.

monochloromonohydroxybis-*s*-triazine (B) and the bis(monohydroxy-*s*-triazine) (H) components of the dye was integrated.

All of these components have about the same extinction coefficients, hence their relative ratio of concentrations is equal to their relative ratio of peak areas. Their relative concentrations are plotted as a function of time in Fig. 6. It can be seen that the concentration of the bis(monochloro-*s*-triazine)

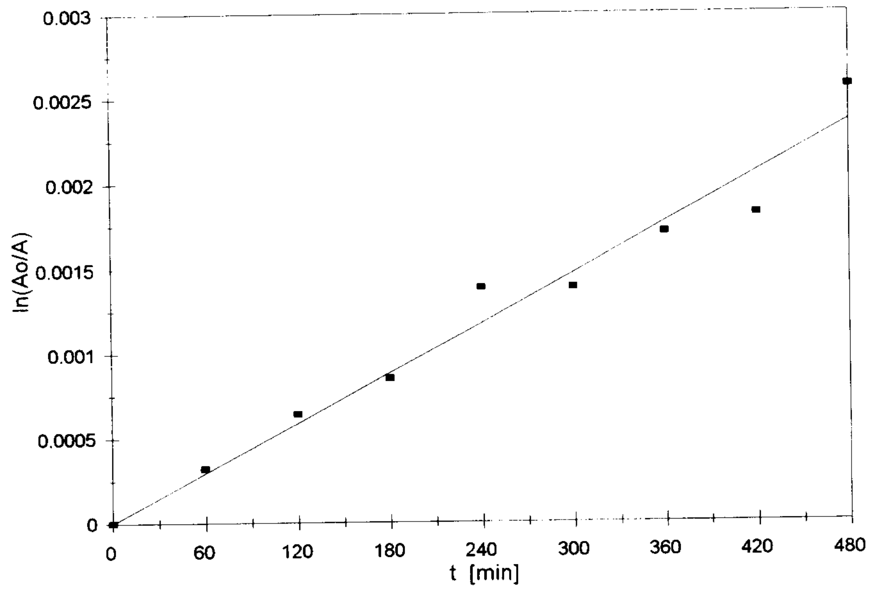
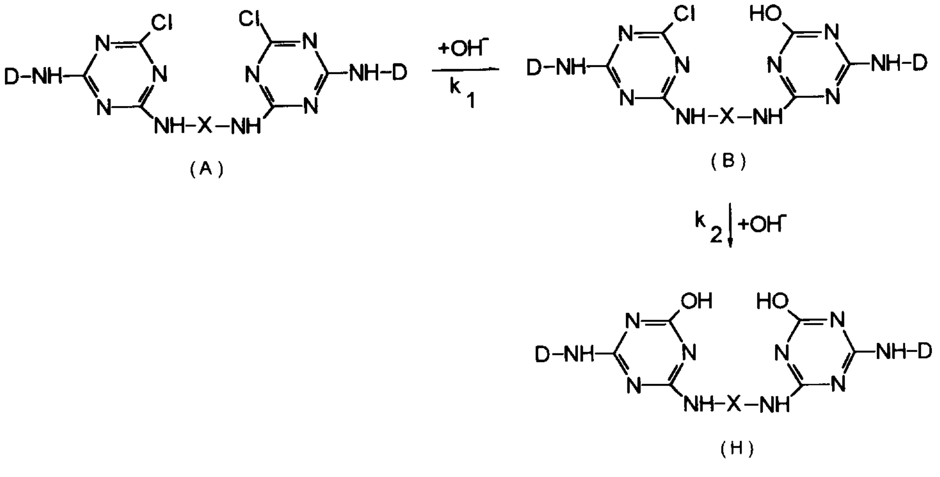


Fig. 4. Plot of $\ln(A_0/A)$ vs time of hydrolysis t at 20 °C in buffer of pH 11 for the monochloro-*s*-triazine reactive dye.



Scheme 2. Hydrolysis of bis(monochloro-*s*-triazine) dye.

compound exponentially decreases, that of the monochloromonohydroxybis-*s*-triazine compound rapidly rises to a maximum and then asymptotically falls, and that of the bis(monohydroxy-*s*-triazine) compound rises with increasing hydrolysis time (Fig. 6). This plot corresponds to the assumed mechanism of consecutive first-order reactions.[25]

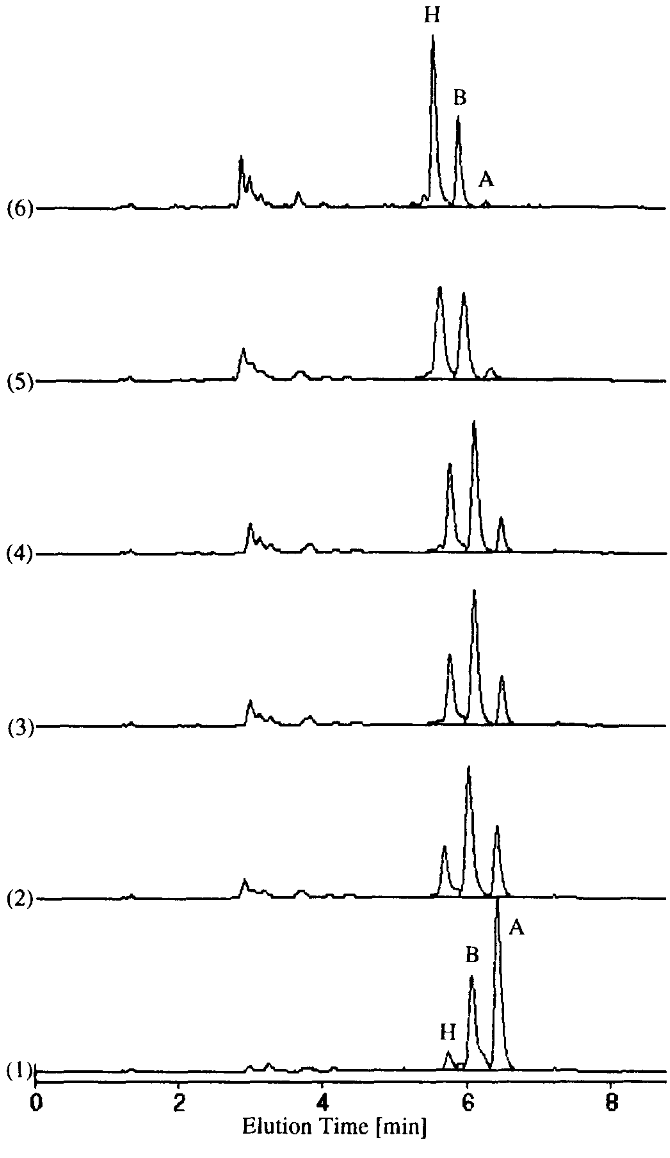


Fig. 5. Chromatograms of the commercial bis(monochloro-*s*-triazine) reactive dye in buffer of pH 11 recorded after various times of hydrolysis at 80 °C: (1) 0 min, (2) 40 min, (3) 60 min, (4) 80 min, (5) 120 min, (6) 180 min; where components A, B and H represent bis(monochloro-*s*-triazine) and monochloromonohydroxybis-*s*-triazine and bis(monohydroxy-*s*-triazine) forms.

The concentration decrease of the bis(monochloro-*s*-triazine) form of the bifunctional dye can also be expressed by eqn (1), in which A_0 and A are the values of the peak areas of the bis(monochloro-*s*-triazine) form at time $t = 0$

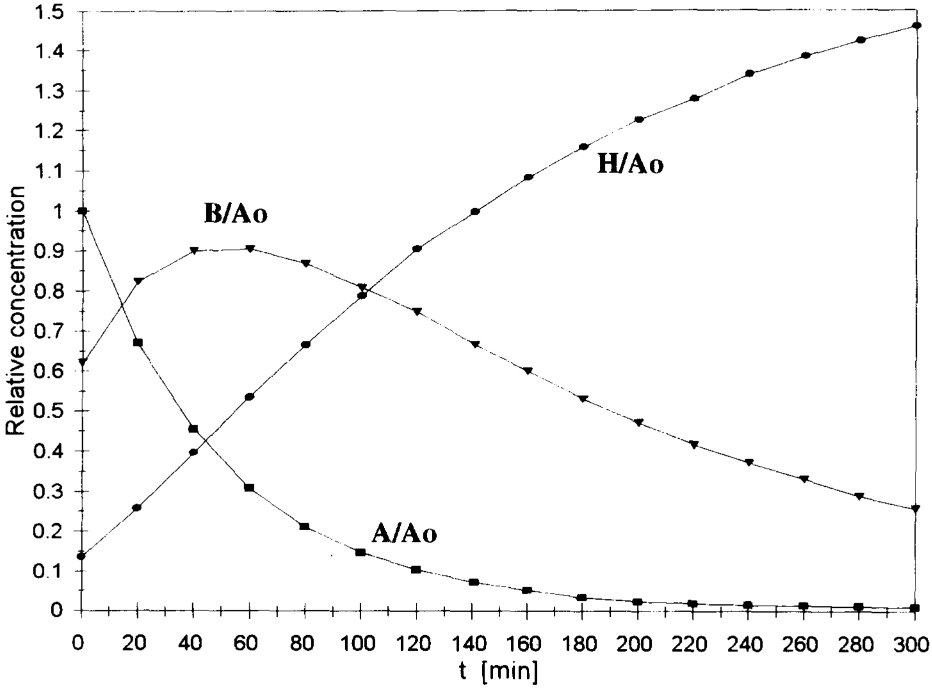


Fig. 6. Plot of relative concentrations of bis(monochloro-*s*-triazine) form (A), monochloromonohydroxybis-*s*-triazine form (B) and bis(monohydroxy-*s*-triazine) form (H) to the initial concentration of bis(monochloro-*s*-triazine) form (Ao), as a function of hydrolysis time *t* at 80 °C in buffer of pH 11.

and at a later time *t*. The pseudo-first-order rate constant of hydrolysis of the bis(monochloro-*s*-triazine) form (k_{ps1}) is calculated as the slope of the straight line in the plot of $\ln(A_0/A)$ vs. time within 220 min (Fig. 7). After a time longer than 220 min the kinetics of hydrolysis deviates from a linear relationship and therefore cannot be considered as pseudo-first-order.

The average value of the pseudo-first-order rate constants of hydrolysis of the bis(monochloro-*s*-triazine) dye form, C.I. Reactive Red 141, (k_{ps1}) at 80 °C and pH 11 is 0.0186 ($\pm$0.0001) min^{-1}, the average square of the correlation coefficient in the linear regression (R^2) being 0.998.

The rate of formation of the monochloromonohydroxybis-*s*-triazine form (B) of the bifunctional dye can be expressed as:

$$\frac{d[B]}{dt} = k_{ps1}[A] - k_{ps2}[B] \qquad (3)$$

where [A] is the concentration of the bis(monochloro-*s*-triazine) form and [B] is the concentration of the monochloromonohydroxybis-*s*-triazine form of

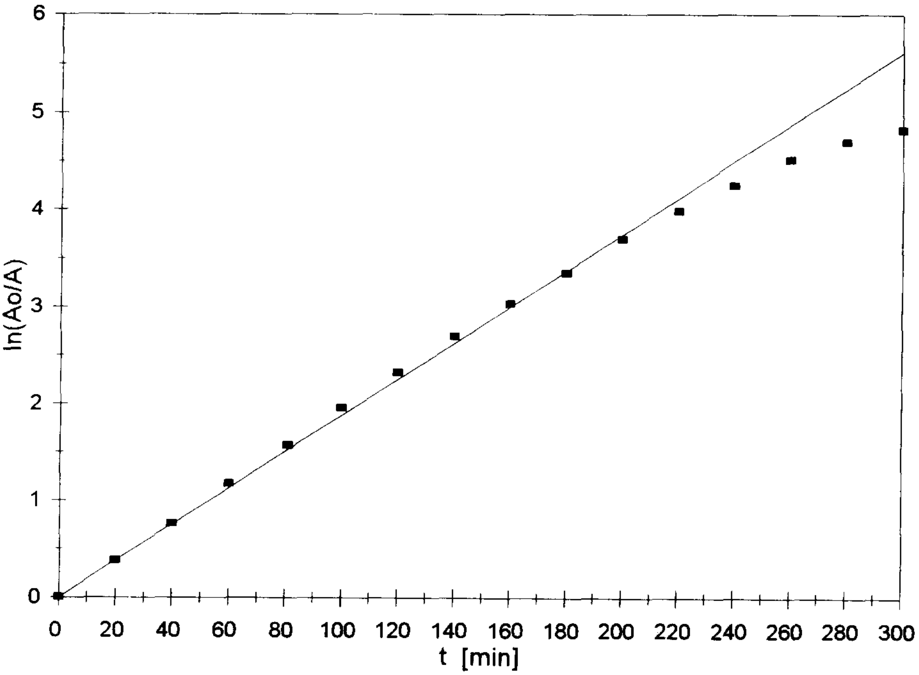


Fig. 7. Plot of $\ln(A_0/A)$ vs time of hydrolysis t at 80 °C in buffer of pH 11 for the bis(monochloro-*s*-triazine) reactive dye.

the bifunctional dye, k_{ps1} is the pseudo-first-order rate constant of hydrolysis of the bis(monochloro-*s*-triazine) form and k_{ps2} is the pseudo-first-order rate constant of hydrolysis of the monochloro-*s*-triazine group in the monochloromonohydroxybis-*s*-triazine dye.

The pseudo-first-order rate constant of hydrolysis of the monochloromonohydroxybis-*s*-triazine form (k_{ps2}) is determined at a time of 60 min when the concentration of this form is at a maximum. By using the differential form of eqn (3) and considering at that time the value of $d[B]/dt = 0$, k_{ps2} can then be calculated from:

$$k_{ps2} = k_{ps1} \frac{[A]}{[B]} \tag{4}$$

The pseudo-first-order rate constant of hydrolysis of the monochloromonohydroxybis-*s*-triazine form of the bifunctional dye (k_{ps2}) determined at 80 °C and pH 11 is 0.0064 (±0.0001) min^{-1}. The hydrolysis of one triazine reactive group causes the deactivation of the other and, because of this, the reactivity of the monochloromonohydroxybis-*s*-triazine dye form (k_{ps2}) is about three times smaller than that of the bis(monochloro-*s*-triazine) form (k_{ps1}).

CONCLUSIONS

HPLC chromatograms recorded at different times of hydrolysis enable a good insight into the time-dependent changes of the amounts of the active and the hydrolysed forms of the dyes. Changes of other, unknown components in the commercial samples of dyes can also be seen. A reason for their appearance could be the complexity of the hydrolysis mechanism of monochlorotriazine dyes containing an imino bridging link[15,26,27] in alkaline buffers.[16,20] Additionally, impurities present in the commercial samples could also be contributory.

The hydrolysis of the monochloro-*s*-triazine and the bis(monochloro-*s*-triazine) dyes in the buffered solution of pH 11 at constant temperature follows the assumed pseudo-first-order kinetics.

The monochloro-*s*-triazine dye has about 2700 times lower reactivity at 20 °C than at 80 °C. At 80 °C the pseudo-first-order rate constant of the bis(monochloro-*s*-triazine) form of the bifunctional dye is about three times higher than that of the monochloromonohydroxybis-*s*-triazine form.

When the rate constants of hydrolysis of the investigated monofunctional and bifunctional dyes are compared in the buffer at pH 11, 80 °C, it is seen that the reactivity of the monochloro-*s*-triazine monofunctional dye is slightly lower than that of the bis(monochloro-*s*-triazine) form of the bifunctional dye, and at the same time about twice as much as that of the bifunctional dye containing one monochlorotriazine and one monohydroxytriazine group. When the rate constants of both active forms of the bifunctional dye C.I. Reactive Red 141 are considered, the reactivity of the bifunctional dye is almost twice as high as that of the monofunctional dye C.I. Reactive Red 43.

The determined rate constants of hydrolysis enable the evaluation of an important factor, i.e. the chemical reactivity of dyes, which has a primary significance in each study of reactive dyeing. However they cannot give us a complete picture of the dyeing behaviour, which is influenced also by the rate of diffusion of the dye into cellulose and by the affinity of the dye for cellulose.[28]

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