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KINETIC INVESTIGATION OF REACTIVE DYEING

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SUMMARY

A modified mathematical model has been derived for the description of the reactive dyeing mechanism of cellulose. For the experiments film and fabric based on regenerated cellulose and a dye of monochlorotriazine type (C.I Reactive Red 43) have been used The calculated diffusion coefficient could be applied as an acceptable approximation. The dependence of dyeing efficiency on different parameters (dye and electrolyte concentration, pH, temperature, pretreatment, etc) has been investigated separately For the improvement of dye utilization hot mercerizing pretreatment proved to be the most effective

1 INTRODUCTION

One of the cardinal problems of economic reactive dyeing is to increase the proportion of the dyestuff quantity bonded covalently to the fibrous material. Though numerous research groups are dealing all over the world with the theoretical and practical problems of reactive dyeing, the dyestuff fraction fixed on the substrate is still less than desired.

Based on simple organic chemical reactions, reactive dyeing is nevertheless a complicated process which is difficult to grasp. The submicroscopic true-phase structure of the cellulosic fibrous material necessitates the consideration of many factors.

The dye is applied from an aqueous solution to the fibre. The formation of the covalent bond is preceded by sorption and diffusion processes Consideration has to be given to the hydrolysis of the dye and the decomposition of the dyestuff–cellulose bond already formed. In the investigation of the dyeing mechanism the secondary

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binding forces must be taken into consideration as well as the formation of the covalent bond

The heterogeneous chemical processes proceeding in the reactive dyestuff–cellulose system have been studied by a reaction kinetics approach. The exact formulation of all the processes proceeding in the fibrous system presents almost inextricable difficulties The problem can be approached only by neglecting some more or less substantial factors All the kinetic models published in the technical literature, describing various processes of reactive dyeing, involve such approximations

Our investigations have concerned the control of parallel and overlapping processes and the establishing of the relative optimum of dyeing at which the dyestuff–cellulose bond is dominant and the hydrolysis of the dyestuff is suppressed For practical purposes a new linearized kinetic relationship was selected for the modelling of reactive dyeing The model has been used to describe the reactive dyestuff uptake by substrates of regenerated cellulose (rayon) From the change with time of the total and the chemically bonded quantity of dyestuff sorbed on the substrate,

(a) the effective diffusion coefficient,
(b) the second order rate constant of the chemical reaction,
(c) the interfacial concentration of the reactive dyestuff, and
(d) the apparent quantity of the active sites of the substrate

have been calculated A relationship was found between the efficiency of fixation and the constants characteristic of dyeing

In the quantitative description of the reactive dyeing process some authors have over-estimated the importance of the chemical reaction and followed this by investigations using model compounds Others have given preference to the transport processes and assigned only a secondary role to the formation of the covalent bond Sizing up the actual situation, most of the researchers have started from the kinetic equation of diffusion linked with chemical reaction Applying different boundary conditions, they have used different solutions for the description of the kinetics of reactive dyeing The resulting relationships and equations are similar to one another in many respects since all are based on the same kind of approximation Some researchers have extended the kinetic model of reactive dyeing by giving prominence to single parts of the complicated heterogeneous process and by their mathematical formulation

In the initial period of the application of reactive dyestuffs some authors[1–3] examined the batching stage of the pad-batch process However, diffusion coefficients and substantivity values would not be deduced from these results Danckwerts' equations[4,5] have been used by some researchers The equations describe diffusion with either a plane semi-infinite slab[4] or a semi-infinite cylinder,[5] thus taking no account of many characteristics of the heterogeneous dyestuff–fibre system, the accessibility of the fibrous material, its surface properties and porous structure The equations can deal only with a chemical reaction of first order and are valid only for the initial stage of dyeing. They have the great deficiency of not enabling the calculation of the characteristic constants of dyeing (diffusion coefficient, substantivity, reactivity), so that these must be determined under idealized conditions, separate from the dyeing process investigated. The value of the diffusion coefficient, obtained under idealized conditions without chemical reaction, does not agree with the value measured under real conditions

For example, in exhaustion dyeing in a neutral medium, a dynamic equilibrium is established between the dyestuff quantities in the solution and on the fibre before the addition of the alkali After the addition of alkali the diffusion of the dye from the solution phase to the surface and into the bulk of the substrate does not proceed at the same rate as the chemical reaction. In response to the continued adjustment and restoration of a dynamic equilibrium more and more dye diffuses into the substrate and reacts to an extent approaching 30–40 % of the total sites available for reaction Thus, in the fixation of the dye, transport and sorption phenomena play equally important roles

Our investigations began in the middle of the 1960s This was the time when research groups engaged in work on reactive dyeing extended and complemented the kinetic model of reactive dyeing known so far In the formulation of his kinetic model, Rattee[6, 7] took into consideration that the reactive dye reacts in a double-phase system with cellulose swollen in water. He took into account conditions prevailing in the external and internal aqueous phases, and attributed an important role to diffusion, sorption and the surface charge of the substrate Zollinger *et al.* used for the description of the kinetics of reactive dyeing the pore model of Weisz [8] The basis of their calculation was Fick's second equation modified by porosity and tortuosity factors, in which diffusion is independent of concentration [9] To deduct chemisorption and desorption Langmuir's sorption mechanism has been used The chemical reaction of the sorbed dye with the fibrous material and the hydrolysis of the dye in the liquid filling the pores were considered as reactions of second order [10] Kricsevskij and co-workers[11–14] used for the description of the reactive dyeing kinetics of cellulose-based fibrous material both the stepwise approximation method and the analytical solution of Fick's second equation The elaborated correlations are valid in the diffusive and kinetic sections of dye fixation They do not give information for the case when rates of true chemical reaction and dye diffusion are comparable On the basis of the investigation of dye penetration new mathematical correlations were found[15–17] for the modelling of reactive dyeing kinetics. These cannot be applied for practical dyeing, because the experimental methods are very different from the usual dyeing techniques.

A common insufficiency of the kinetic models mentioned so far, is that the determination of the constants characteristic of dyeing is based upon experimental conditions other than the dyeing process itself. It is almost impossible under practical conditions to find an expression for describing the kinetics of heterogeneous chemical reaction and its efficiency, that takes into account all the influencing parameters. However, some of the difficulties have been overcome by modelling the kinetics of reactive cellulose dyeing on the basis of a new mathematical correlation. While this too is not free of approximations, it does make possible during the dyeing process investigated, assuming second order reaction kinetics, the study and quantitative determination of dyeing characteristics and the elucidation of their complicated interactions.

2 EXPERIMENTAL DETAILS

2.1 *Dye*

For most of the investigations dye C.I. Reactive Red 43, and for a small proportion C.I. Reactive Red 12, were used. The commercial dye proved to be single-component on the basis of thin-layer chromatography.

2.2 *Substrate*

The cellophane film was manufactured by the Magyar Viscosa Gyar by the viscose process. Thickness, 4×10^{-3} cm, mass per unit area, 60 g m^{-2}, glycerol content, 10·3%, density, $1{\cdot}5 \times 10^{-3}$ kg m^{-3}, average degree of polymerization, 235, copper number, 1·35 mg copper g^{-1} cellulose; Methylene Blue sorption, 2·39 mg COOH g^{-1} cellulose; alkali sorption, 16·5 mg NaOH g^{-1} cellulose.

'Fibrella' bleached rayon was also used. Yarn count per 10 cm^2, in the warp direction 285/20 tex per 10 cm, in the weft direction 258/20 tex per 10 cm; weight per unit area, 114 g m^{-2}, density, $1{\cdot}52 \times 10^{-3}$ kg m^{-3}, average degree of polymerization, 262, copper number, 1·18 mg copper g^{-1} cellulose; Methylene Blue sorption, 2·14 mg COOH g^{-1} cellulose, alkali sorption, 19·7 mg NaOH g^{-1} cellulose.

2.3 *Dyeing*

Dyeing was carried out by exhaustion procedures using a liquor to goods ratio of 1000:1 for both the cellophane film and the viscose fabric. Alkali and electrolyte were added at the beginning of dyeing to the system.

Glycerol was extracted from the cellophane film with hot water, and the cellophane film was then soaked at room temperature for 24 h in a dyestuff-free, 'blank', dyebath (i.e. with alkali and electrolyte only).

To increase the reactivity of the monochlorotriazine dye, an equimolar quantity of either triethylamine or tributylamine was added as catalyst in a few experiments.

Several alternative pretreatments were used in the case of the viscose fabric:

(a) 60°C in 10 g dm^{-3} trisodium phosphate dodecahydrate (the same concentration as used for dyeing) until the equilibrium value of the alkali sorption isotherm is attained (about 2 h)

(b) 2 h at 60 °C in aqueous solutions containing 10 g dm^{-3} trisodium phosphate dodecahydrate and 50–100 g dm^{-3} sodium chloride.

(c) 90 min at 60 °C in solutions of 0·25–1 0 g dm^{-3} dye and 50 g dm^{-3} salt, until the equilibrium value of the dye sorption isotherm is attained.

(d) 2 min either cold (20 °C) or hot (90 °C) in 38 g dm^{-3} sodium hydroxide solution followed by rinsing, acid neutralization, then rinsing again

General specification of dyeing conditions

Dye concentrations (g dm^{-3}). 0 25, *0 50*, 1·00
Sodium chloride concentrations, (g dm^{-3}) 0; 10, 25, *50*, 100
Alkali concentrations· *10 g dm*$^{-3}$ $Na_3PO_4 \cdot 12H_2O$, 4 g dm^{-3} NaOH
Temperature (°C) 50; *60*; 75
Italicized data are values selected as constant by changing the other parameters

In order to follow the kinetics of dyeing, separate samples were dyed for the times specified Each sample was divided into two parts. Using half of the sample the total quantity of dye taken up was determined From the other half of the sample loosely bonded dye was extracted with hot water and solvent. From the data, the quantity of chemically bonded dye was calculated by difference

2 4 *Determination of the dye content of the dyed substrate*

The dye content of the cellophane film was determined by direct colorimetry That of the regenerated cellulose (rayon) fabric was determined by spectrophotometry after dissolution in cadmium–diethylenediamine reagent. The colour depth of the dyed fabric was determined with a tristimulus colour measuring instrument

2 5. *Determination of dye hydrolysis*

Dye hydrolysis was followed by potentiometric titration of the chloride ions present. Measuring solution, 0 01 M-$AgNO_3$ solution; electrodes, chloride ion selective membrane electrode (OP-Cl-7111 C Radelkisz), double salt bridge reference electrode (OP-8212 Radelkisz).

3 MATHEMATICAL DEDUCTION OF THE KINETIC MODEL USED AND INVESTIGATION OF ITS VALIDITY

3 1. *Deduction of the kinetic model*

For the description of diffusive processes associated with chemical reaction, the approximate solution of Fick's second diffusion equation, elaborated by Levai and coworkers,[18] has been used

The change in concentration in unit volume of the dye diffusing into the film and undergoing chemical reaction is described by the following equation:[19]

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial y^2} - \frac{\partial c_s}{\partial t} \tag{1}$$

where c and c_s are the concentrations (g dm^{-3}) of the reactive and of the chemically bonded dye, y (cm) is a local coordinate in the direction of diffusion, and D (cm^2 min^{-1}) is the diffusion coefficient.

The quantity of reactive dye, N (mg g^{-1} substrate), which diffuses into the film but does not form covalent bonds, and the quantity of chemically bonded dye, S (mg g^{-1} substrate), are determined by the integrals of concentrations c and c_s with respect to y.

$$N = \int_0^\infty c\,\mathrm{d}y \qquad \text{and} \qquad S = \int_0^\infty c_s\,\mathrm{d}y \tag{2}$$

The kinetic model considers the concentration distribution of the diffusion zone as linear along the y axis.[18] This linear distribution is shown by the straight line in Fig. 1.

If the concentration distributions were actually linear, quantities N and S would be equal to the areas of the triangles under the straight lines. However, the true values of N and S are given only by the areas enclosed by the concentration distribution curves, so that the area of the triangles can be used for their calculation only after the introduction of appropriate correction factors (α, β, γ).

$$N = \alpha\frac{c_0\xi}{2} \tag{3}$$

where c_0 is the internal dye concentration (g dm^{-3}) at the interface

$$S = \beta\frac{c_s\xi}{2} \tag{4}$$

where ξ is the slope of the concentration distribution curve (Fig. 1).

From the starting equations (1) and (2) and considering relationships (3) and (4), the general relationship (5) can be deduced for the chemical reaction associated with diffusion.

$$N = \sqrt{D\alpha}\,\frac{\sqrt{\int c_0^2\left(1+\gamma\frac{c_s}{c_0}\right)\mathrm{d}t}}{1+\gamma\left(\frac{c_s}{c_0}\right)} \tag{5}$$

$$S = N\gamma\left(\frac{c_s}{c_0}\right) \tag{6}$$

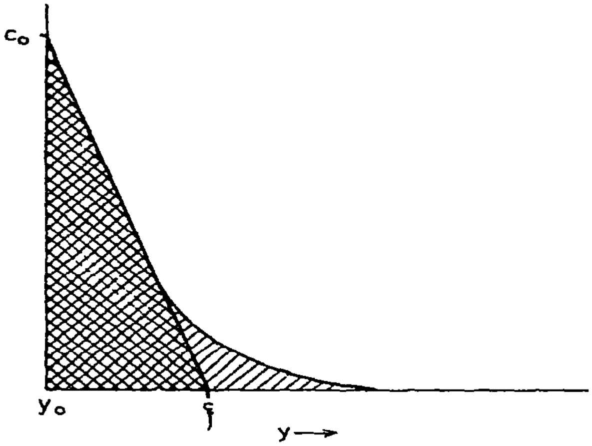

Fig 1 Linearized and actual concentration profiles

On comparing the results of the linearized diffusion equation with calculations from the literature,[20]

$$\gamma = 0.722 \text{ in the range } kt = 0\text{–}1 \text{ and}$$
$$\gamma = 0.770 \text{ in the range } kt = 1\text{–}2^{18}$$

where k ($dm^3 g^{-1} min^{-1}$) is the dye–substrate second order rate constant.

During the chemical reaction, the concentration of the reactive reagent diminishes also because of hydrolysis If this decrease is sufficiently small, the hydrolysis rate constant can be omitted from the equation on the basis of mathematical considerations [18,21]

$$M = N + S = c_0\sqrt{\frac{D}{kn_0}}\,\sqrt{2\gamma kn_0(1+\gamma R)t - 2\gamma^2R^2[1-\exp(-kc_0t)]} = c_0\sqrt{\frac{D}{kn_0}}\cdot\phi(t)_M \tag{7}$$

$$S = c_0\sqrt{\frac{D}{kn_0}}\,\frac{\gamma R[1-\exp(-kc_0t)]}{1+\gamma R[1-\exp(-kc_0t)]}\,\phi(t)_M = c_0\sqrt{\frac{D}{kn_0}}\cdot\psi(t)_s \tag{8}$$

$$\frac{S}{N} = \gamma R[1-\exp(-kc_0t)] \tag{9}$$

where $R = n_0/c_0$, and γ is a dimensionless constant.

Considering the fibrous material as of circular cross-section, Levai has used the analogy between the diffusion equation for films and cylinders He took into consideration that the quantity of reactive dye diffusing towards the interior of the cylinder, changes as the volume element of the cylindrical ring, and that it is not constant with time The dyeing of the fibre is described by the relationship:

$$N = \frac{c_0}{\rho}\left\{2.35\sqrt{\frac{2D\gamma}{r^2kc_0}}\,\frac{\sqrt{(1+\gamma R)t-\gamma R[1-\exp(-kc_0t)]}}{1+\gamma R[1-\exp(-kc_0t)]} - 1.5\frac{2D\gamma}{r^2kc_0}\,\frac{(1+\gamma R)t-\gamma R[1-\exp(-kc_0t)]}{\{1+\gamma R[1-\exp(-kc_0t)]\}^2}\right\} \qquad (10)$$

where r is the radius of the cylinder (cm), and ρ the density of the fibre (10^{-3} kg m^{-3})

Equations (7)–(10) describe with satisfactory approximation the progress of the diffusion process associated with chemical reaction in a body bounded by planes (in the film) and in the fibre considered as an infinite cylinder Further assumptions are the linear distribution of dye concentration, constant dye concentration at the surface of the substrate and a negligibly small rate of hydrolysis of the dye.

Constants characteristics of dyeing were calculated from our data in the case of cellophane film numerically by graphical integration (eqns (7)–(9)), and for the viscose rayon fabric with a computer (eqn (10))

3.2 *Investigation of the validity of the kinetic model*

(a) *Example of the reactive dyeing of cellophane film* It has been estimated that the kinetic model is valid only in systems in which the concentration of the adsorbed

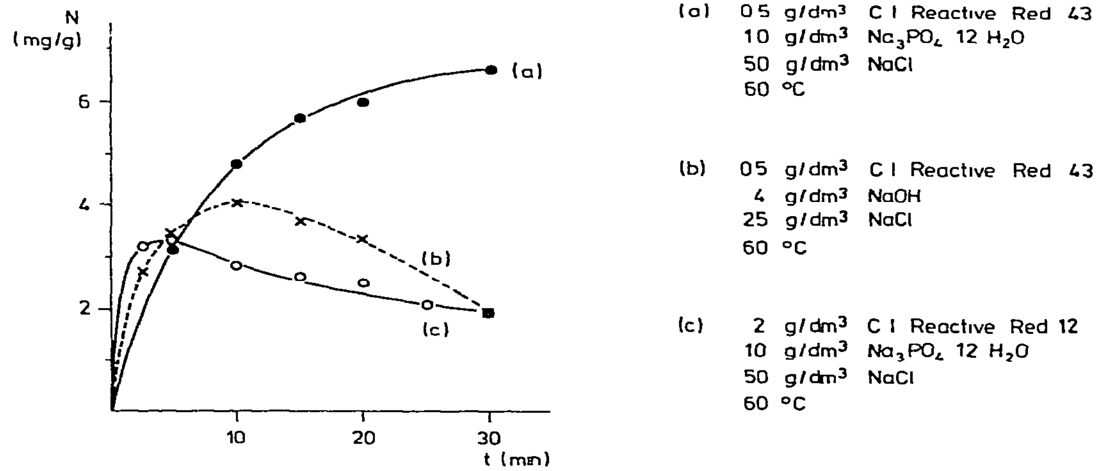

Fig 2 Change in reactive dye concentration as a function of time in various dyeing systems

reactive dye (N) increases monotonically with time, and asymptotically approaches a limiting value (Fig. 2, curve a). In this case good agreement was obtained between calculated and measured values.

The good agreement of calculated and measured values is shown in Fig. 3.

The agreement is much less when the electrolyte is changed to sodium hydroxide (Figure 2, curve b) The relationship is valid only in the initial, ascending, branch of the curve

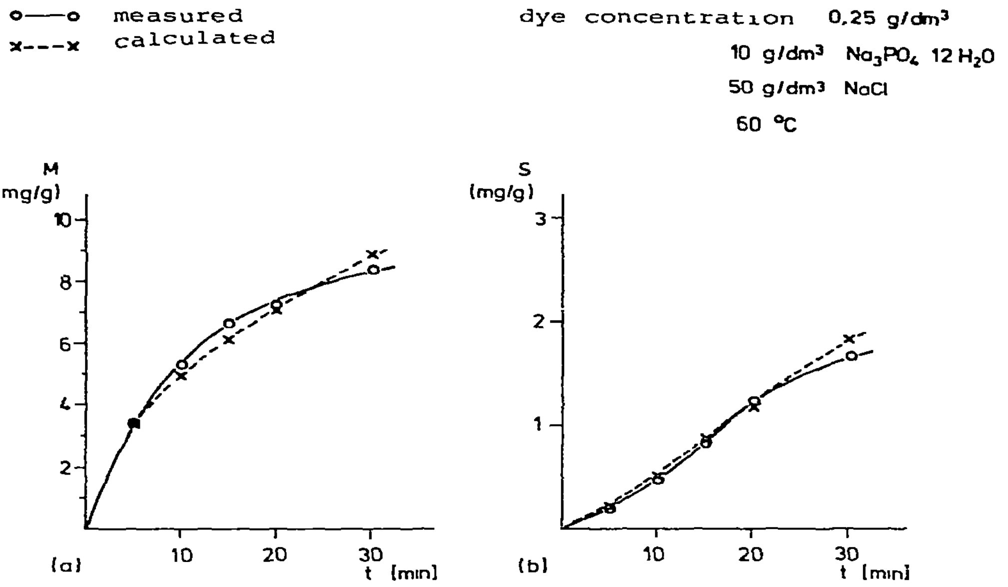

Fig 3 Comparison of calculated and measured quantities (a) total dye on the fibre, (b) covalently bonded dye on the fibre

Dyeing carried out with C I Reactive Red 12 could not be evaluated with the linearized diffusion equation The affinity of the dye is low, its diffusion rate high, and maximal dye concentration is reached in a few minutes at the surface of the substrate (Fig 2, curve c) The process is controlled by the rate of the chemical reaction

It has been established that for the kinetic description of the dyeing of cellophane film the linearized diffusion equation, under appropriate dyeing conditions, is valid only in given reactive dye systems, in which the fixation of the dye is affected equally by the rate of diffusion and the rate of the chemical reaction, i.e. the process proceeds in the transitory region Experience shows that due to numerous approximations, the new kinetic model describes only the initial stage of the process far from equilibrium and the accuracy of description worsens as equilibrium is approached

(b) *Example of the reactive dyeing of regenerated cellulose (rayon) fabric* · The adaptation of the kinetic model used in the dyeing of cellophane film to the reactive dyeing of viscose fabric is not an easy task The difficulty of application and its complexity lie on the one hand in the interpretation of the the physical model, and on the other hand in the mathematical solution of the linearized diffusion equation. It has been assumed that the fibres have a circular cross-section and that dyeing is uniform However, it was possible using the overall data relating to the dyeing of the fabric to calculate the constants characteristic of dyeing, and to estimate, on this basis, the effect of these parameters on the efficiency of fixation, etc

(c) *Comparative analysis of the applicability of the calculated diffusion coefficients* Additional experiments were designed to determine whether the diffusion coefficient determined without chemical reaction (in an idealized system) can be applied to the real conditions of dyeing

Investigations were carried out using neutral hydrolyzed dye solution The diffusion coefficient was determined by the multilayer membrane method It was established that changes in temperature and electrolyte concentration had a similar effect whether dye fibre reaction was allowed to proceed or not. However, the numerical values of the calculated constants, diffusion coefficients and substantivities were different in the two processes For example, dyeing at 60 °C in a bath containing 0 50 g dm^{-3} dye, 10 g dm^{-3} $Na_3PO_4 \cdot 12H_2O$, 50 g dm^{-3} NaCl, in the solution of the hydrolyzed dye the diffusion coefficient is $6\ 2 \times 10^{-7}$ cm^2 min^{-1}, and in the solution of the reactive dye, under the conditions of dyeing $5\ 6 \times 10^{-8}$ cm^2 min^{-1}

Since in the equation describing efficiency the characteristic constants of dyeing are in complicated correlation with one another, the use of the linearized diffusion equation, which takes into account the real conditions of dyeing and the associated interactions, gives a closer approach to the representation of reality

The new linearized kinetic model selected for the quantitative description of reactive dyeing describes with good approximation the reactive dyeing of cellophane film, and in the dyeing of viscose fabric the trends can be estimated. The relationship gives a good approximation of the initial stages of dyeing, far from equilibrium. In addition the model only functions in situations where the fixation of the dye is affected to an identical degree by the transport process and the chemical reaction

4 RESULTS AND THEIR EVALUATION

4 1. *Dyeing of cellophane film*

Constants calculated for the characterization of dyeing on the basis of our measurement are summarized in Table 1, while the tendencies of changes are outlined in Fig 4

On increasing the temperature, the diffusion coefficient, the reaction rate

TABLE 1

CONSTANTS CHARACTERISTIC OF THE REACTIVE DYEING OF CELLOPHANE FILMS

Dye C.I. Reactive Red 43

Temperature (°C)	*Initial dye concentration* c_s ($g\,dm^{-3}$)	*Concentration* ($g\,dm^{-3}$)		*Catalyst in equimolar quantity*	c_0 ($g\,dm^{-3}$)	q_0/c_s	n_0 ($g\,dm^{-3}$)	$k \times 10^2$ ($dm^3\,g^{-1}\,min^{-1}$)	$D \times 10^8$ ($cm^2\,min^{-1}$)
		Alkali	*Electrolyte*						
50	0.25	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	30.6	122.5	13.8	0.46	5.68
50	0.50	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	45.2	90.5	15.2	0.46	5.40
50	1.00	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	77.1	77.1	17.1	0.47	3.71
60	0.25	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	29.6	118.4	13.8	1.22	5.52
60	0.50	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	42.1	84.3	17.8	1.21	5.61
60	1.00	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	48.3	48.3	19.7	1.20	14.50
75	0.25	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	24.4	97.5	15.3	2.09	5.62
75	0.50	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	36.5	73.3	26.7	2.13	9.61
75	1.00	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	—	39.0	39.0	23.8	2.05	22.60
60	0.50	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	Triethylamine	40.5	81.1	19.9	1.99	5.71
60	0.50	$10Na_3PO_4 \cdot 12H_2O$	50NaCl	Tributylamine	41.5	83.0	17.7	2.21	5.68
60	0.50	4NaOH	—	—	6.7	13.4	10.2	1.5	3.1
60	0.50	4NaOH	10NaCl	—	11.5	23.0	22.3	2.2	16.2
60	0.50	4NaOH	25NaCl	—	18.2	36.4	20.2	3.1	14.3
60	0.50	4NaOH	50NaCl	—	20.9	41.8	26.1	3.0	14.4
60	0.50	4NaOH	100NaCl	—	24.0	48.0	46.5	2.1	15.0

c_0 = internal interfacial dye concentration
c_s = substantivity

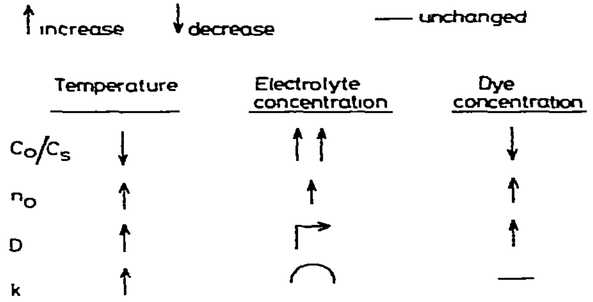

Fig. 4 The change of reactive dyeing as a function of dyeing parameters on cellophane film

coefficient and apparent quantity of active sites increase, but substantivity diminishes. An increase in the initial dye concentration does not affect the value of the rate constant but brings about an increase in the apparent number of active sites and a decrease in the substantivity. At temperatures above 50 °C the diffusion coefficient is increased. A small quantity of electrolyte added increases the diffusion coefficient, while further additions have no significant effect. Catalysts actually increase only the reaction rate constant, as compared to dyeing in the absence of catalyst, while the constants characteristic of dyeing remain unchanged. Neither does the quantity of dye fixed on the substrate change.

Using C.I. Reactive Red 12 for dyeing, it can be generally established that the quantity of dye adsorbed at the surface of the substrate becomes constant after 5–10 min. The quantity of covalently bonded dye increases with time, so that the concentration of unfixed reactive dye in the fibre is characterized by a sudden increase which is then followed by gradual decrease. As mentioned already, the kinetic model based on the linearized diffusion equation is not suitable for the calculation of the characteristic constants in this case.

Substantivity, as expected, decreases with increasing temperature. At small external concentrations its value falls by approximately 20%, while at higher external concentrations the change is more substantial. The phenomenon can be interpreted in two ways. On the one hand, it can be assumed that physical sorption and chemisorption proceed simultaneously in the internal volume of cellophane. On the other hand, association may play an important role in the control of the process. On increasing the electrolyte concentration, substantivity increases and approaches a limiting value. Substantivity decreases with increasing alkalinity, due to the fact that with increasing pH the number of anions and thereby the negative electric charge of the cellulose phase increases by dissociation of the cellulose, which decreases dye sorption.

In the kinetic model the quantity n_0 represents the apparent quantity of the fixation sites of cellulose. No assumptions have been made about their chemical characterization. It has been shown[22,23] that the number of cellulose hydroxyl groups participating in the reactive dye–cellulose reaction is limited by accessibility. With increasing dye sorption during the fixation process, the number of the accessible hydroxyl groups decreases at a higher rate than that corresponding to the degree of substitution. The phenomenon is due to the high space requirement of the dye molecule, and gives rise to an effective saturation value.

For the determination of the fixation sites in cellulose the saturation value seemed to be a good parameter In one of our early communications,[24] the effective saturation value obtained on the basis of repeated dyeing has been used in the calculations for the determination of the active hydroxyl groups, and unusually high concentrations were obtained. Later, saturation values were determined from chemically bonded dye·

Temperature (°C)	50	60	75
Saturation value (mg dye g^{-1} cellulose)	12 22	14 81	24 58

These effective saturation values increase with increasing temperature On the other hand, the n_0 value calculated on the basis of the kinetic model depends on the initial dye concentration, and is about 50 % less than the quantity determined on the basis of the effective saturation value The reason of the numerical difference appears to be the formation of aggregation centres by the dye linked covalently. The associated dye molecules cannot be removed by solvent extraction, so that they appear to be covalently bonded Thus, instead of presuming monomolecular dyeing, the association of the dye must also be taken into consideration

With decreasing substantivity the diffusion coefficient passes through a minimum value It increases with decreasing substantivity at 60 °C and 75 °C but at 50 °C it decreases. This is consistent with the findings of Crank.[25] The magnitude of the diffusion coefficient is determined by two opposing effects, the changes of the electric surface charge and of substantivity. At 60 °C, the diffusion coefficient first increases with increasing electrolyte concentration, reaches a maximum, and then decreases gradually Similar results were obtained by Neale and Stringfellow,[26] who found that the diffusion coefficients of substantive dyes change along a maximum curve with increasing electrolyte concentration

In the calculation of the rate constants the reaction between cellulose and reactive dye can be considered as kinetically second order, proceeding between the Cell O$^-$ ions and the dye molecule in the internal volume of cellulose, and thus its rate is $k\ c_0 . n_0$. According to sorption theory, the dye molecules in the internal volume may be bound by physical and chemical sorption forces to the cellulose surface Thus, it may be assumed that dye molecules in different states of sorption have also a different reactivity. Therefore, c_0 in itself is insufficient for the characterization of the reaction rate. This is actually manifested by the fact that the temperature dependence of k in Table 1 does not follow Arrhenius' equation.

The reaction of the reactive dye and the cellulose substrate is promoted by the alkalinity of the medium The rate constant increased by a factor of about 2 5 on increasing the pH from 11·5 to 12 5

4 2 *Dyeing of viscose fabric*

The constants calculated on the basis of our measurements for the characterization of dyeing are summarized in Tables 2 and 3.

In general similar relationships between the dyeing and fixation behaviour and dyeing process variables were observed on viscose rayon fabric to those found to apply in dyeing cellophane film

Substantivity Pretreatment, involving the pretreatment of the fabric with reactive dye in a neutral medium, makes possible the penetration and the uniform distribution of the dye in the interior of the fibre before the beginning of the chemical reaction The reactive dye reaches the active sites of cellulose, and on alkali addition the dye reacts rapidly with the polymer The rate constant is by half to one order of magnitude higher than the value measured or calculated for the fabric not pretreated with dye The rate of the chemical reaction is proportional to the concentration of the sorbed reactive dye

The effect of the change in initial dye concentration is the same as has been found in the dyeing of fabric without pretreatment with dye A decrease of the diffusion coefficient with increasing dye concentration has been observed. This is contrary to the tendency to change of the diffusion coefficient measured in a medium containing sodium hydroxide (Table 3) but agrees with the findings of other authors [12 27 28] Presumably, with increasing dye concentration trisodium phosphate promotes dye association, and this masks the effect of the increased dye concentration gradient on the diffusion coefficient At a dye concentration of 1 g dm^{-3}, conditions in the dyeing of the fabric are likely to favour the formation of associates, with a resulting decrease of the reaction rate constant

Effect of the electrolyte In the presence of electrolyte a compacted diffuse double layer is produced at the fibre surface and the dissociation of the hydroxyl groups is suppressed This facilitates the approach of the dye anions of identical charge to the cellulose fibre surface The electrolyte increases the substantivity of the reactive dye,[29] but it also enhances dye association, resulting in a decrease in diffusion rate [30] It also affects the distribution between the external and internal phases of the hydroxyl ions, introduced into the system by the addition of alkali According to the Donnan membrane model, in alkaline medium the pH of the internal phase of cellulose is always lower than that of the external phase [31] The addition of electrolyte decreases this difference,[32] and thereby increases the rate of fixation of the reactive dye Other researchers[22 33] have observed that the hydrolysis rate of the dye increases with increasing electrolyte concentration.

TABLE 2

CONSTANTS CHARACTERISTIC OF THE REACTIVE DYEING OF VISCOSE FABRIC

Pretreatment					Dyeing[a]			c_0 ($g\,dm^{-3}$)	n_0 ($g\,dm^{-3}$)	$k \times 10^2$ ($dm^3\,g^{-1}\,min^{-1}$)	$D/r^2 \times 10^3$ (min^{-1})
Temperature (°C)	Time (min)	Concentration ($g\,dm^{-3}$)			Temperature (°C)	Concentration ($g\,dm^{-3}$)					
		Alkali	Electrolyte	Dye		Dye	Electrolyte				
—	—	—	—	—	50	0.50	50NaCl	9.35	11.56	8.74	1.15
—	—	—	—	—	60	0.50	50NaCl	10.46	21.00	8.25	3.02
—	—	—	—	—	75	0.50	50NaCl	9.16	36.93	19.00	3.86
—	—	—	—	—	60	0.25	50NaCl	4.79	12.35	8.25	13.10
—	—	—	—	—	60	1.00	50NaCl	17.09	45.53	1.99	2.15
60	90	—	50NaCl	0.25	60	0.25	50NaCl	5.80	15.47	17.10	16.4
60	90	—	50NaCl	0.50	60	0.50	50NaCl	12.07	26.01	18.70	21.4
60	90	—	50NaCl	1.00	60	1.00	50NaCl	20.86	30.65	11.00	19.3
—	—	—	—	—	60	0.50	—	1.83	2.77	4.55	24.20
—	—	—	—	—	60	0.50	100NaCl	7.70	14.56	1.53	17.50
60	120	10Na_3PO_4 $12H_2O$	—	—	60	0.50	—	2.65	2.00	14.6	100.9
60	120	10Na_3PO_4 $12H_2O$	50NaCl	—	60	0.50	—	27.26	42.55	3.17	0.57
60	120	10Na_3PO_4 $12H_2O$	100NaCl	—	60	0.50	—	12.74	25.24	0.64	6.03
60	120	10Na_3PO_4 $12H_2O$	—	—	60	0.50	50NaCl	9.03	9.69	17.0	7.03
20	2	38 NaOH	—	—	60	0.50	50NaCl	24.93	30.85	0.65	1.31
90	2	38 NaOH	—	—	60	0.50	50NaCl	22.04	27.70	0.68	17.3
—	—	—	—	—	60	0.50	50NaCl	28.69	40.57	0.69	7.83
190	10	—	—	—	60	0.50	50NaCl	18.09	32.47	0.51	2.46

[a] 10 g litre^{-1} Na_3PO_4 $12H_2O$ was used for dye fixation in all cases with C I Reactive Red 43

TABLE 3

CONSTANTS CHARACTERISTIC OF THE DYEING OF VISCOSE RAYON

Temperature (°C)	*Time* (*min*)	*Pretreatment*	*Dyeing*[a]			c_0 ($g\,dm^{-3}$)	n_0 ($g\,dm^{-3}$)	$k \times 10^2$ ($dm^3\,g^{-1}\,min^{-1}$)	$D/r^2 \times 10^3$ (min^{-1})
		Alkali concentration ($g\,dm^{-3}$)	*Temperature* (°C)	*Concentration* ($g\,dm^{-3}$)					
				Dye	*Electrolyte*				
—	—	—	50	0 50	50NaCl	9 75	6 74	2 26	7 20
—	—	—	60	0 50	50NaCl	5 97	15 72	4 53	11 06
—	—	—	75	0 50	50NaCl	3 03	16 33	18 80	14 30
—	—	—	60	0 25	50NaCl	3 04	10 14	2 33	4 16
—	—	—	60	1 00	50NaCl	9 84	19 86	1 04	16 20
—	—	—	60	0 50	—	0 68	1 47	3 30	0 20
—	—	—	60	0 50	100NaCl	8 77	32 27	4 16	3 44
60	120	4NaOH	60	0 50	50NaCl	4 24	8 00	9 92	17 20

[a] 4 g litre^{-1} NaOH was used for dye fixation in all cases with C I Reactive Red 43

Factors influencing changes in dyeing and fixation can assert themselves through a chain of very complicated interactions thus making their interpretation and explanation difficult. With the changing of conditions different components of the complex action may predominate. Quantitative changes often result in qualitative transformations. For the explanation of the results, those characteristics and effects which prove decisive in the given circumstances must be used.

An analysis of the data relating to the effect of electrolyte concentration shows that different effects are evident in the 0–50 g dm^{-3} and in the 50–100 g dm^{-3} NaCl concentration ranges. The lower quantities of electrolyte increase substantivity, the reaction rate constant and the apparent quantity of active sites. A larger quantity of sodium chloride promotes the association of the dye molecules, so that the internal dye concentration decreases at the interface, and this in turn decreases the effective rate constant The diffusion coefficient passes through a maximum with increasing salt concentration in the same way as observed in the dyeing of the cellophane film.

A smaller increase in the negative surface potential of cellulose occurs in the presence of trisodium phosphate as compared with sodium hydroxide at the same pH The relatively small amount of dye on the fabric is located in the vicinity of the surface and reacts at a high rate with the active sites of cellulose.

Pretreatment with NaCl solution of 50 g dm^{-3} concentration nearly trebles the dye concentration at the inner interface. However, in spite of the abundant dye supply, reaction rate constant and diffusion coefficient decrease Presumably, sorbed dye in the vicinity of the inner interface associates, and by clogging the pores, it hinders penetration and chemical reaction too In accordance with the Donnan equilibrium a higher pH is established in the interior of the fibre in the presence of salt, and this increases the apparent quantity of the active sites

At high electrolyte concentration dye association is even more important at the surface. Therefore, the value of c_0 is lower than with a treatment with NaCl solution of 50 g dm^{-3} concentration, but somewhat higher than in the case of fabric not pretreated The reaction rate decreases because, presumably, the dye hydrolysis rate comes strongly to the fore

In a medium containing sodium hydroxide, the changes with electrolyte concentration revealed a similar tendency, as compared with the dyeing of the cellophane film.

The role of the accessibility of cellulose. In the case of the viscose fabric, the effect of two physical modifications has been studied The accessibility of the fibrous material has been increased on one hand by pretreatment with alkali, and has been decreased on the other hand by repeated dyeing and thermal treatment.

When the fabric is saturated with alkali under the conditions of dyeing, during the relatively long treatment time (2 h) the swelling of the fibrous material becomes important, independently of the nature of the alkali, and the ionization of cellulose also increases As a result of this double effect, the reaction rate constant and the diffusion coefficient become about twice as great as in the dyeing of the untreated fabric. Unexpectedly, the value of n_0 decreases.

Cold pretreatment with sodium hydroxide solution of 38 g dm^{-3} concentration increases primarily the availability of the fibrous material with respect to physical adsorption and chemisorption, the values of c_0 and n_0 increase. This is reflected in dyeing by an increase of both M, the total dye quantity taken up by the fabric, and S, the chemically bonded ratio As the dyeing time increases, the increase of M surpasses that of S. This double dye supply cannot be utilized, presumably because of association The chemical reaction rate is also lower than in the case of the untreated fabric

By cold alkaline pretreatment accessibility increases mainly at the surface of the fibrous material This effect decreases towards the interior of the fibre Penetration into the interior of the fibre is hindered also by the increasing association of the dye

Hot (90 °C) alkaline pretreatment increases accessibility almost uniformly across the fibre As a result of this, the diffusion coefficient is larger by almost an order of magnitude than the value obtained by cold alkaline treatment, that is to say the large dye quantity accumulated at the internal interface penetrates the interior of the fibre Although the reaction rate constant is not higher than that measured for the fabric treated with cold alkali, more of the dye on the fibre is bonded chemically. The apparent quantity of active sites is further increased by hot alkaline treatment

The efficiency of fixation (S/M) is 13 % less on dyed fabric pretreated with cold alkali as compared with untreated dyed fabric, while on fabric pretreated with hot alkali the fixation efficiency is 2 % higher

An increase in availability is produced by alkaline treatment, which results in a high rapid initial dye uptake by definite surface layers of the fibrous fabric In a fabric treated with hot alkali the dye penetrated in 5 min to 68 5 % of the total thickness, while in the fabric treated with cold alkali a similar depth was penetrated only after 60 min Repeated dyeings change to such an extent the predicted physical content of the kinetic model that experimental results cannot be analyzed with the linearized diffusion equation deduced for a cylindrical substrate.

Heat treatment decreases accessibility, the structure of cellulose becomes more compact, it swells to a lesser degree and its specific surface is smaller than that of untreated cellulose This is manifested in a decrease of the internal interfacial dye concentration, of the diffusion coefficient and of n_0

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