Kinetics of Hydrolysis of Halogeno-s-triazine Reactive Dyes as a Function of Temperature

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The kinetics of alkaline hydrolysis of azo reactive dyes: monofunctional with one monohalogeno-s-triazine reactive group and bifunctional with two identical monohalogeno-s-triazine reactive groups was studied in the temperature range from 50 °C to 80 °C by means of high performance liquid chromatography. From the determined pseudo-first order hydrolysis rate coefficients, the chemical reactivity of particular dyes and their sensitivity to temperature changes according to the Arrhenius equation were evaluated.

The hydrolysis rate coefficient of monofunctional dyes is more temperature dependent than that of homobifunctional dyes. Reactive dyes with a less reactive monochloro-s-triazine group are more sensitive to temperature variations than reactive dyes with a more reactive monofluoro-s-triazine group. Among the studied dyes, the bis(monofluorotriazine) form of the homobifunctional dye exhibits the lowest sensitivity to temperature variations.

Key words:
Reactive dye, hydrolysis, rate coefficient, temperature dependence, Arrhenius equation, HPLC

Introduction

Reactive dyes are the most important class of dyes for cellulose fibres due to their good washing fastness, bright shades, and versatile dyeing methods.[1] A characteristic structural feature of these dyes is the reactive group attached (over a bridging group or directly) to the chromogenic system.[2] The reactive group, generally based on halogenoheterocycle or vinyl sulphone, is capable of forming a covalent bond with a fibre under alkaline conditions. However, in alkaline dyebaths, the hydrolysis reaction of a reactive dye, always accompanies the fixation reaction of the dye with cellulose fibres. The competitive hydrolysis reaction causes lower fixation levels and is therefore of great environmental and economic importance. When a reactive group of dyes hydrolyzes, it cannot link covalently to a cellulose fibre. The hydrolyzed dye is a waste of the dyeing process and is discharged as colored effluent.[3]

In order to achieve a higher degree of fixation and, consequently, lower water pollution, the investigations of dye manufacturers have been focused on developing reactive dyes with two reactive groups, i.e. bifunctional dyes, which are now widely commercialized.

The study of kinetics and mechanism of hydrolysis is also very significant for understanding the dye – fibre reaction. Reactive dyes react with hydroxide ions (OH^-) and with nucleophilic groups of cellulose (cell-O^-) by the same mechanism, and therefore the hydrolysis reaction can be used as a model reaction for elucidating the fixation.[2] From the hydrolysis rate coefficient of a reactive dye, measured at defined pH and temperature conditions, its chemical reactivity can be evaluated.

The temperature dependence of hydrolysis rate coefficients of monofunctional reactive dyes has already been studied.[4-12] However, there was no data on the influence of temperature on the hydrolysis kinetics of the bifunctional reactive dyes in comparison with that of the monofunctional dyes of the same reactive system, which is a subject of this investigation.

In this study, all dyes contain a monoazo-based chromogen moiety and a monohalogeno-s-triazine group chemically reacting with cellulose in the same manner under alkaline conditions at elevated temperatures. Bifunctional dyes that have two chromogens and two halogenotriazine reactive groups linked together by an aryl or an alkyl diamine group are generally characterized by a greater substantivity towards cellulose and therefore achieve higher exhaustion levels, as well as fixation efficiency compared with analogous monofunctional dyes that contain only one reactive group per chromogenic unit. One of the investigated dyes is a bis(monofluorotriazine) Cibacron LS dye, a representative of an economical and ecologically-friendly progressive range of reactive dyes that require very low salt concentrations for exhaustion dyeing.

The temperature range investigated was selected according to application temperatures of the fixation phase for the studied dyes with cellulose fibres. The optimal temperature in exhaustion dyeing with monochloro-s-triazine and bis(monochloro-s-triazine) dyes is usually 80 °C, with bis(monofluoro-s-triazine) dyes about 70 °C, and with monofluoro-s-triazine dyes about 50 °C.

Hydrolysis of the dyes was monitored chromatographically by observing the relative changes in peak areas of the active and hydrolyzed dye forms in alkaline solution at constant temperature after various reaction times.

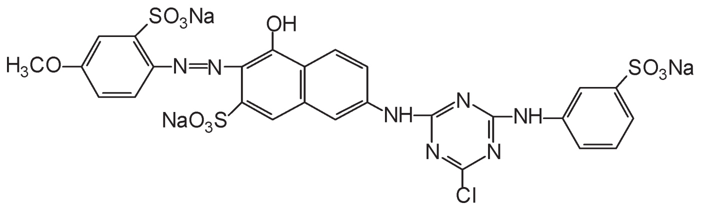
Experimental

Dyes

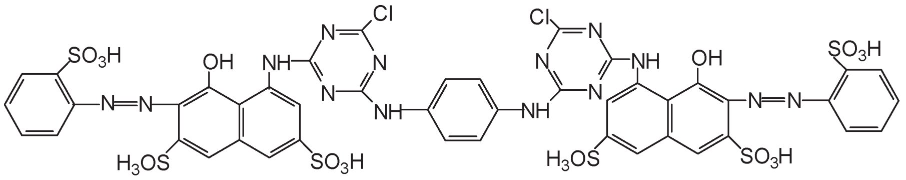
The reactive dyes used were commercial samples of: monochloro-s-triazine dye Procion Scarlet H-2G (C.I. Reactive Red 43) further denoted as (I), bis(monochloro-s-triazine) dye Procion Red HE-3B (C.I. Reactive Red 120) further denoted as (II), monofluoro-s-triazine dye Cibacron Scarlet F-3G (C.I. Reactive Red 183) further denoted as (III), and bis(monofluoro-s-triazine) dye Cibacron Scarlet LS-2G (C.I. Reactive Red 268) denoted as (IV). In general structures of (III) and (IV) dyes, group D incorporates a monoazo-based chromogen moiety unknown chemical structure. R in dye structure (III) can be hydrogen, alkyl or aryl, and Y in dye structure (IV) alkyl $–(CH_2)_n–$.[13]

Hydrolysis of dyes at 50 °C, 60 °C, 65 °C, 70 °C and 80 °C

0.025 g of dye was dissolved in a mixture of 5 mL of buffer of pH 7 (from Carlo Erba) and 25 mL of deionized water. The stock dye solution was heated to a determined temperature and then added to 220 mL of buffer of pH 11 (from Riedel-de Haën AG) that was preheated to the same temperature in a thermostatically controlled bath. After various times of hydrolysis, 10 mL aliquots were withdrawn from the prepared dye solution ($pH_{20°C}$ 10.9), which were constantly stirred and maintained at the determined temperature. The dye samples removed were immediately cooled and neutralized by the addition of dilute HCl (p.a., KT Podnart) to stop further reaction.



(I)



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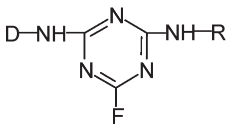

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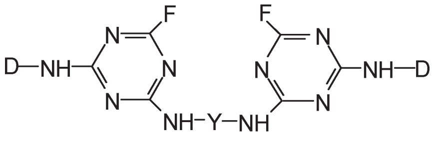


(IV)

HPLC analysis

HPLC analysis of hydrolyzed dye samples was carried out on a Thermo Separation Products liquid chromatograph using a Hypersil ODS 3 μm column (l = 250 mm · d_i = 4 mm, from Säulentechnik Knauer) as the stationary phase and a mixture of solvents 1 and 2 as the mobile phase.[14] Solvent 1 was a 100 % acetonitrile (CHROMASOLV® for HPLC, Riedel-de Haën AG) containing c = 0.025 mol L^{-1} tetrabutylammonium bromide (p.a., Fluka Chemie AG). Solvent 2 was a 30/70 mixture of acetonitrile containing c = 0.025 mol L^{-1} tetrabutylammonium bromide and deionized water containing c = 0.05 mol L^{-1} ammonium dihydrogen phosphate (p.a., Kemika). The composition of the solvents 1 and 2 was altered according to the gradient systems shown in Tables 1 and 2 at a constant flow rate of Q = 1.3 mL min^{-1}. The injected volume of the analyzed samples was V = 20 μL. Solutions of the monochlorotriazine dye Procion Scarlet H-2G were analyzed at a wavelength of λ = 500 nm, of the bis(monochlorotriazine) dye Procion Red HE-3B at λ = 541 nm, of the monofluorotriazine dye Cibacron Scarlet F-3G at λ = 499 nm and of the bis(monofluorotriazine) dye Cibacron Scarlet LS-2G at a wavelength of λ = 502 nm by using a Spectra Focus Forward Optical Scanning detector.

Table 1 – *Linear gradient system for monofunctional dyes*

Time t/min	Solvent 1/%	Solvent 2/%
0	20	80
5	30	70
10	40	60

Table 2 – *Linear gradient system for homobifunctional dyes*

Time t/min	Solvent 1/%	Solvent 2/%
0	20	80
2	30	70
7	40	60
12	20	80

Results and discussion

Reactive dyes that contain halogeno-s-triazine groups react with hydroxide ions by the nucleophilic bimolecular (heteroaromatic) substitution mechanism.[15] The reaction mechanism involves a specific base catalyzed addition of a hydroxide ion to the electrophilic carbon of the reactive group, followed by the elimination of a halogenide ion. The alkaline hydrolysis of a monofunctional monohalogeno-s-triazine dye and a symmetrical homobifunctional bis(monohalogeno-s-triazine) dye can be represented in simplified form as shown in Figs. 1 and 2, where D in the chemical structures denotes a dye chromogen and X a halogen.

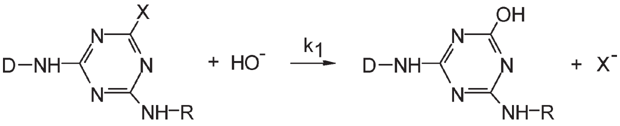


Fig. 1 – *Alkaline hydrolysis of a monohalogeno-s-triazine reactive dye*

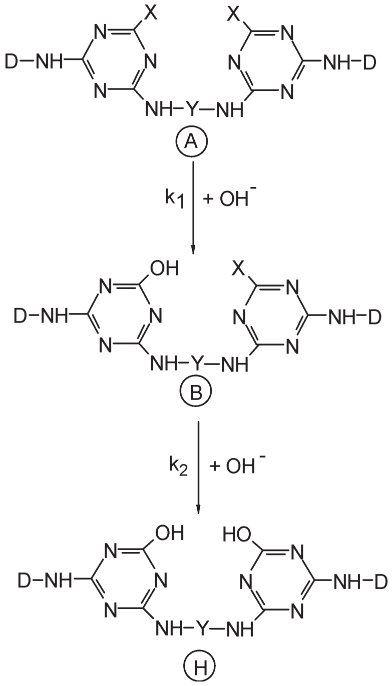


Fig. 2 – *Alkaline hydrolysis of a bis(monohalogeno-s-triazine) reactive dye*

If the addition of a hydroxide ion to the electrophilic carbon of the triazine group is the rate-determining step of the hydrolysis reaction, and the hydroxide ion concentration remains constant during the reaction, the rate of decrease in the concentration of a monohalogeno-s-triazine or a bis(monohalogeno-s-triazine) dye form at constant temperature may be expressed by the equation for a pseudo-first order reaction:[3]

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1 \cdot [\mathrm{A}] \tag{1}$$

where [A] is the concentration of the monohalogeno-s-triazine or the bis(monohalogeno-s-triazine) dye form at any reaction time t, and k_1 is the pseudo-first order rate coefficient of hydrolysis.

k_1 can be determined from the integrated form of eq. (1) as the slope of the straight line passing through the origin in the graph of $\ln(S_0/S)$ against reaction time, where S_0 and S are the peak areas of the active monohalogeno-s-triazine or the bis(monohalogeno-s-triazine) form at the time $t = 0$ and at a later reaction time t, respectively, at constant temperature.

The plots of $\ln(S_0/S)$ against hydrolysis time at various temperatures for the particular reactive dyes examined are shown in Figs. 3–6. Pseudo-first order kinetics can be confirmed for all dyes at the studied temperatures within an initial reaction time interval for which the dependence of $\ln(S_0/S)$ on reaction time is still linear.

By increasing the time of the reaction the amount of the bis(monohalogeno-s-triazine) form exponentially decreases, that of the bis(monohydroxy-s-triazine) form increases, and the amount of the monohalogenomonohydroxybis-s-triazine form first increases to a maximum and then slowly decreases (Figs. 7 and 8). These time-dependent changes in the amounts of the dye forms confirm the mechanism of two consecutive hydrolysis reactions assumed in Fig. 2.

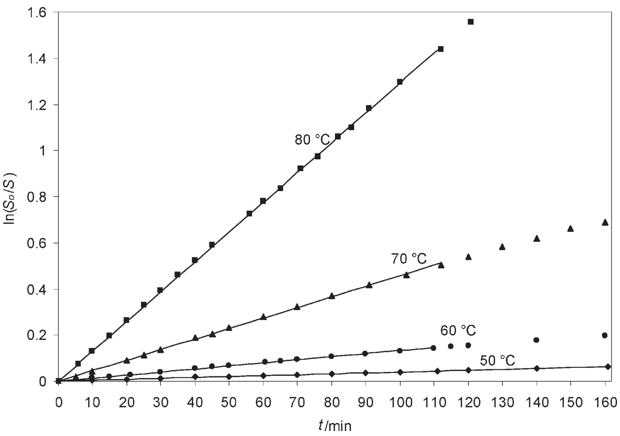


Fig. 3 – *Plot of ln(S$_0$/S) vs. time of hydrolysis (t) at different temperatures for the monochloro-s-triazine dye (I)*

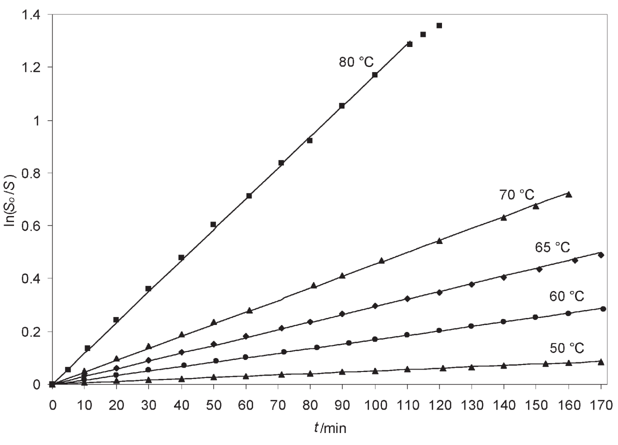


Fig. 4 – *Plot of ln(S$_0$/S) vs. time of hydrolysis (t) at different temperatures for the bis(monochloro-s-triazine) dye (II)*

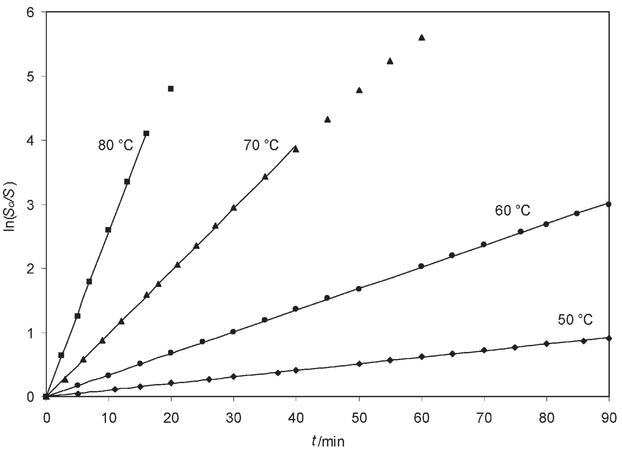


Fig. 5 – *Plot of ln(S$_0$/S) vs. time of hydrolysis (t) at different temperatures for the monofluoro-s-triazine dye*

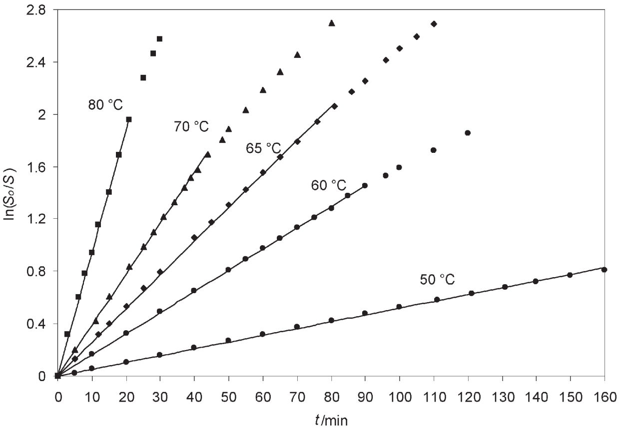
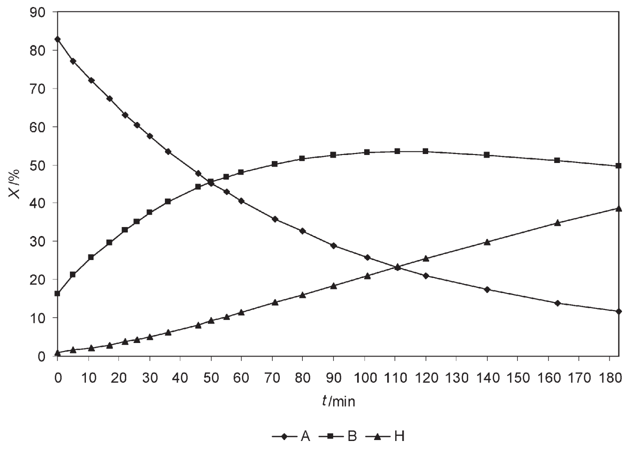


Fig. 6 – *Plot of ln(S$_0$/S) vs. time of hydrolysis (t) at different temperatures for the bis(monofluoro-s-triazine) dye (IV)*

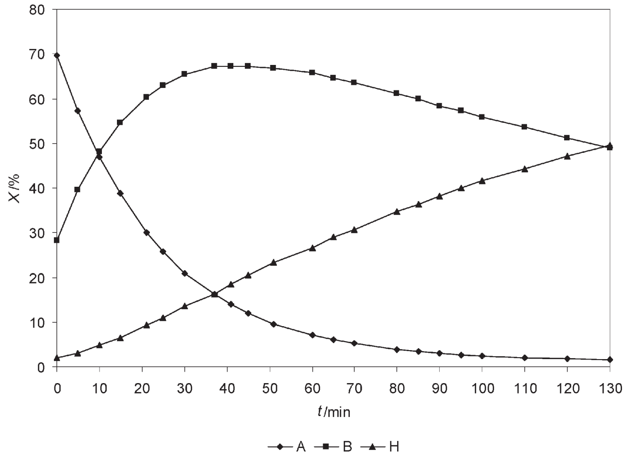
The rate equation for the formation of the partly hydrolyzed monohalogenomonohydroxy-bis-s-triazine form of a homobifunctional dye at constant temperature can be written as following:

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_1 \cdot [\mathrm{A}] - k_2 \cdot [\mathrm{B}] \qquad (2)$$

where [A] and [B] represent the concentrations of the bis(monohalogeno-s-triazine) and the monohalogenomonohydroxybis-s-triazine forms at any time t, k_1 and k_2 are the pseudo-first order rate coefficients of the hydrolysis of the monohalogeno-s-triazine reactive group in the bis(monohalogeno-s-triazine) and in the monohalogenomonohydroxybis-s-triazine forms, respectively.



F i g . 7 – *Plot of peak areas of bis(monochloro-s-triazine) form (A), monochloromonohydroxybis-s-triazine form (B) and bis(monohydroxy-s-triazine) form (H) of dye (II) against hydrolysis time (t) at 80 °C*



F i g . 8 – *Plot of peak areas of bis(monofluoro-s-triazine) form (A), monofluoromonohydroxybis-s-triazine form (B) and bis(monohydroxy-s-triazine) form (H) of dye (IV) against hydrolysis time (t) at 70 °C*

At the time, when the concentration of the partly hydrolyzed dye form reaches its maximum value, the rate d[B]/dt is equal to zero and the hydrolysis rate coefficient k_2 can be calculated from eq. (2) as:

$$k_2 = k_1 \cdot \left[\frac{\mathrm{A}}{\mathrm{B}}\right] \tag{3}$$

where [A] and [B] are the concentrations of the corresponding dye forms at the time, when the partly hydrolyzed form B reaches its maximum.

Calibration graphs[16] of the homobifunctional dyes in alkaline solution show that the absorption detector responds equally to the bis(monohalogeno-s-triazine) form and the monohalogenomonohydroxybis-s-triazine form of the same dye at the wavelength used. Therefore, in eq. (3), instead of the concentration ratio of corresponding dye forms, the ratio of their integrated peak areas can be used.

Hydrolysis rate coefficients of the studied dyes, determined in the alkaline buffer solution at chosen temperatures, are summarized in Table 3. During the measurements of the hydrolysis reaction of the bis(monochloro-s-triazine) dye at 50 °C, 60 °C, 65 °C and 70 °C, its monochloromonohydroxybis-s-triazine form (B) did not reach its maximum value and hence the rate coefficient k_2 could not be calculated at these temperatures. For the same reason, the hydrolysis rate coefficient of the monofluoromonohydroxybis-s-triazine form could not be computed at 50 °C. Hydrolysis of the monofunctional dyes was not carried out at 65 °C. All pseudo-first order hydrolysis rate coefficients of the dyes determined as a function of the temperature are gathered in Table 3. The correlation coefficients (R^2) in Table 3 show a very good agreement to the proposed pseudo-first order kinetics.

T a b l e 3 – *Pseudo-first order hydrolysis rate coefficients (k) of reactive dyes and the squares of the correlation coefficients in linear regression (R^2) at different temperatures (T)*

Reactive dye	T/°C	k/min^{-1}	R^2
monochloro-s-triazine (I)	50	$3.94 \cdot 10^{-4}$	0.9960
	60	$1.33 \cdot 10^{-3}$	0.9991
	70	$4.45 \cdot 10^{-3}$	0.9991
	80	$1.30 \cdot 10^{-2}$	0.9997
bis(monochloro-s-triazine) form of (II)	50	$5.08 \cdot 10^{-4}$	0.9975
	60	$1.68 \cdot 10^{-3}$	0.9994
	65	$2.93 \cdot 10^{-3}$	0.9994
	70	$4.54 \cdot 10^{-3}$	0.9994
	80	$1.17 \cdot 10^{-2}$	0.9991
monochloromonohydroxy-bis-s-triazine form of (II)	80	$5.07 \cdot 10^{-3}$	
monofluoro-s-triazine (III)	50	$1.04 \cdot 10^{-2}$	0.9993
	60	$3.36 \cdot 10^{-2}$	0.9998
	70	$9.78 \cdot 10^{-2}$	0.9997
	80	$2.56 \cdot 10^{-1}$	0.9987
bis(monofluoro-s-triazine) form of (IV)	50	$5.18 \cdot 10^{-3}$	0.9992
	60	$1.62 \cdot 10^{-2}$	0.9998
	65	$2.57 \cdot 10^{-2}$	0.9992
	70	$3.92 \cdot 10^{-2}$	0.9995
	80	$9.35 \cdot 10^{-2}$	0.9985
monofluoromonohydroxy-bis-s-triazine form of (IV)	60	$3.42 \cdot 10^{-3}$	
	65	$5.55 \cdot 10^{-3}$	
	70	$9.45 \cdot 10^{-3}$	
	80	$2.56 \cdot 10^{-2}$	

As expected, the monofunctional monofluoro-s-triazine dye (III) has the highest values of hydrolysis rate constants, which are from 2 to 2.7 times higher at temperatures from 50 °C to 80 °C than that of the bis(monofluoro-s-triazine) form of dye (IV). The reactivity of the monofluoro-s-triazine reactive group in the homobifunctional dye is reduced due to the deactivation effect of the alkyl diamine linking group present between the two triazine groups.

The partly hydrolyzed monofluoromonohydroxybis-s-triazine form of dye (IV) has 4.7 to 3.7 times lower reactivity (at temperatures of 60 °C to 80 °C) than its bis(monofluoro-s-triazine) form. The ionization of the hydroxyl group on the triazine ring in the partly hydrolyzed form of the homobifunctional dye causes the deactivation of the remaining monofluoro-s-triazine group.[17] With increasing temperature, the difference in reactivity of the monofluorotriazine reactive group in the partly hydrolyzed form and in the initial bis(monofluorotriazine) form to nucleophilic attack by hydroxide ions gradually decreases.

The monochloro-s-triazine dye (I) is about 26 to 20 times less reactive than the monofluoro-s-triazine (III) at the temperatures from 50 °C to 80 °C. The rate coefficient of the monochloro-s-triazine dye at 80 °C has a value of similar order as that of the monofluoro-s-triazine dye at 50 °C, which is in agreement with the general recommendations[18,19] for dyeing with these dyes. The higher reactivity of dye (III) is mainly the result of the more reactive monofluoro-s-triazine group, due to the greater electronegativity of fluorine compared with chlorine. However, dye reactivity can also be influenced by a non-labile substituent attached to the triazine ring, a bridging group linking the triazine group to the chromogen, as well as by substituents present in the chromogenic part of the dye.[3]

Despite different chemical structures of their chromogens, the monochloro-s-triazine dye (I) and the bis(monochloro-s-triazine) dye (II) studied show almost the same level of reactivity. The hydrolysis rate constant of the scarlet monochloro-s-triazine dye (I) at the temperatures of 50 °C and 60 °C is a little lower, at 70 °C about the same and at 80 °C slightly higher than that of the bis(monochloro-s-triazine) form of dye (II). An advantage of homobifunctional dyes containing two reactive groups compared with monofunctional dyes is a greater probability of chemical reaction with cellulose fibres. However, at 80 °C the reactivity of the monochloro-s-triazine group in the monochloromonohydroxybis-s-triazine form of dye (II) is reduced by 2.3 times compared with that in its bis(monochloro-s-triazine) dye form.

It is noticeable that as the temperature is increased from 50 °C to 60 °C, the rate coefficients of all dyes increase by more than 3 times. However, at higher temperatures the increase in hydrolysis rate coefficients with a rise of 10 °C is lower. The possible dissociation of imino-bridging groups in the dye molecules, which is more pronounced at higher temperatures, as well as the reduced concentration of hydroxide ions at elevated temperature could be the reasons for a lower change of the hydrolysis rate coefficients when the temperature is increased from 70 °C to 80 °C compared to the rate coefficient change observed for the same 10 °C increase at lower temperatures.

The linearity of plots of the logarithm of the hydrolysis rate coefficients of the dyes against the reciprocal of absolute reaction temperature (shown in Fig. 9) and their calculated correlation coefficients R^2 (in Table 4) indicates that the hydrolysis rate coefficients of the dyes vary with the temperature according to the Arrhenius equation:[20]

$$\log k = -\frac{E_\mathrm{a}}{2.303 \cdot R \cdot T} + \log A \tag{4}$$

in which k is the hydrolysis rate coefficient, A is the pre-exponential or frequency factor, E_a is the activation energy of the hydrolysis reaction, R is the gas constant and T is the absolute temperature of hydrolysis.

From the intercept of the linear plot at $1/T = 0$ being log A and from the slope of the line being $-E_\mathrm{a}/(2.303 \cdot R)$, the pre-exponential factor A and the activation energy E_a of the hydrolysis can be calculated. The values for the Arrhenius parameters of the studied dyes are summarized in Table 4.

With regard to the values of the correlation coefficients R^2 (Table 4), the temperature dependence of rate coefficients of the monofunctional dyes fits

Table 4 – *Activation energies E_a, pre-exponential factors A and the squares of the correlation coefficients R^2 in the linear Arrhenius plot for alkaline hydrolysis of the halogeno-s-triazine dyes*

Reactive dye	E_a/kJ · mol^{-1}	A/min^{-1}	R^2
monochloro-s-triazine (I)	111.03	$3.4 \cdot 10^{14}$	0.9999
bis(monochloro-s-triazine) form of (II)	98.88	$5.1 \cdot 10^{12}$	0.9981
monofluoro-s-triazine (III)	101.41	$2.6 \cdot 10^{14}$	0.9997
bis(monofluoro-s-triazine) form of (IV)	90.89	$2.7 \cdot 10^{12}$	0.9976
monofluoromonohydroxybis-s-triazine form of (IV)	99.03	$1.1 \cdot 10^{13}$	0.9995

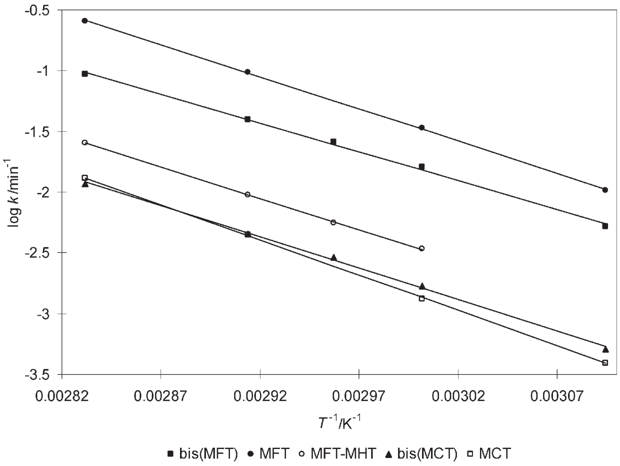


Fig. 9 – *Plot of log k against 1/T for alkaline hydrolysis of reactive dyes, where bis(MFT) denotes bis(monofluoro-s-triazine) form of dye (IV), MFT monofluoro-s-triazine dye (III), MFT-MHT monofluoromonohydroxybis-s-triazine form of dye (IV), MCT monochloro-s-triazine dye (I), bis(MCT) bis(monochloro-s-triazine) form of dye (II).*

a little better with the Arrhenius equation than that of the homobifunctional dyes. It is noticeable that the plots of log *k* vs. 1/*T* of both homobifunctional dyes (Fig. 9) show a slight curvature at 60 °C.

It is obvious from the Arrhenius parameters (in Table 4) that the rate coefficient of the monofunctional monochlorotriazine dye (I) depends on temperature more than that of any other dyes. A high sensitivity of the rate coefficient to temperature variations also exhibits the monofluoro-s-triazine dye (III), followed by the monofluoromonohydroxybis-s-triazine form of dye (IV), which has almost the same value of the activation energy as the bis(monochloro-s-triazine) form of dye (II). Among the studied dyes, the bis(monofluoro-s-triazine) form of dye (IV) is the least sensitive to changes in temperature conditions, which is an advantage of this type of dye.

Conclusions

The pseudo-first-order hydrolysis rate coefficients of the monofunctional and the homobifunctional halogeno-s-triazine dyes follow the Arrhenius equation in the temperature range of 50 °C – 80 °C. In general, as the temperature is raised by 10 °C the pseudo-first order hydrolysis rate coefficients of the most reactive dyes approximately triple, although the rate increase is a little greater at lower than at higher temperatures. However, the hydrolysis rate coefficient of the monofunctional dyes is more temperature-dependent than that of the homobifunctional dyes. The reactive dyes with a less reactive monochloro-s-triazine group are more sensitive to temperature variations than the reactive dyes with a more reactive monofluoro-s-triazine group.

The rate coefficients of the monofunctional monofluorotriazine dye are about 2 to almost 3 times greater than that of the bis(monofluorotriazine) form of the homobifunctional dye. Among the studied dyes, the bis(monofluorotriazine) form of the homobifunctional dye exhibits the lowest sensitivity to temperature variations and it is also about 4 to 5 times more reactive than its partly hydrolyzed monofluoromonohydroxybis-s-triazine form in the temperature range investigated. With the rising temperature, the difference in reactivity between these two forms of the homobifunctional dye gradually decreases.

The monochlorotriazine dye and the bis(monochlorotriazine) form of the homobifunctional dye show almost the same level of reactivity. The bis(monochloro-s-triazine) form of the investigated homobifunctional dye is about twice as reactive as its partly hydrolyzed monochloromonohydroxybis-s-triazine form.

Although this study only investigates the reactivities of the halogeno-s-triazine dyes and the effect of temperature on them, it needs to be emphasized that the substantivity and diffusional properties of the dyes, as well as the influence of other dyeing quantities such as pH, electrolyte concentration and liquor ratio are also essential determinants of their dyeing behaviour.

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List of symbols

[A], [B], c – concentration, mol L^{-1}
A – pre-exponential factor, min^{-1}
d_i – inner diameter, mm
E – activation energy, J mol^{-1}
l – length, mm
k – hydrolysis rate constant, min^{-1}
Q – volume flow rate, mL min^{-1}
S – peak area
R – gas constant, J K^{-1} mol^{-1}
R^2 – correlation coefficient
T – temperature, K, °C
t – time, min
V – volume, μL, L
λ – wavelength, nm

References

1. *Broadbent, A. D.*, Basic Principles of Textile Coloration, Society of Dyers and Colourists, Bradford, 2001, pp 332-357.
2. *Rys, P., Zollinger, H.*, Reactive dye-fibre systems, in Johnson, A. (Ed.), The theory of coloration of textiles, 2nd edn., Society of Dyers and Colourists, Bradford, 1989, pp 428-476.
3. *Hunter, A., Renfrew, M.*, Reactive dyes for textile fibres, Society of Dyers and Colourists, Bradford, 1999, pp 168-209.
4. *Bohnert, E., Weingarten, R.*, Melliand Textilber. **40** (1959) 1036.
5. *Hildebrand, D., Beckmann, W.*, Melliand Textilber. **45** (1964) 1138.
6. *Hildebrand, D.*, Bayer Farben Revue No. **9** (1964) 29.
7. *Rattee, I. D., Murthy, K. S.*, JSDC **85** (1969) 363.
8. *Fisichella, S., Occhipinti, G., Alberghia, G., Amato, M. E.*, Textile Res. J. **51** (1981) 683.
9. *Renfrew, A. H. M., Taylor, J. A.*, JSDC **105** (1989) 441.
10. *Dongzhi, L., Kunyu, G., Lubai, C.*, Dyes and Pigments **33** (1997) 87.
11. *Klančnik, M.*, Int. J. Polym. Mater. **47** (2000) 735.
12. *Karapinar, E., Phillips, D. A. S., Taylor, J.A.*, Dyes and Pigments (2006), doi:10.1016/j.dyepig.2006.06.026.
13. *Phillips, D. A. S.*, Advances in Colour Science & Technology No. 1 (1998) 1.
14. *Smith, C. B., Thakore, K. A.*, Text. Chem. Colorist **23** (1991) 23.
15. *Zollinger, H.*, Color Chemistry, 2nd edn., VCH, Weinheim; New York; Basel; Cambridge, 1991, pp 167-179.
16. *Klančnik, M.*, Ph. D. Thesis, University of Ljubljana, 1999.
17. *Klančnik, M.*, Chem. Biochem. Eng. Q. **14** (2000) 87.
18. Technical documentation of Procion H dyes, BASF.
19. Technical documentation of Cibacron F dyes, Ciba Specialty Chemicals.
20. *Bunnet, J. F.*, Techniques of Chemistry. Investigation of Rates and Mechanisms of Reactions, in Lewis, E. (Ed.), Part I, 3rd edn., Wiley, New York; London; Sydney; Toronto, 1974, pp 131-204.