

INVESTIGATION OF CELLULOSE-REACTIVE DYE HETEROGENEOUS SYSTEMS

By

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(Received June 30, 1974)

1. Introduction

Owing to their vivid colour, good colour fastness and relatively simple use, reactive dyes spread quickly in textile dyeing and printing.

The fixing of water-soluble reactive dyes on cellulose fibres is a heterogeneous reaction. For the description of the reaction, factors arising from the heterogeneity of the reaction (availability, diffusion, affinity, submicroscopic steric effects, dye distribution between the two phases, etc.) must also be taken into consideration besides the parameters influencing the homogeneous reactions (rate and equilibrium constants, concentration of the reactants, etc.).

The quantitative description of the complicated heterogeneous process has been attempted first by SUMNER and VICKERSTAFF [1], PRESTON and FERN [2], and later by most of the researchers studying reactive dyes, with the modified form of Danckwerts' equation. According to RATTEE [3], the kinetics of dyeing is influenced also by the ionization of cellulose, its surface potential, and by the structure of the dye. On the basis of the kinetic analysis of the results, he assumed a certain acid-base equilibrium to exist in alkaline dye solutions and ascribed also a role to the dye aggregations. SZADOV and co-workers [4] explained the mechanism of cellulose dyeing with monochlorothiazine reactive dyes on the basis of the model of the Langmuir isotherm.

As an approach to the complex heterogeneous processes, one part of the researchers, thus DAWSON et al. [2, 5], SUMNER et al. [6], ZOLLINGER et al. [7, 8], HILDEBRAND and BECKMANN [9, 10] and BAUMGARTEN et al. [11] used model substances. They used mono- and polyhydric alcohols in their dyeing experiments, and studied the self-decomposition of the dye in aqueous, alkaline medium. They established relationships between the two systems, and concluded from the homogeneous reactions on the heterogeneous phase reaction, i.e. on practical dyeing.

For heterogeneous phase dyeing, no method of calculation is known so far, which would take into consideration all the chemical and physical-chemical processes in reactive dyeing, that is to say, which would describe reliably the complex process under consideration of the combined effect of adsorption, diffusion and all the possible chemical reactions.

Though DANCKWERTS' equation relates to the steady state of chemical reaction, without consideration of hydrolysis, from the practical aspect the knowledge of the rate relationships of the processes leading to the steady state is of particular interest. Danckwerts' equation is valid also, — at a small deviation — for the initial section. The deviation arises from the fact that the equation suits to describe the kinetics of first-order reactions alone, while it cannot be solved for complex processes of second order.

Our experiments were aimed at elaborating a method of calculation, suitable for the description of complex processes.

2. Method of experiment

Our experiments involved a C. I. Reactive Red 43 dye of monochlorothiazine type, that proved to be a single-component dye in a chromatographic test. In alkaline medium, these dyes enter substitution reactions with cellulose-based fibre substances.

To facilitate diffusion measurements, a viscous sheet was dyed. Before dyeing, the sheets were pre-swelled in accordance with the conditions of dyeing.

Dyeing was carried out at constant temperature, with the dye solution in contact with only one side of the sheet. The concentration and the quantity of the dye solution were selected so that the quantity of dye diffusing into the cellophane should cause only a negligible change in the dye concentration. After the completion of dyeing, the total quantity of the dye taken up by the sheet, and the reactively bound part were determined.

The dyed sheet was investigated by spectrophotometry at a fair reproducibility of results. Dye contents determined in this way agreed well with the values of dye quantities determined by other methods.

3. Evaluation of the experimental results

In the course of our experiments, the quantity S of the dye bound chemically on cellulose, and the quantity N of the dye present in the cellulose have been determined as a function of dyeing time. Further measurements were carried out for the investigation of the effect of temperature and electrolyte concentration.

It was attempted to describe the results of measurements by solving the differential equations relevant to diffusion associated with chemical reaction for that case, valid for a body limited on one side by a plane surface, and of infinite extension in the direction of diffusion (semi-infinite membrane). The solution for this case of the kinetically first-order reaction is known from the

work of DANCKWERTS [12], but the differential equations can be calculated also by the method of Laplace transformation. The calculations give relationships for the change with time of the active dye content (N) and the chemically bound dye content (S) of cellophane, and of the S/N ratio.

A comparison of the calculated and measured results shows the time function of the measured S/N values to differ from that of the calculated curve. The slightly concave curve corresponding to theory lies above the convex curve calculated from the measured values (Fig. 1). It follows from this devia-

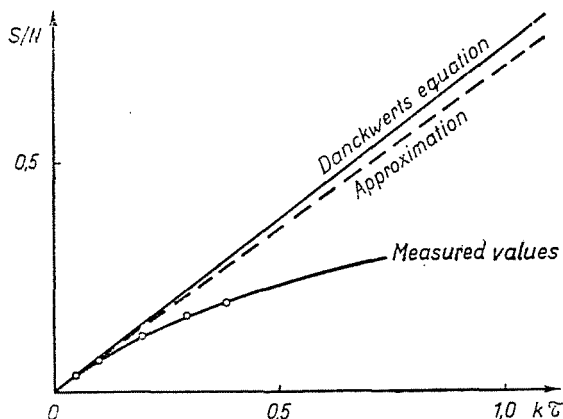


Fig. 1

tion that the actual reaction rate decreases with time, as compared to the reaction rate calculated on the basis of first-order kinetic. This deviation was attributed to the decrease in active hydroxy groups of cellulose or to the hydrolysis in alkaline medium of the dye. In either case, evidently the solution obtained for diffusion combined with first-order chemical reaction was unsuitable to describe our measurement results. Therefore, a mathematical solution had to be found for the case of second-order chemical reaction and diffusion. Since this solution should take into consideration also the consumption of the active hydroxy groups, the determination of their quantity became necessary. The determination of the quantity of the active hydroxy groups was attempted first by repeated reactive dyeing. In addition, the hydrolysis of the dye was measured.

Repeating six times the reactive dyeing on the same sample for determining the active hydroxy groups, 105 mg/g of dye was found to be bound on cellulose. In a previous publication [13] this value was used in our calculations, yielding unusually high internal concentration values. Further investigations showed the structure of cellulose to substantially change upon repeated dyeing,

so that the limit value of 105 mg/g could not be used for evaluating the results obtained in a single dyeing.

For determining the hydrolysis of the dye, kinetic measurements were carried out. The rate constant of hydrolysis at 60°C (in the presence of 10 g/l of Na₃PO₄ and 50 g/l of NaCl, at pH 11.4) was found to be 0.003 min⁻¹. In consideration of the time of reactive dyeing, about 20 min, this rate constant corresponds to about 8% of dye hydrolysis. In our estimation, this value and the consumption of the hydroxy groups can already cause a sensible deviation from the course of the kinetically first-order curve shown in Fig. 1. This recognition induced us to model calculations for investigating the combined role of diffusion and the second-order chemical reaction, and dye hydrolysis.

Our calculations were based on a model, assuming linear concentration distribution of the diffusion zone along the x axis (Appendix 1).

On the basis of the model, the following relationship of general validity has been deduced for the chemical reaction combined with diffusion

$$N = \sqrt{Dz} \frac{\int_0^z c_0^2 (1 + \gamma s_0/c_0) dt}{1 + \gamma s_0/c_0} \quad (1)$$

and

$$S = N\gamma s_0/c_0 \quad (2)$$

where: t is the time; S the quantity of dye bound chemically; N is the quantity of unreacted dye, M/cm²; c_0 and s_0 are the internal concentration of the active and chemically bound dye, respectively, at the interface, M/ml; α , γ are dimensionless correction constants, D is the diffusion coefficient, cm²/min. In the table the dye concentrations are understood in g/l.

The equation is related to a body limited on one side by a plane surface, and of infinite extension in the direction of penetration, hence it is valid for a membrane only up to the time of break-through (i.e. for the time required for the diffusion of the dye to reach the other side), which is about 30 minutes. The equation has the advantage that c_0 and s_0 are concentrations taken at the interface, so that the local co-ordinate does not change, and therefore, not partial differential equations have to be integrated. Eq. 1 applies to any type of homogeneous reaction and can be integrated with respect to time. Calculations made under consideration of hydrolysis showed during the measuring period a negligible hydrolysis corresponding to a rate constant of 0.003 min⁻¹ (Appendix 1). The solution of Eqs 1 and 2 for the cases of second-order reaction is:

$$M = c_0 \sqrt{D/kn_0} \varrho(t)_M \quad (3)$$

$$S = c_0 \sqrt{D/kn_0} \psi(t)_S \quad (4)$$

where: M is $S + N$, the total dye content of cellulose;
 n_0 is the number of the active hydroxy groups;
 k is the rate constant of the second-order chemical reaction;
 $\varrho(t)_M$ and $\psi(t)_S$ are time functions (see Appendix).

The solutions obtained were applied to our results, and they proved to describe satisfactorily the process measured. M and S values, plotted in Figs 2, 3 and 4, as a function of $\varrho(t)_M$ and $\psi(t)_S$, respectively, are seen to lie

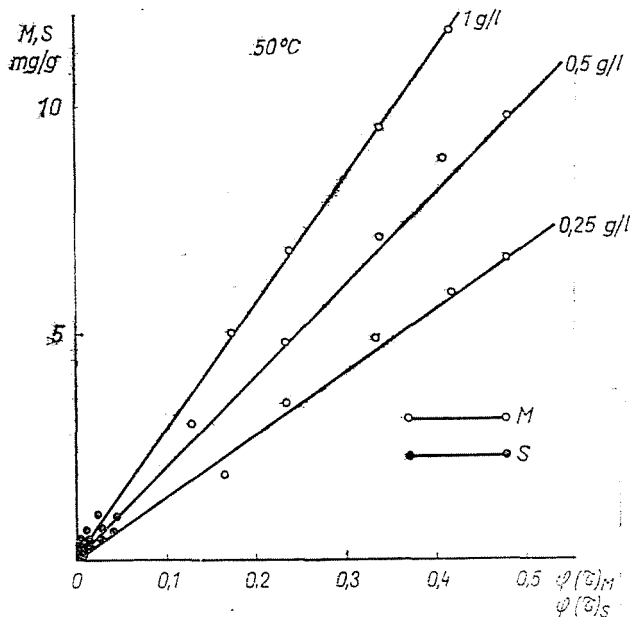


Fig. 2

actually on a common straight line, sloping at $c_0 \sqrt{D/kn_0}$. The measuring point obtained at various temperatures and external (constant) solution concentrations determine various slopes, depending on the internal interfacial concentration, the diffusion coefficient, the rate constant and the concentration of the active hydroxy groups. These quantities can only be calculated if the value of one of the (c_0) is known. The calculation of the values of c_0 , n_0 , k and D is given in the Appendix. The results of the calculations, as described in the Appendix, are compiled in Table 1 and shown in Figs 5, 6, 7 and 8.

3.1 Internal concentrations

For the interpretation of the effect of the internal concentrations c_0 , Table 1 gives also the values of the affinities $\Delta\mu'_0$, calculated in the usual way ($\Delta\mu'_0 = -RT \ln (c_0/c_{\text{external}})$).

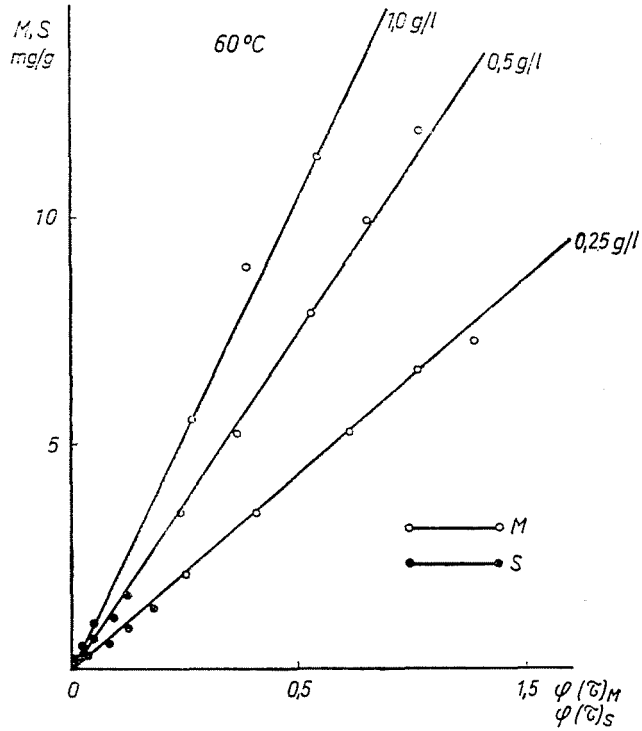


Fig. 3

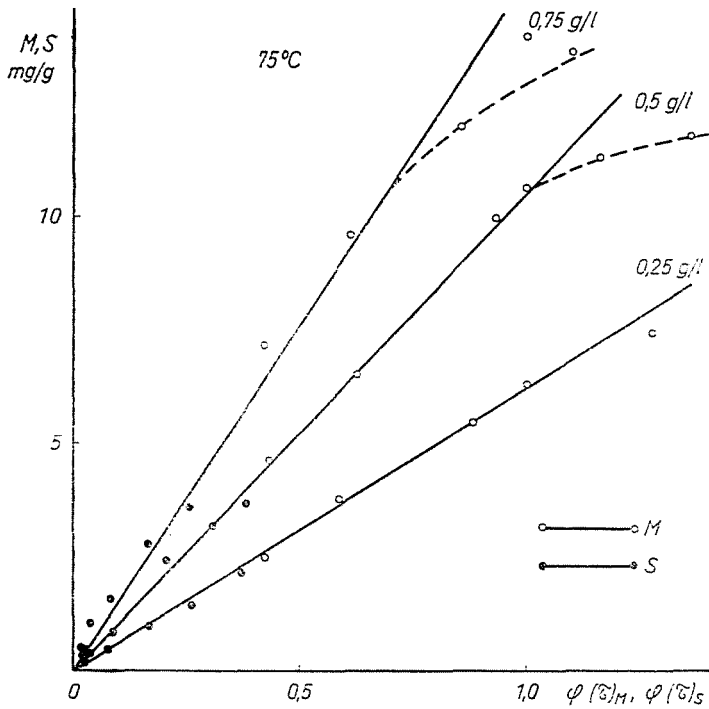


Fig. 4

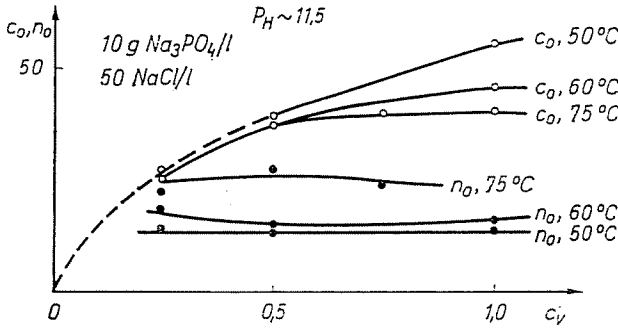


Fig. 5

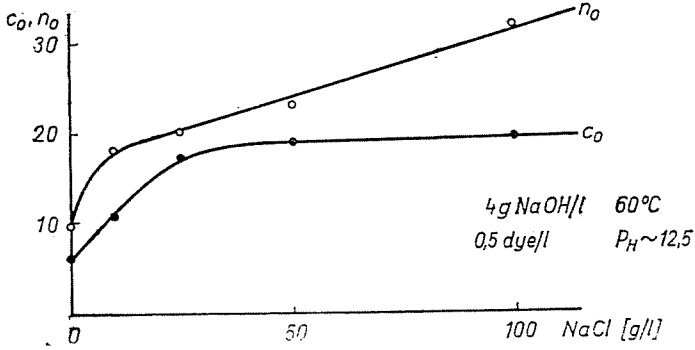


Fig. 6

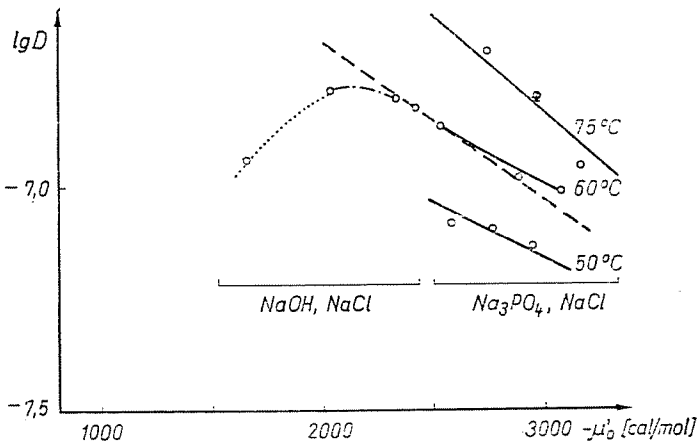


Fig. 7

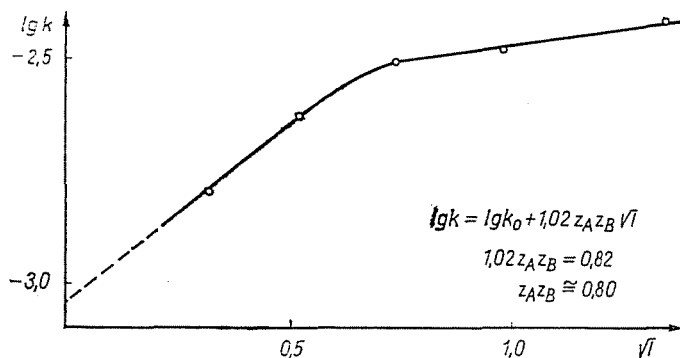


Fig. 8

Table 1
Kinetical parameters of the reactive dyeing reaction

Exp. No.	Temperature °C	Dye concentration g/l	Salt and basis concentration	pH	$k \cdot 10^{-3}$ $\text{min}^{-1} (\text{g/l})^{-1}$	c_0 g/l	n_0 g/l	$D \cdot 10^{-8}$ $\text{cm}^2 \cdot \text{min}^{-1}$	$\Delta \mu_0$
1	50	0.25	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	0.56	25.0	13.9	7.6	-2950
2	50	0.50	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	0.56	37.6	13.6	8.0	-2760
3	50	1.0	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	0.56	55.4	14.0	8.3	-2580
4	60	0.25	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	1.3	26.8	18.6	9.8	-3080
5	60	0.50	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	1.3	39.1	13.6	10.5	-2880
6	60	1.00	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	1.3	46.0	15.3	13.7	-2530
7	75	0.25	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	2.0	25.0	22.6	11.0	-3180
8	75	0.50	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	2.0	37.5	27.1	16.0	-2980
9	75	0.75	10 g/l Na_3PO_4 + 50 g/l NaCl	11.4	2.0	40.0	23.3	20.5	-2750
10	60	0.50	4 g/l NaOH + 0 g/l NaCl	12.7	1.60	6.22	9.5	10.4	-1665
11	60	0.50	4 g/l NaOH + 10 g/l NaCl	12.6	2.35	10.65	17.7	16.2	-2020
12	60	0.50	4 g/l NaOH + 25 g/l NaCl	12.5	3.16	17.75	19.8	15.9	-2360
13	60	0.50	4 g/l NaOH + 50 g/l NaCl	12.45	3.36	18.65	23.4	15.7	-2390
14	60	0.50	4 g/l NaOH + 100 g/l NaCl	12.4	3.90	19.55	32.7	15.0	-2420

It should be noted that these are only apparent affinity values, because they were determined from the active dye content measured during the chemical reaction, so that no true equilibrium can be assumed between the external and the internal volumes, and at most an equilibrium approaching the steady state can be spoken of.

According to Fig. 5, with increasing c_e external concentration c_0 approaches a limit value. With increasing temperature, c_0 does not change unequivocally. At low external concentrations, the change in temperature has practically no effect on c_0 , at higher external concentration, however, c_0 decreases with increasing temperature. This phenomenon is indicative of the fact that several kinds of adsorption processes, maybe physical and chemical adsorptions take place simultaneously in the internal volume of cellophane. At low concentrations, chemical adsorption can still compensate the change with temperature of physical adsorption, which is of apposite direction to that of chemical adsorption. Therefore, in this region, c_0 is practically independent of temperature. However, at higher external concentrations, owing to its topochemical character, chemisorption attains a saturation state, so that physical adsorption predominates. Therefore, at higher external concentrations the change with temperature of physical adsorption prevails, and c_0 decreases with increasing temperature.

Measurements for investigating the effect of the electrolyte (NaCl) show c_0 and the apparent affinity value to increase unequivocally with increasing salt concentration, to approach a limit value (Fig. 6). This phenomenon is known already in connection with substantive dyes, its theory has been cleared, so that its reasons will not be discussed here in detail.

More interesting results were obtained in investigating the effect of the change in pH on the internal concentration. Since Na_3PO_4 would have interfered strongly in the investigation of the effect of electrolyte concentration, NaOH has been used for the adjustment of pH in investigating the effect of NaCl concentration. Therefore, the pH of these solutions (Table 1, experiments 10 to 14) is approximately by one pH higher (about 12.5), than that of the solutions of the preceding series (experiments 1 to 9, pH about 11.5). Data of experiments 5 and 13 clearly show the increase in the alkalinity of the solutions to bring about the decrease of the internal concentration c_0 . Again, the corresponding curves of Figs 5 and 6 show the range of the c_0 values to decrease with increasing alkalinity, while at the same time the range of concentration n_0 of the active sites is increasing. If the electrolytically dissociated hydroxyl ions of cellulose are considered as active (see next subchapter), the decrease in c_0 value can be explained by the fact that with increasing pH the number of the dissociated cellulose- O^- ions, and consequently the negative charge of the cellulose phase increases, so that the adsorption of the dye decreases.

3.2 Reactive sites of cellulose

In our kinetic equations, the number of the active sites of cellulose was denoted by n_0 , however, no stipulation was made concerning its chemical properties. From data in Table 1 the n_0 values clearly increase with increasing pH and temperature, indicating that n_0 can be identified as the cell-O⁻ ions, formed by the electrolytic dissociation of the hydroxy groups of cellulose. However, the value of n_0 increases also with increasing electrolyte concentration (Fig. 6, experiments 10 to 14). This finding cannot be ascribed anymore to the dissociation of the active hydroxy groups of cellulose, because an increase in Na⁺ ion concentration would further the formation of cellulose-Na and would result therefore in just the opposite effect, i.e. the decrease of the n_0 values. It seems more probable that the increase in electrolyte concentration increases the availability by the change in charge produced in the electric double layer, so that more active hydroxy groups become free at the internal surface of cellulose.

An approximate idea of the proportion of internal surface of cellulose occupied by the chemically bound dye can be obtained by calculating what a surface would be occupied by the dye, if all the n_0 active sites would enter into reaction. At the same time, this calculation is informative on how far the numerical values obtained for n_0 can be considered as realistic, since the surface calculated from these values cannot be greater than the total internal surface of cellulose. As an approximate value of the latter, a surface of $30 \cdot 10^4$ cm²/g was accepted on the basis of data in the literature [14]. Calculations with the lowest and highest n_0 values in Table 1 (experiments 10 to 14), yielded surfaces of $4 \cdot 10^4$ and $16 \cdot 10^4$ cm²/g, so that the dye bound chemically would not occupy more than 50% of the total surface, even if the reaction was complete. (It should be noted that the surface of $30 \cdot 10^4$ cm²/g, taken the basis of comparison, has not been measured in alkaline medium, and actually a greater surface than this is to be expected.) In our calculations, the space required by one dye molecule was obtained from the relationship $1.091 (M/N\rho)^{2/3}$, where M is the molecular weight of the dye, N is Avogadro's number and ρ is the density.

3.3 Diffusion coefficient

The relationship between the diffusion coefficient and the activity is shown in Fig. 7. With increasing affinity, the value of the diffusion coefficient increases in the beginning, and after a maximum it gradually decreases. The diffusion coefficients, determined by NEALE and STRINGFELLOW [15] for substantive dyes, changed according to a similar maximum curve when the electrolyte concentration was changed. Since also the maximum exhibited in Fig. 7 is within the range of the change of electrolyte concentration, it is evident that

the change of the diffusion constant is a resultant of two opposite effects, i.e. the change of the electric surface charge and that of the affinity. For describing these two effects, CRANK [16] suggested relationship (5):

$$D = D_0 e^{-\frac{\psi EZ}{RT}} \cdot \frac{c_v}{c_0} \quad (5)$$

where D_0 and D are diffusion coefficients measured in the pure solvent, and in the electrolyte, resp., ψ is the surface potential, z the valency of the ion, ε the unit of the electric charge, c_v the external and c_0 the internal dye concentration. Expressing the quotient c_v/c_0 by the affinity, and writing the relationship in logarithmic form:

$$\lg D = \lg D_0 = \frac{\psi \varepsilon z}{2,3 kT} + \frac{\Delta\mu'_0}{2,3 RT} \quad (6)$$

The second term on the right side of Eq. (6) describes the effect of the electrolyte, the third term the effect of the affinity. With increasing salt concentration, the ψ value of the electric charge initially decreases faster than the affinity increases ($\Delta\mu'_0$ is negative), and therefore the diffusion coefficient increases initially with the affinity. With a further increase in salt concentration, the electric charge approaches a limit value, while the affinity continues to increase, so that the diffusion coefficient begins slowly to decrease. Thus, in conformity with the equation of CRANK, the diffusion coefficient must actually change along a maximum curve with the increase of affinity. The slope of the nearly linear section of the curve, calculated from Crank's equation, is $1/2,3 RT = 0.65 \cdot 10^{-3}$. The dotted straight line in Fig. 7 indicates the value of the slope, and support at the same time the validity of the relationship. A deeper investigation is prevented by the inherent error of the diffusion constant determination.

3.4 Rate constants

In the calculation of the rate constants, the reaction between cellulose and the reactive dye has been considered as a kinetically second-order process, which proceeds between the cell-O⁻ ions and the dye molecule in the internal volume of cellulose, at a rate of kc_0n_0 . In connection with the investigation of the internal concentration values, it has been mentioned that in the internal volume the dye molecules can be bound by various (physical and chemical) adsorptive forces to the surface of cellulose. Therefore, it is justified to assume that the reactivity of the dye molecules in different adsorption states is also different. Therefore, c_0 alone is not an adequate quantity for characterizing the reaction rate. This is actually manifest from the fact that the temperature

dependence of the k values in Table 1 does not follow the Arrhenius equation. The activation energy values calculated from k values measured at 50 to 60°C and 50 to 75°C (17 000 and 12 200 cal/mole, respectively) unambiguously show the activation energy to decrease with increasing temperature. Starting from the plausible assumption that the reactive dye reacts predominantly in chemisorbed state with the cellulose molecule, the exact form of the rate equation has to be written for the c_A concentration of the chemisorbed dye molecules. Be k' the true rate constant, then it is related with the (measured) rate constant k as:

$$k' c_A n_0 = k c_0 n_0 \quad (7)$$

The equilibrium constant of chemisorption is:

$$K = A \cdot \exp \cdot (-Q/RT) = \frac{c_A}{c_0 - c_A} \quad (8)$$

and

$$c_A = \frac{c_0}{1 + K}$$

and thus, from Eq. (7), under consideration of the temperature dependence, $k' = A' \exp \cdot (-E/RT)$:

$$k = \frac{k'}{1 + K} = \frac{A \cdot \exp \cdot (-E/RT)}{1 + A' \exp \cdot (-Q/RT)} \quad (9)$$

The change with temperature of the (measured) rate constant k is seen not to follow Arrhenius' equation; k does not change proportional to, but at a gradually decreasing rate with $\exp(-E/RT)$.

The assumption of chemisorption as intermediate step is supported also by the values of the activation energies calculated from the Arrhenius equation, which are considerably lower than expected, as follows directly from the above deduction.

The increase in electrolyte concentration (Table 1, experiments 10 to 14) brings about a decisive but diminishing increase of the rate constants. As concerns the electrolyte effect, mainly the primary electrolyte effect can come into consideration. The energy barrier of the surface charge of cellulose cannot play here a role, it representing a hindrance only for the adsorption, for the development of the c_0 values. The presence of the electrolyte can change the reaction rate of the adsorbed (chemisorbed) dye molecule primarily by its action on the activity of the dye molecule. According to Debye—Hückel's theory, the rate constant of ionic reactions

$$\lg k = \lg k_0 + 1,02 z_A z_B \sqrt{I} \quad (10)$$

changes in very dilute solutions proportional to the square root of the ionic strength I (where k is the rate constant measured in ion-free solutions, z_A, z_B are the values true-to-sign of the ion charge numbers of the reactants).

The k values in Table 1 (experiments 10 to 14) are plotted according to the Debye—Hückel equation in Fig. 8. The linearity of the initial section supports the validity of the equation. In this section, the close to $+1$ value of the slope indicates the reaction of two monovalent ions of identical, evidently negative charge. Actually, in completely dissociated state, the dye molecule carries three negative charges ($-\text{SO}_3^-$), however, the large size of the molecule, its strong deviation from spheric-symmetrical and the too high concentration of the solutions used for the measurement do not permit to conclude from the value of the $z_A z_B$ slope on the valency of the ions.

As is well known, the reaction of dyes of monochlorotriazine type is furthered by the alkalinity of the medium. The comparison of the k constants of experiments 5 and 13 in Table 1 shows the catalyzing action of the OH^- ions to be considerable in the pH range of about 11.5—12.5; a unit increase in the pH value increases the rate to about 2.5-fold.

Summary

The kinetics of the reaction between cellulose and reactive dye has been studied on cellophane sheet. An approximative method has been developed for the calculation of the kinetics of the heterogeneous process, which permits to establish the diffusion coefficient, the rate constant of the chemical reaction and the concentration relationships in the internal volume of cellulose. From results, physical, chemical and electrochemical factors controlling the reaction between cellulose and reactive dye can be concluded on. The diffusive transport process is influenced by the negative surface charge of cellulose and by the adsorption (affinity) of the dye. Both factors much depend on the electrolyte concentration. The reaction of the dye and cellulose is kinetically of second order, a process between two negative ions, the rate constant of which depends on the ionic strength. The experimental method did not permit to clear, whether the reaction proceeds through dye molecules dissolved in the internal volume or through adsorbed dye molecules. The low value of the activation energies calculated, as well as the anomalies encountered in applying Arrhenius' equation support the chemical activity of the adsorbed dye. Active sites (surface occupied by dye equivalent to the cell- O^- ions) calculated from experimental data are within the limits of the values known from the literature and accepted for cellulose surface. The number of active sites changes with electrolyte concentration, indicative of the fact that the availability of cellulose is a function of the electric surface charge.

Appendix

The change in concentration in the elementary cell of the dye molecule diffusing into the cellophane sheet and entering with it into a chemical reaction, is described by the relationship

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{\partial s}{\partial t} \quad (1)$$

where c and s are the concentration of the reactive dye and of the dye bound chemically on cellulose, resp., x is the locus co-ordinate and t is the time. The quantity N of the dye diffused into the film (not chemically bound) and the quantity S of the chemically bound dye are determined by the integral of c and s with respect to x :

$$N = \int_0^{\infty} c dx \quad \text{and} \quad S = \int_0^{\infty} s dx$$

In an analogous way, the integral of Eq. (1) with respect to x gives the differential equation of the change of N with time:

$$\frac{dN}{dt} = -D \frac{\partial c}{\partial x} - \frac{\partial S}{\partial t}. \quad (2)$$

The solution of Eq. (2) for reactions of first order is known from the works of DANCKWERTS [12]. For second-order reactions ($\partial s/\partial t = ken$) the equation cannot be integrated, no exact solution in closed form is known. Therefore, elaboration of an appropriate approximative solution became necessary.

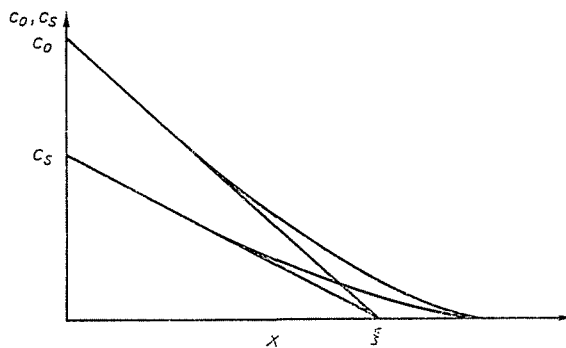


Fig. 9

Our approximate solution is based on assuming the distribution of concentrations c and s in the sheet to be linear. This linear distribution is shown by the straight lines in Fig. 9, originating from points c_0 and s_0 (interfacial concentration values of the free and the chemically bound dye), and meeting at the axis in the common intersection. The straight line starting from point c_0 is the tangent of the curve of actual concentration distribution c at $x = 0$. If concentration distributions were actually linear, the quantities N and S would be equal to the area of the triangles below the straight lines. However, the true values of N and S are given by the areas below the curves c and s . Therefore, the area of the triangles can only be used after introducing correction factors for the calculation of N and S . Expressing the functional relationship between the areas below the curves and the straight lines, and as to their properties, they can be either constant or depend on N , S or t . After introducing the corresponding correction factors α and β , the values of N and S , expressed from the triangles areas are:

$$N = \alpha \frac{c_0 \xi}{2} \quad (3)$$

$$S = \beta \frac{c_0 \xi}{2} \quad (4)$$

and the S to N ratio:

$$\frac{S}{N} = \frac{\beta}{\alpha} \frac{s_0}{c_0} = \gamma \frac{s_0}{c_0} \quad (5)$$

Since the straight line originating from point c_0 is the tangent to curve c , at $x = 0$, the partial derivative in the second equation $(\partial c/\partial x)_{x=0}$ can be substituted by the quotient c_0/ξ . This substitution, further the substitution of S from Eq. (5) and of ξ from Eq. (3) gives:

$$\frac{dN}{dt} = D \frac{c_0}{\xi} - \frac{dS}{dt} = D\alpha \frac{c_0^2}{2N} - \gamma \frac{d(Ns_0/c_0)}{dt} \quad (6)$$

The integration of the equation (considering α and γ to be constant) gives the general integral equation:

$$N = \sqrt{D\alpha} \frac{\sqrt{\int c_0^2(1 + \gamma s_0/c_0) dt}}{1 + \gamma s_0/c_0} \quad (7)$$

In integrating Eq. (7), only the concentration value taken at $x=0$ has to be substituted. In the case of chemical reaction, the differential equation corresponding to the equation of the reaction is also written for point $x=0$ alone, and the function $s_0 = F(t)$ is calculated by its integration, to be substituted into Eq. (7).

Eq. (7) has been checked on a few examples, the exact solutions of which are known from the literature. Thus, e.g. when diffusion is not associated with chemical reaction ($s_0 = 0$), and c_0 is constant, the solution obtained by integrating Eq. (7) is:

$$N = c_0 \sqrt{D\alpha_1 t} \quad (\text{the exact solution})$$

$$N = 2 c_0 \sqrt{Dt/\pi}$$

For $c_0 = kt$:

$$N = kt \sqrt{D\alpha_2 t/3} \quad (\text{the exact solution})$$

$$N = \frac{4}{3} kt \sqrt{Dt/\pi}$$

For $c_0 = kt^{1/2}$:

$$N = k \sqrt{D\alpha_3/2t} \quad (\text{the exact solution})$$

$$N = k \sqrt{D\pi/4t}$$

The function of the approximate solutions is seen to be of the same form as the exact solution. The value of the correlation factors varies, however, from case to case: $\alpha_1 = 1.272$; $\alpha_2 = 1.692$; $\alpha_3 = 1.572$. The deviations can be reduced, if contrary to the original interpretation, α is considered as the correction factor of time, and the corrected time $\tau = \alpha^2 t$ is used in the calculations. Thus: $\alpha'_1 = \alpha_1$ and $\alpha'_1 = 1.272$; $\alpha'_2 = \alpha_2^{1/3}$ and $\alpha'_2 = 1.192$; $\alpha'_3 = \alpha_3^{1/2} = 1.255$.

If the chemical reaction concomitant to diffusion is of first order:

$$\frac{ds_0}{dt} = kc_0, \text{ and } c_0 \text{ is constant,}$$

integration yields:

$$s_0 = kc_0 t.$$

Substituting s_0 into Eq. (7) and considering c_0 and k as constant, the integration gives

$$N = c_0 \sqrt{D\alpha/2\gamma k} \sqrt{1 - \frac{1}{(1 + \gamma kt)^2}} \quad (8)$$

and from (5)

$$S = \gamma N kt. \quad (9)$$

According to the exact solution:

$$N = c_0 \sqrt{D/k} \operatorname{erf} \sqrt{kt} \quad (10)$$

For $t \rightarrow \infty$, the N values of both solutions (9 and 10) tend to the limit value N_∞ , and diffusion becomes stationary. It follows from the comparison of the limit values of the approximative solution $N_\infty = c_0 \sqrt{D\alpha/2\gamma k}$ and of the exact solution $N_\infty = c_0 \sqrt{D/k}$ that $\alpha/2\gamma = 1$. Thus, this correction factor is of unit value in Eq. (8). When γ is constant, the s/N ratio must change linearly with time in the sense of Eq. (9). However, S/N values calculated from the exact solution have an other than linear course (Fig. 1), therefore γ can only be considered approximatively constant. Our calculations showed in the values $\gamma = 0.722$, and $\gamma = 0.770$ to give a fair approximation in the ranges $kt = 0 \dots 1$ and $kt = 1 \dots 2$, respectively.

The analysis of the S/N values calculated from our experimental results showed the dependence of S/N on time not to be linear, but to increase ever slower with time (Fig. 1). Thus, the reaction is not of first order. This deviation can be traced back to the consumption of the active hydroxy groups or to the hydrolysis of the dye. In the latter case, the c_a concentration of the active dye decreases continuously, due to hydrolysis. Be c_0 the initial concentration at the interface, then

$$c_a = c_0 e^{-ht}$$

where h is the rate constant of hydrolysis. Considering the reaction between dye and cellulose as a second-order process:

$$\frac{ds_0}{dt} = kc_a(n_0 - s_0) = kc_0 e^{-ht}(n_0 - s_0),$$

where n_0 is the initial concentration of the active hydroxy groups at the interface, and k is the rate constant of the chemical reaction.

The integration of the equation gives:

$$s_0 = n_0 [1 - \exp.k(c_0/h) (e^{-ht} - 1)]. \quad (11)$$

Substituting the value of s_0 in the general integration equation (7), another integration would be needed bound to serious difficulties owing to the twice exponential factor of the equation. Since the k value determined experimentally is low enough (0.003 min^{-1}), the approximation $\exp.(-kt) - 1 \sim -kt$ can be used in the measuring range. Thereby k is eliminated, and

$$s_0 = n_0 [1 - \exp(-kc_0 t)]. \quad (12)$$

Substituting this equation into Eq. (7) facilitates integration:

$$N = c_0 \sqrt{D/kn_0} \frac{\sqrt{2\gamma kn_0(1 + \gamma R)t - 2\gamma^2 R^2 [1 - \exp(-kc_0 t)]}}{1 + R(1 - \exp.(-kc_0 t))}. \quad (13)$$

Similarly as in the solutions related to the first-order reaction, the value of the factor $\alpha/2\gamma$ has been taken as unit:

$$R = n_0/c_0.$$

Further, from Eqs (11) and (5):

$$\frac{S}{N} = \gamma R [1 - \exp.(-kc_0 t)]. \quad (14)$$

Apparently, according to Eq. (14), the S/N value actually does not change linearly with time in the case of second-order chemical reaction.

In our numerical calculations, the kc_0 value has been obtained from the S/N value-pairs using Eq. (14), while the γR values have been calculated from the kc_0 values, and plotting graphically the S/N and the $[1 - \exp.(-kc_0 t)]$ values. Hence all the constant groups of Eq. (13), except factor $c_0 \sqrt{D/kn_0}$, were known. The $c_0 \sqrt{D/kn_0}$ value has been determined from the $M = N + S$ quantities measured at various times, and from the quantity S of the dye chemically bound, using the relationships deduced from Eqs (13) and (14):

$$M = N + S = c_0 \sqrt{D/kn_0} \sqrt{2\gamma kn_0(1 + \gamma R)t - 2\gamma^2 R^2 [1 - \exp.(-kc_0 t)]} = c_0 \sqrt{D/kn_0} \varphi(t)_M \quad (15)$$

and

$$S = c_0 \sqrt{D/kn_0} \varphi(t)_M \frac{\gamma R [1 - \exp.(-kc_0 t)]}{1 + \gamma R [1 - \exp.(-kc_0 t)]}$$

$$s = c_0 \sqrt{Dk/n_0} \cdot \psi(t)_S. \quad (16)$$

Plotting the S and M values vs. $\varphi(t)_M$ and $\psi(t)_S$, respectively, the measuring points lie along a straight line of slope $c_0 \sqrt{Dk/n_0}$. From the constant groups γR , kc_0 and $c_0 \sqrt{Dk/n_0}$, the values of D , k , c_0 and s_0 can be calculated, if the value of one of them is known. c_0 was found to be the easiest to determine. Since at times after break-through the N value tends to a limit estimable by plotting, the value of c_0 can be calculated from Eq. (3). Indeed, in this case ξ can be replaced by the thickness l of the cellophane sheet, so that $c_0 = 2\alpha N/l$. According to our calculations, the values of α and γ are given by the relationship $\alpha/2\gamma = 1$: $\alpha = 1.444$ and $\gamma = 0.722$ (using the γ value calculated for first order reaction).

Summary

The kinetics of reactive dyeing of cellophane sheet have been investigated on the basis of a new mathematical approximation method. This method allows the evaluation of the kinetic characteristics (diffusion coefficients, bimolecular rate constant, concentration of non reacted dye in the surface layer and concentration of the active sites in the cellophane sheet of the dyeing process. The results obtained suggest a bimolecular mechanism for the reaction between the reactive dye and the cellulose hydroxyl groups. From the kinetic parameters conclusions can be drawn concerning the influence of pH, electrolyte concentration, dye concentration and temperature on the various reaction steps.

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