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**COMPUTER SIMULATION OF BATH DYEING  
OF FIBROUS MATERIALS**

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*A mathematical model has been formulated for the dyeing process of a fibrous substrate in aqueous dyeing bath of finite ratio. The model has been constructed for the isothermal process kinetically controlled by the diffusion of dyestuff into the mass of fibre polymer for the case of nonlinear partition function of the dyestuff between the phases of fibre and bath. The numerical simulation by the Schmidt method of finite differences has been used to find the functions of concentration fields of dyestuff in cylindrical space of fibre and the transfer function of kinetic integral amount of dyestuff to fibre. The model has been formulated on the basis of dimensionless criteria of the theory of similarity. On the basis of the model suggested, the dimensionless criterial parameters have been found for the dyeing system which crucially affect the rate of dyestuff transfer from bath to fibre, the development of concentration field of dyestuff in fibre, and the degree of utilization of dyestuff in dyeing processes. The results found can be applied in selecting and developing the dyestuffs for optimized and high-speed processes for the dyestuffs of disperse and reactive technological classes.*

## Introduction

The bath dyeing process is formed by a complex of simultaneous processes which are cogently summarized elsewhere<sup>1-3</sup>.

The basic processes involve:

- the transport of dyestuff through the continuous liquid of dyeing bath to the substrate surface; it is usually kinetically determined by the convection due to stirring of dyeing bath,
- the transfer through the phase interface between the liquid of dyeing bath and the fibre polymer; usually considered is the kinetic effect of transport resistance through the laminar boundary layer of the liquid by-passing the fibre,
- the transport of dyestuff in the polymer mass; these are usually diffusion processes whose driving force is given by the concentration gradient, the gradient of chemical or electrochemical potential; in more complex cases of dyestuff-polymer interactions the diffusion behaviour is manifested formally by nonconstant diffusion coefficient which usually depends on the dyestuff concentration, which was interpreted by various models of diffusion behaviour in polymers (porous "matrix" models<sup>4-6</sup> or free-volume diffusion models<sup>3,7-9</sup>).

A detailed mathematical description of the simultaneous processes is complex and results in a formulation of a system with high-capacity transfer characteristic considering several kinetically significant partial processes, the so-called discontinuous system<sup>1-3</sup>.

This model of dyeing system is considered by Navrátil<sup>1</sup>, who formulated a relatively complex solution taking into account the kinetic effect of the processes preceding the dyestuff-in-fibre diffusion transport itself.

The problem is substantially simplified by the presumption that the slowest and hence rate-limiting process is the diffusion of dyestuff in fibre. This simplifying presumption is more or less justified. The kinetic effect of transport of dyestuff through the liquid of dyeing bath is excluded if there is sufficient stirring of the bath. Also the effect of transport resistance at the phase interface of fibre and liquid of dyeing bath, which is usually interpreted by the necessity of diffusion of dyestuff through the laminary boundary layer of liquid in close neighbourhood of the fibre surface, has not yet been satisfactorily experimentally proved. Particularly in the case of diffusion of dyestuffs into fibres with compact structure (e.g. PES fibres) the diffusion coefficients of dyestuffs in the liquid of dyeing bath are several orders of magnitude higher than those in the fibre polymer<sup>4</sup>, which excludes the kinetic effect of diffusion through the laminary boundary layer.

The facts given make it possible to formulate a simpler kinetic case of transport problem - the so-called continuous system<sup>2,3</sup>. Here the process of dyeing of cylindrical fibre is kinetically controlled by the diffusion of dyestuff in fibre mass. The processes preceding this diffusion are faster by orders of magnitude and can establish equilibrium states. The result is a mathematical function of partition equilibrium of dyestuff between the phases of bath and

fibre which defines the limiting conditions of the diffusion problem.

For the cases of isothermal dyeing of usual fibrous materials with various application classes of organic dyestuffs the function of equilibrium partition of dyestuff between the PES substrate and liquid of dyeing bath (the sorption isotherm) most frequently has a concave curved course<sup>3,8</sup> (Fig. 1). The function deviates from the linear Nernst partition coefficient (1) which can be interpreted as the limit for infinite dilution of dyeing bath:

$$K = \lim_{c_L \rightarrow 0} \left[ \frac{dc_R}{dc_L} \right] \quad (1)$$

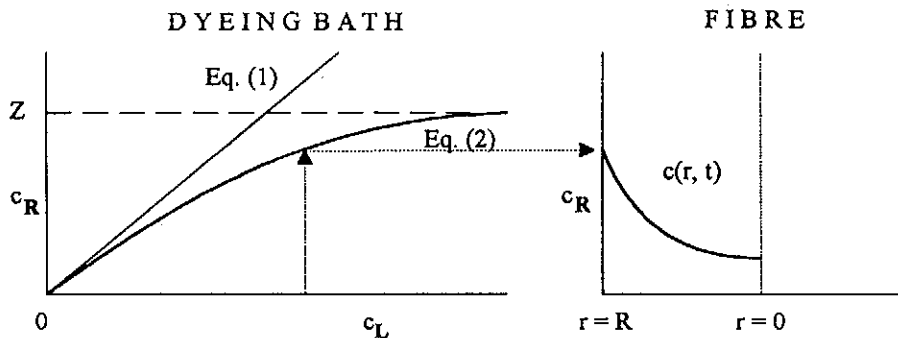


Fig. 1 The principle of dyeing system

The partition function has the limit in the maximum  $Z$  for the bath concentration  $c_L \rightarrow \infty$  and it represents the "ceiling" of concentration saturation of fibre with dyestuff. The partition function course mentioned is interpreted theoretically on the basis of e.g. the gradient models (gradient potential, activity gradient) and several other models of sorption behaviour in polymers<sup>10-12</sup>.

Most often the partition equilibrium is formulated by the Langmuir function (2) (Fig. 1) which follows from the gradient models of sorption behaviour and satisfactorily reflects the reality in the majority of practical cases:

$$c_R = \frac{K c_L}{1 + \frac{K}{Z} c_L} \quad \text{where } Z = \lim_{c_L \rightarrow \infty} c_R \quad (2)$$

## Experimental

### *Mathematical Description of Dyeing System*

The dyeing system is formed by:

- the fibrous substrate of the mass  $Hs$  [kg],
- the liquid of dyeing bath of the mass  $Hl$  [kg]
- the dyestuff charged with the mass of  $Hd$  [kg].

The substrate has the form of cylindrical fibre of the radius  $R$ . The transport of dyestuff in fibre is realized by radial diffusion at the diffusion coefficient  $D$  in real time  $t$ . In a more general case, the diffusion coefficient can be a function of concentration,  $D(c)$ , or it can depend on other variables.

Before the diffusion starts, the fibre contains no dyestuff. The driving force of diffusion is the concentration gradient whose source is the surface concentration on the fibre,  $c_R$ , which forms the limit conditions of the diffusion problem. The surface concentration is determined by the functional relation of the partition equilibrium of dyestuff between the phases of bath and substrate. For the case of the Langmuir type of partition function,  $c_R$  depends on the dyestuff concentration in the bath  $c_L$ , according to Eq. (2) (Fig. 1).

In the course of diffusion the dyestuff forms a time-dependent concentration field  $c(r,t)$  in the fibre cylinder. The problem can be effectively solved by introducing the dimensionless variables according to the theory of similarity:

$$\text{- dimensionless radius in fibre cylinder: } \rho = \frac{r}{R} \quad (3)$$

$$\text{- dimensionless time - Fourier number: } Fo = \frac{Dt}{R^2} \quad (4)$$

$$\text{- dimensionless concentration in cylinder: } v(\rho, Fo) = \frac{c(r,t)}{Z} \quad (5)$$

$$\text{- mass ratio of dyeing bath ("bath ratio"): } L = \frac{Hl}{Hs} \quad (6)$$

In the course of dyeing process there gradually proceeds a transfer of dyestuff from bath into the mass of fibre. In the general case of dimensionless time  $Fo$ , a part of dyestuff of the mass  $Q(Fo)$  will be in the fibre and the rest of dyestuff of the mass  $Hd - Q(Fo)$  will be in the bath.

Let the amount of dyestuff in the fibrous substrate as a function of  $Fo$  be referred to the mass of the substrate treated and expressed by the fraction:

$$p(Fo) = \frac{Q(Fo)}{Hs} \quad p(Fo=0) = p_0 = \frac{Hd}{Hs} \quad (7)$$

In the colouristic practice it is usual to express the amount of dyestuff in the dyeing system by the dyeing percentage  $S\%$ :

$$S\% = \frac{H_D}{H_S} 100 \quad (8)$$

Hence it is:

$$p_0 = \frac{S\%}{100} \quad (9)$$

Let the concentration of dyestuff in bath be also expressed by the dimensionless mass fraction:

$$c_L(F_0=0) = \frac{H_D}{H_L} = \frac{p_0 H_S}{L H_S} = \frac{p_0}{L} \quad (10)$$

- in the course of dyeing in a general point of dimensionless time  $F_0$ :

$$c_L(F_0) = \frac{H_D - Q(F_0)}{H_L} = \frac{1}{L} [p_0 - p(F_0)] \quad (11)$$

The concentration changes of dyestuff in bath  $c_L$  make themselves felt in the values of the surface concentration  $c_R$  according to the function of partition equilibrium of dyestuff between the two phases.

For the case of the Langmuir type of partition equilibrium given by the function (2) and with the application of the relations (10, 11) it is:  
Let us introduce further dimensionless variables:

$$v_R = \frac{c_R}{Z} = \frac{\frac{K}{Z} c_L}{1 + \frac{K}{Z} c_L} = \frac{\frac{K}{L} \left[ \frac{p_0}{Z} - \frac{p(F_0)}{Z} \right]}{1 + \frac{K}{L} \left[ \frac{p_0}{Z} - \frac{p(F_0)}{Z} \right]} \quad (12)$$

$$\text{- Relative amount of dyestuff in substrate} \quad X(F_0) = \frac{p(F_0)}{Z} \quad (13)$$

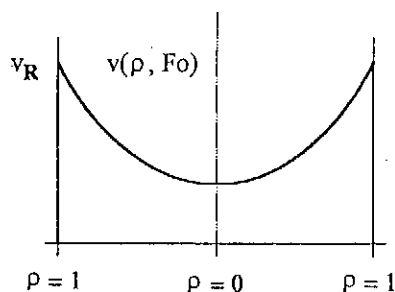
$$\text{theoretical maximum} \quad X_0 = \frac{p_0}{Z} \quad (14)$$

$$\text{- Partition parameter} \quad A = \frac{K}{L} \quad (15)$$

For the driving force of diffusion - the relative surface concentration  $v_R$  - we have:

$$v_R(F_0) = \frac{A[X_0 - X(F_0)]}{1 + A[X_0 - X(F_0)]} \quad (16)$$

The quantity  $X(F_0)$  represents the amount of dyestuff in the substrate expressed relatively. It is determined by the integration as the volume under the curve of dimensionless concentration field  $v(\rho, F_0)$  in the cross section of cylindrical fibre (Fig. 2):



Kubatur - volume  
(under curve of conc. field):

$$X(Fo) = \frac{1}{\pi} \int_{\rho=0}^{\rho=1} 2\pi \rho v(\rho, Fo) d\rho \quad (17)$$

Fig. 2 Determination of amount of dyestuff in fibre by integration of concentration field

The relative amount of dyestuff transported from bath into fibre by the dimensionless time  $Fo$  represents the percentage of exhaustion of dyeing bath:

$$\% Ex = \frac{X(Fo)}{X_0} 100 \quad (18)$$

### Formulation of Diffusion Problem

The 2<sup>nd</sup> Fick law for diffusion into an infinite cylinder (fibre) reads as follows:

$$\frac{\partial c}{\partial t} = \frac{1}{r} \left[ \frac{\partial}{\partial r} \left( rD \frac{\partial c}{\partial r} \right) \right] \quad (19)$$

In a more general case, the diffusion coefficient  $D$  is a function of concentration. The transformation of relation (19) into the dimensionless quantities (3) to (6) /and for the case of the concentration dependence of diffusion coefficient in the general form (20)/ will give Eq. (21).

$$D(v) = D_0 \Phi(v) \quad (20)$$

$$\frac{\partial v}{\partial Fo} = \Phi(v) \left[ \frac{1}{\rho} \frac{\partial v}{\partial \rho} + \frac{\partial^2 v}{\partial \rho^2} \right] + \frac{\partial \Phi(v)}{\partial v} \left[ \frac{\partial v}{\partial \rho} \right]^2 \quad (21)$$

For the case of isothermal dyeing of a fibrous substrate which at the beginning of the process did not contain any dyestuff, the limit conditions of the diffusion problem can be formulated as follows:

$$Fo < 0 \quad v(\rho) = 0 \quad (22a)$$

$$Fo = 0 \quad v(\rho=1) = \frac{AX_0}{1+AX_0} \quad v(0 \leq \rho < 1) = 0 \quad (22b)$$

$$Fo > 0 \quad v(\rho=1, Fo) = v_R(Fo) = \frac{A[X_0 - X(Fo)]}{1 + A[X_0 - X(Fo)]} \quad (22c)$$

$X(Fo)$  being given by Eq. (13). Moreover it is:

$$\left[ \frac{\partial v}{\partial \rho} \right]_{\rho=0, Fo} = 0 \quad (23)$$

### The Solution by Numerical Simulation

The solution was carried out by the Schmidt difference method. A difference analogue has been constructed for the differential equation (21). The cylindrical volume was divided along the coordinate of dimensionless radius into  $M$  discrete equal intervals  $\Delta \rho$ . The dimensionless time  $Fo$  was divided into  $N$  identical differences  $\Delta Fo$ . Hence, in any general point of space and time  $(i, j)$  it is:

$$\rho_{i,j} = i\Delta\rho = \frac{i}{M} \quad \Delta\rho = \frac{1}{M} \quad (24)$$

$$\left[ \frac{\partial v}{\partial \rho} \right]_{i,j} = \frac{v_{i+1,j} - v_{i-1,j}}{2\Delta\rho} = \frac{M}{2}(v_{i+1,j} - v_{i-1,j}) \quad (25)$$

$$\left[ \frac{\partial^2 v}{\partial \rho^2} \right]_{i,j} = \frac{v_{i+1,j} + v_{i-1,j} - 2v_{i,j}}{\Delta\rho^2} = M^2(v_{i+1,j} + v_{i-1,j} - 2v_{i,j}) \quad (26)$$

$$\left[ \frac{\partial v}{\partial Fo} \right]_{i,j} = \frac{v_{i,j+1} - v_{i,j}}{\Delta Fo} \quad \text{where} \quad \Delta Fo = \frac{Fo}{N} \quad (27)$$

Introduction of the difference relations (24) - (27) into Eq. (21) gives:

$$v_{i,j+1} = v_{i,j} + M^2 \left\{ \Phi(v_{i,j}) \left[ \left(1 + \frac{1}{2i}\right) v_{i+1,j} + \left(1 - \frac{1}{2i}\right) v_{i-1,j} - 2v_{i,j} \right] + \left[ \frac{\partial \Phi(v)}{\partial v} \right]_{i,j} \left[ \frac{v_{i+1,j} - v_{i-1,j}}{2} \right]^2 \right\} \Delta Fo \quad (28)$$

The relation (28) will simplify for the case of ideal Fick diffusion ( $D = \text{const.}$ ) because

$$\Phi(v_{i,j}) = 1 \quad \left[ \frac{\partial \Phi(v)}{\partial v} \right]_{i,j} = 0 \quad (29)$$

In a more general case the diffusion coefficient is a function of concentration. In accordance with the published data following from the models of diffusion behaviour in polymers<sup>4-9</sup>, the following functions of concentration dependence were formulated:

- a linear one in the form:

$$\Phi(v) = 1 + kv \quad k = \text{const.} \quad (30)$$

therefrom it follows:

$$\left[ \frac{\partial \Phi(v)}{\partial v} \right] = k \quad (31)$$

- an exponential one:

$$\Phi(v) = \exp(kv) \quad k = \text{const.} \quad (32)$$

therefrom it follows:

$$\left[ \frac{\partial \Phi(v)}{\partial v} \right] = k \exp(kv) \quad (33)$$

- a hyperbolic one:

$$\Phi(v) = \frac{1}{1 - kv} \quad k = \text{const.} \quad (34)$$

therefore it follows:

$$\left[ \frac{\partial \Phi(v)}{\partial v} \right] = \frac{k}{(1 - kv)^2} \quad (35)$$

A repeated iteration calculation according to the recurrent relation (28) respecting the limiting conditions (22, 23) with continuous determination of surface concentration  $v_R(Fo)_j$  in every cycle of the iteration calculation gave the concentration field in the fibre cylinder in the form of dependence of dimensionless concentration upon the dimensionless radius  $\rho$  for parametrical values of the quantities  $Fo$ ,  $A$ ,  $Xo$ :

$$v = \{f(\rho)\}_{Fo, A, Xo} \quad (36)$$

A continuous integration of concentration fields according to Eq. (17) then gave the kinetic dependence of the percentage of exhaustion of bath % $Ex$  as a function of  $Fo$  for various parametrical values of the quantities  $A$ ,  $Xo$  (the



so-called exhaustion curve):

$$\% Ex = \{\varphi(Fo)\}_{A, X_0} \quad (37)$$

### Test of Accuracy of the Numerical Solutions

An estimate of accuracy of the approximate numerical solutions was obtained from the comparison of results of numerical solutions with one of the few known analytical solutions, viz. the Wilson equation for calculating the kinetic function of transport into an infinite cylinder from a liquid of finite volume at the partition equilibrium of the form of the Nernst constant partition coefficient (Fig. 3).

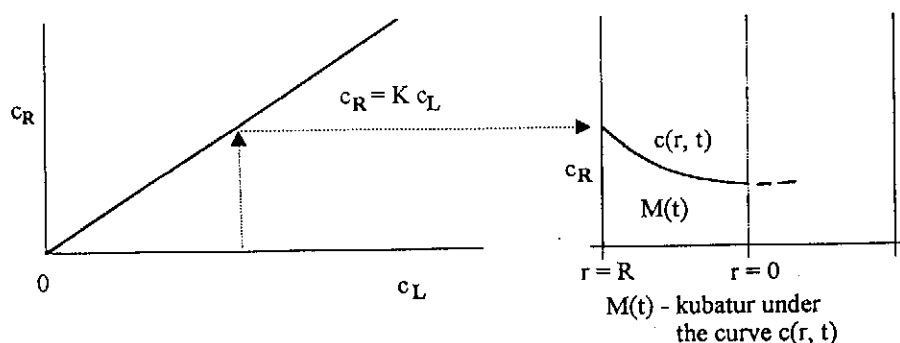


Fig. 3 Scheme of diffusion problem described by Wilson kinetic equation

The amount of the medium (dyestuff) in the cylinder (fibre) at the time  $t$  is given by the relation:

$$\frac{M(t)}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2\gamma_n^2} \exp(-\gamma_n^2 Fo) \quad (38)$$

where  $M(t)$  represents the mass amount of the medium (dyestuff) which has penetrated by diffusion into the cylinder (fibre) by the time  $t$ ,  $M_\infty$  stands for the equilibrium amount (for  $t \rightarrow \infty$ ),  $L = H_L/H_s$  is the bath ratio, so that it is  $\alpha = 1/A$ ,  $Fo = Dt/R^2$  is the Fourier number for a cylinder, and  $\gamma_n$  means the  $n$ -th positive root of Eq. (39):

$$\alpha \gamma_n J_0(\gamma_n) - 2J_1(\gamma_n) = 0 \quad (39)$$

The degree of exhaustion of bath given by the mass % corresponds to the following relation:

$$\% Ex = 100 \frac{1}{1 + \alpha} \frac{M(t)}{M^\infty} = 100 \frac{A}{1 + A} \frac{M(t)}{M^\infty} \quad (40)$$

For the equilibrium exhaustion of bath ( $t \rightarrow \infty$ ) it is

$$\% Ex(F_0 \rightarrow \infty) = \% Ex(\infty) = 100 \frac{1}{1 + \alpha} = 100 \frac{A}{1 + A} \quad (41)$$

The calculations were carried out with a PC with double precision (16 valid digits). The Bessell functions  $J_0(x)$ ,  $J_1(x)$  were calculated with the precision of 7 valid digits. The roots  $\gamma_n$  of Eq. (39) were calculated with the precision of 5 valid digits, and the sum in Eq. (38) with the precision of 4 valid digits. These results were compared with those of numerical solution (see Table I).

The numerical simulation of the same diffusion problem was carried out by the procedure given above. The only modification concerns the functional relation of partition equilibrium which was correspondingly modified to the form of the Nernst constant partition coefficient and the therefrom following relation for the driving force of diffusion - the dimensionless surface concentration  $v_R$ . It was chosen  $Z = 1$ ,  $p_0 = 1$ , and the corresponding relation (42) was used instead of Eq. (16).

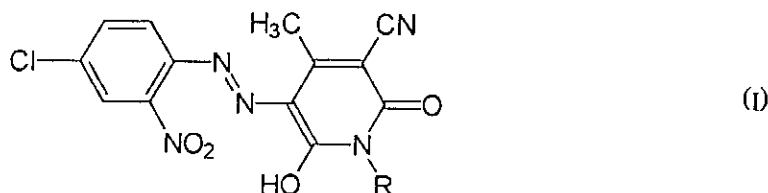
$$v_R = A[X_0 - X(F_0)] = A[1 - X(F_0)] \quad (42)$$

From the results given in Table I it can be seen that the two independent solutions agree very well, the difference being of the order of  $10^{-1} - 10^{-2} \%$ . Hence the results of numerical solutions are obviously correct.

### *A Practical Example of Application of the Results of Solution*

The practical application of computer simulation is illustrated with an example of HT-dyeing of PES fibres with disperse dyes.

Two yellow disperse dyes of azo pyridone type were used. Their structure was similar



to (I) but they differed in their sorption characteristics.  $R = \text{CH}_3$  and  $\text{C}_2\text{H}_5$  for the dyestuffs denoted as B-Me and B-Et, respectively.

Table 1 Comparison of results of analytical and numerical solution of the Wilson equation. The relative difference is expressed in %

$A = K/L$	$F_0 = (Dt)/R^2$	Analytically		Numerically		Difference %
		$M(t)/M_\infty$	%Ex	$M(t)/M_\infty$	%Ex	
$A = 1$	0.0050	0.24963	12.48	0.2502	12.51	0.220
	0.0100	0.36657	18.32	0.3669	18.35	0.090
	0.0200	0.47893	23.94	0.4798	23.99	0.150
	0.0500	0.65361	32.68	0.6538	32.69	0.030
	0.1000	0.79301	39.65	0.7932	39.66	0.030
	0.1500	0.86896	43.45	0.8694	43.47	0.050
	0.2000	0.91571	45.78	0.917	45.85	0.140
	0.5000	0.99381	49.69	0.9938	49.69	0.002
$A = 10$	0.0010	0.48709	44.28	0.4878	44.35	0.150
	0.0020	0.58862	53.51	0.5887	53.52	0.020
	0.0050	0.71847	65.32	0.7164	65.13	0.290
	0.0100	0.80064	73.05	0.8010	72.81	0.330
	0.0200	0.87304	79.36	0.8714	79.22	0.190
	0.0500	0.93986	85.44	0.9396	85.42	0.028
	0.1000	0.97345	88.49	0.9733	88.48	0.015
	0.2000	0.99328	90.29	0.9932	90.29	0.008
$A = 100$	0.0001	0.75164	74.42	0.7481	74.07	0.470
	0.0002	0.81676	80.86	0.8161	80.80	0.081
	0.0005	0.88194	87.32	0.8830	87.43	0.120
	0.0010	0.91835	90.92	0.9186	90.95	0.027
	0.0020	0.94418	93.48	0.9443	93.50	0.013
	0.0050	0.96794	95.83	0.9674	95.78	0.056
	0.0075	0.97465	96.50	0.9745	96.49	0.015
	0.0100	0.97925	96.95	0.9789	96.93	0.036

The dyestuffs were synthesized by azo coupling reaction and finished by means of usual wet pearl milling with dispersants and dried in a fluidized-bed drier up to the final content of about 50% pigment in the dry matter. The corresponding procedures are described elsewhere<sup>13, 14</sup>.

With both the dyestuffs the sorption isotherms were determined at 130 °C using the usual HT-dyeing process from a bath of infinite bath ratio up to the equilibrium and the spectrophotometric determination of the dyestuff on fibre after extraction with hot chlorobenzene. The experimental sorption isotherms (Fig. 4) were verified by nonlinear regression using the Langmuir function (2),

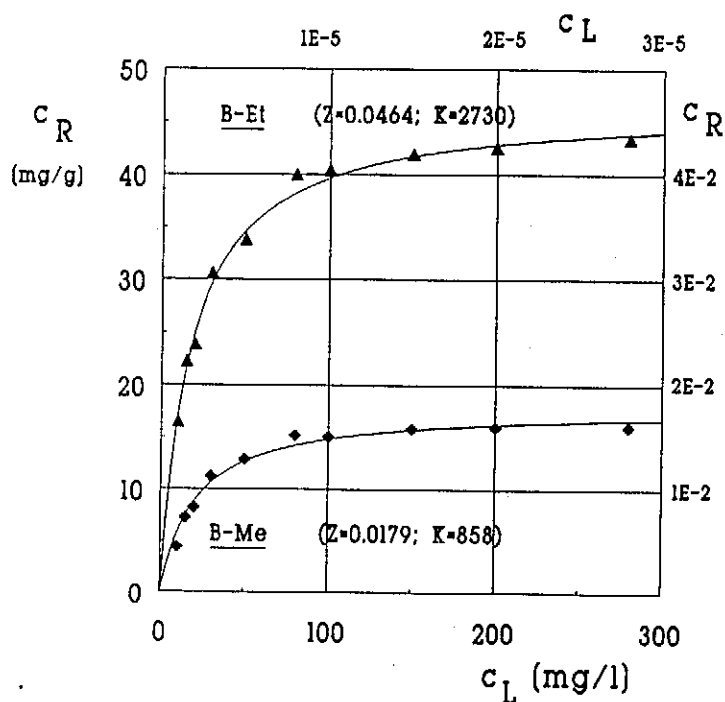


Fig. 4 The sorption isotherms of dyestuffs B-Me and B-Et

and the corresponding values of limit saturation  $Z$  and partition coefficient  $K$  were determined.

The diffusion coefficients of the PES fibre used were estimated by means of microdensitometric analysis of the concentration field of dyestuff at the cross section of the fibre<sup>15</sup>.

For a verification of the model, a standard fabric of PES staple fibre was dyed according to ČSN 800 108 (IS ISO 105/I). The fibre radius was  $R = 9.62 \mu\text{m}$ . The dyeing process was isothermal,  $T = 130 \text{ }^\circ\text{C}$ , at the bath ratio  $L = 40$  using a Linitest apparatus (Original Hanau). For a standard depth 1/1 RT the dyeings of the strengths 0.5% (i.e.  $p_o = 0.05$ ) and 0.45% (i.e.  $p_o = 0.045$ ) were realized for the dyestuffs B-Me and B-Et, respectively. The corresponding parameters of the dyeing system were as follows:

Dye	$Z$	$p_o$	$K$	$L$	$X_o$	$W$	$A$	$R$ $\mu\text{m}$	$D \times 10^{10}$ $\text{cm}^2 \text{s}^{-1}$
B-Me	0.0179	0.0050	858	40	0.279	3.59	21.5	9.62	1.030
B-Et	0.0464	0.0045	2730	40	0.097	10.31	63.3	9.62	0.761

Furthermore we also carried out dyeings by the nonisothermal VT- procedure.

The initial temperature of 60 °C was linearly increased at the rate of 2.5 °C/min up to the final temperature of 130 °C, and the process was continued isothermally at this temperature for another 15 min. The other conditions were identical with those of the isothermal dyeing procedures.

The calculated kinetic functions of exhaustion curves (as the dependence of % *Ex* vs. time *t*) are given in Fig. 5 together with the experimental values obtained in the isothermal dyeing process. The functions of experimental kinetic exhaustion curves for the nonisothermal process are presented in Fig. 6.

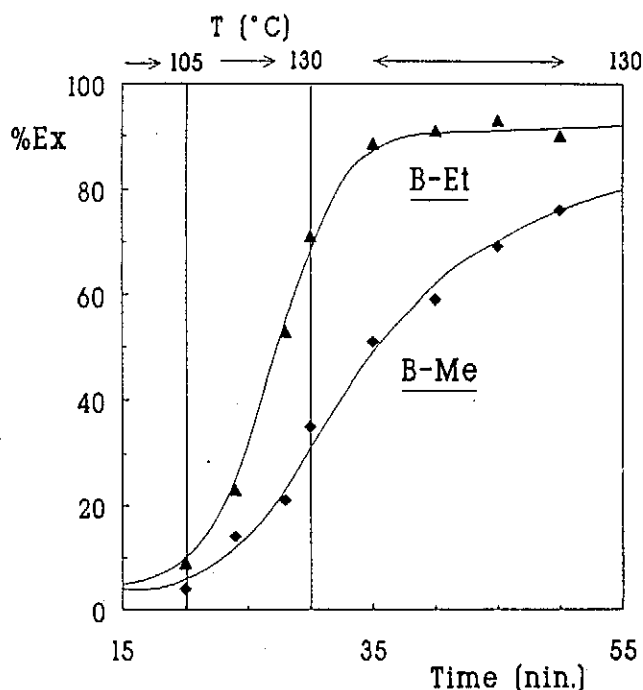


Fig. 5 The kinetic functions of exhaustion curve as a dependence of % *Ex* vs. time *t* for the isothermal case of dyeing - the curves in the graph represent the numerical solution, the points correspond to experimental values

## Results and Discussion

The aim of the mathematical simulation was to find the properties and parameters of the dyeing system allowing the fastest possible transport of the dyestuff from bath to fibre with the highest possible exhaustion of bath and, hence, utilization of the dyestuff.

In order to verify the basic relations and trends, we realized calculations for the case of ideal Fick diffusion ( $D = const$ ) under isothermal conditions.

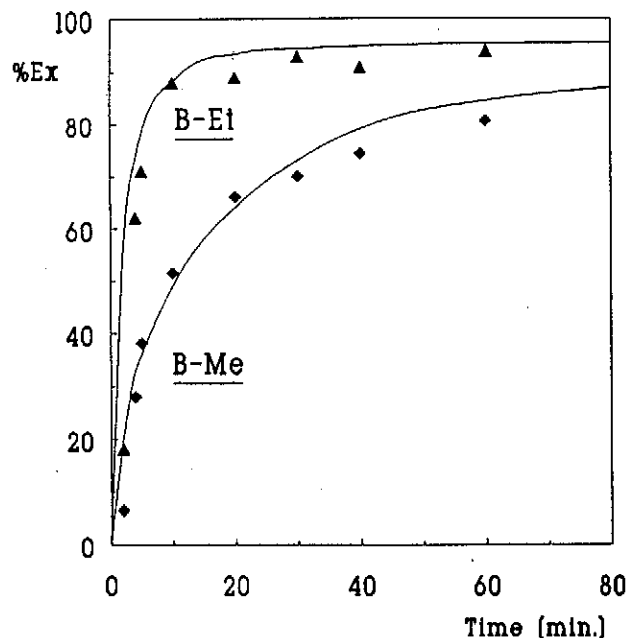


Fig. 6 Experimentally determined kinetic functions of exhaustion curves as a dependence of % Ex vs. time  $t$  for the nonisothermal case of dyeing

The solution of this problem led to:

- finding the development of concentration field in the fibre cylinder in the general functional form of Eq. (36) (examples of the concentration fields see in Table II and Figs 7 - 9)
- finding the integral kinetic function of transfer of dyestuff from bath to fibre (exhaustion curve) as a dependence of percentage of bath exhaustion %Ex upon the dimensionless time  $Fo$  for various parametrical values of the criteria  $A$ ,  $Xo$  in the general functional form of Eq. (37) (for results see Table III and Figs (10), (11)).

The solution was carried out in the ranges of the dimensionless criteria:

$$Xo \in (0.02; 0.4)$$

$$A \in (1; 1000)$$

The intervals given approximately cover the limits in which the real dyeing systems vary. From the results of solution (Figs 10, 11, Table III) it follows that the transport speed of the dyestuff from bath to fibre and the extent of exhaustion of bath after attaining the equilibrium depend upon three dimensionless critical parameters  $Fo$ ,  $A$ ,  $Xo$  (see the definitions in Eqs (4), (14) and (15)).

Table II Numerically calculated concentration fields in fibre cylinder for various values of dimensionless quantities  $Fo$ ,  $A$ ,  $Xo$ . The table presents the concentration in unit expression ( $v/v_R$ )

$Fo = 0.0002$

Radius $\rho_i = i/M$	$Xo = 0.02$		$Xo = 0.04$		$Xo = 0.10$		$Xo = 0.40$	
	$A=10$	$A=1000$	$A=10$	$A=1000$	$A=10$	$A=1000$	$A=10$	$A=1000$
286/300	0.0232	0.0387	0.0222	0.0230	0.0211	0.0201	0.0205	0.0313
288/300	0.0526	0.0868	0.0509	0.0520	0.0487	0.0466	0.0473	0.0686
290/300	0.1084	0.1744	0.1056	0.1052	0.1015	0.0977	0.0987	0.1366
292/300	0.2027	0.3138	0.1986	0.1957	0.1921	0.1858	0.1870	0.1860
294/300	0.3452	0.5036	0.3398	0.3344	0.3308	0.3217	0.3233	0.3218
296/300	0.5365	0.7180	0.5304	0.5245	0.5201	0.5097	0.5112	0.5095
298/300	0.7636	0.9043	0.7588	0.7554	0.7507	0.7423	0.7434	0.7420
300/300	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
$v_R$	0.1344	0.4478	0.2425	0.9091	0.4598	0.9856	0.7894	0.9973

$Fo = 0.001$

Radius $\rho_i = i/M$	$Xo = 0.02$		$Xo = 0.04$		$Xo = 0.10$		$Xo = 0.40$	
	$A=10$	$A=100$	$A=1$	$A=100$	$A=1$	$A=1000$	$A=1$	$A=1000$
272/300	0.0405	0.0807	0.0401	0.0641	0.0400	0.0394	0.0395	0.0388
276/300	0.0799	0.1507	0.0794	0.1230	0.0791	0.0781	0.0783	0.0769
280/300	0.1460	0.2577	0.1452	0.2168	0.1448	0.1432	0.1434	0.1411
284/300	0.2468	0.4034	0.2460	0.3498	0.2454	0.2433	0.2434	0.2399
288/300	0.3880	0.5781	0.3871	0.5187	0.3863	0.3838	0.3837	0.3793
292/300	0.5680	0.7585	0.5673	0.7054	0.5665	0.5642	0.5637	0.5590
296/300	0.7777	0.9106	0.7772	0.8785	0.7766	0.7753	0.7746	0.7711
300/300	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
$v_R$	0.0183	0.1855	0.0361	0.3842	0.0858	0.9689	0.2756	0.9970

$Fo = 0.005$

Radius $\rho_i = i/M$	$Xo = 0.02$		$Xo = 0.04$		$Xo = 0.1$		$Xo = 0.4$	
	$A=1$	$A=10$	$A=1$	$A=100$	$A=1$	$A=100$	$A=1$	$A=1000$
230/300	0.0244	0.0383	0.0243	0.0569	0.0243	0.0386	0.0236	0.0244
240/300	0.0549	0.0812	0.0547	0.1188	0.0547	0.0853	0.0532	0.0510
250/300	0.1122	0.1568	0.1119	0.2229	0.1115	0.1694	0.1090	0.1051
260/300	0.2080	0.2755	0.2076	0.3753	0.2066	0.3021	0.2029	0.1966
270/300	0.3512	0.4397	0.3507	0.5662	0.3492	0.4832	0.3441	0.3355
280/300	0.5416	0.6370	0.5410	0.7650	0.5392	0.6917	0.5336	0.5238
290/300	0.7662	0.8374	0.7658	0.9250	0.7644	0.8828	0.7600	0.7523
300/300	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
$v_R$	0.0170	0.0683	0.0335	0.1727	0.0803	0.4651	0.2639	0.9959

Table II Continued

 $Fo = 0.02$ 

Radius $\rho_i = i/M$	$X_o = 0.02$		$X_o = 0.04$		$X_o = 0.1$		$X_o = 0.4$	
	$A=1$	$A=10$	$A=1$	$A=10$	$A=1$	$A=100$	$A=1$	$A=1000$
80/150	0.0346	0.0779	0.0312	0.0514	0.0313	0.0670	0.0295	0.0272
90/150	0.0711	0.1100	0.0675	0.1061	0.0673	0.1360	0.0641	0.0595
100/150	0.1356	0.2050	0.1327	0.1984	0.1321	0.2482	0.1267	0.1185
110/150	0.2385	0.3425	0.2374	0.3354	0.2362	0.4069	0.2281	0.2153
120/150	0.3866	0.5201	0.3874	0.5122	0.3855	0.5986	0.3752	0.3579
130/150	0.5762	0.7144	0.5782	0.7071	0.5758	0.7904	0.5649	0.5460
140/150	0.7904	0.8879	0.7919	0.8833	0.7900	0.9372	0.7820	0.7677
150/150	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
$v_R$	0.0150	0.0413	0.0297	0.0825	0.0719	0.2321	0.2450	0.9904

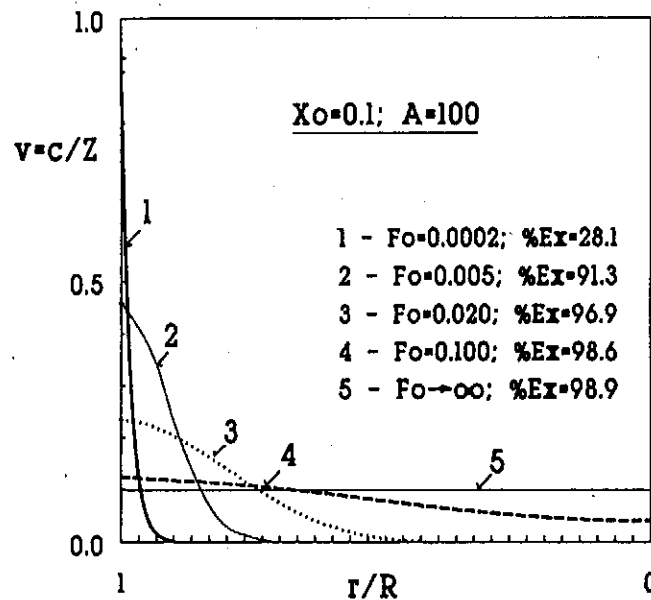


Fig. 7 Example of development of dimensionless concentration field in the course of dimensionless time  $Fo$  for the values of parameters  $A = 100$ ,  $X_o = 0.1$

Beside the generally known and, hence, expected effects of the diffusion coefficient  $D$  and radius of fibre  $R$  upon the transport process (which are involved in the Fourier diffusion criterion  $Fo$ ) it is surprising to find distinct (even in the order of magnitude) effects of the parameters  $A$ ,  $X_o$  upon the rate and degree of exhaustion of dyestuff (Table III, Figs 10, 11).

The parameters  $A$ ,  $X_o$  are connected with the thermodynamic affinity behaviour of the dyestuff in its partition between the phases fibre-bath. Thus



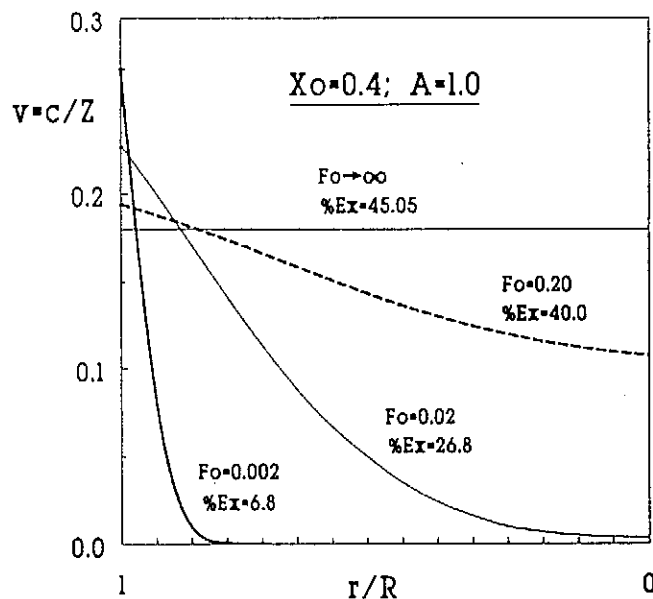


Fig. 8 Example of development of dimensionless concentration field in the course of dimensionless time  $Fo$  for the values of parameters  $A = 1$ ,  $X_0 = 0.4$

their effect is manifested in the definition of the limiting conditions of the diffusion process.

For high  $A$  values and low  $X_0$  values a large driving force of the concentration gradient  $v_R$  is formed at the fibre surface representing a multiple of the equilibrium concentration in fibre at the beginning of the dyeing process. In the course of diffusion, with increasing value of the dimensionless time  $Fo$ , the  $v_R(Fo)$  value markedly decreases (see Table II, Fig. 7).

On the other hand, for low  $A$  values and high  $X_0$  values, the diffusion process takes place with a small driving force  $v_R$  in the whole its course,  $v_R$  being comparable with the value of equilibrium concentration in fibre (Fig. 8). Moreover, from Fig. 9 and Table I it follows that increasing  $A$  and decreasing  $X_0$  result in levelling of the concentration gradients of the ring-form dyeing process in fibre. The results of the computer simulation allow us to explain many cases of rapid uptake of dye from bath to fibre known from practice even at lower  $D$  values as compared with the dyestu. whose diffusion coefficients are higher but the rate of uptake lower. The dyestuffs B-Me and B-Et used in the verification of the model by experiment can serve as examples. The dyestuff B-Et shows a substantially faster, more complete uptake although its diffusion coefficient is by almost a half lower than that of B-Me. The reason lies in the more convenient values of the  $A$ ,  $X_0$  parameters of dyestuff B-Et.

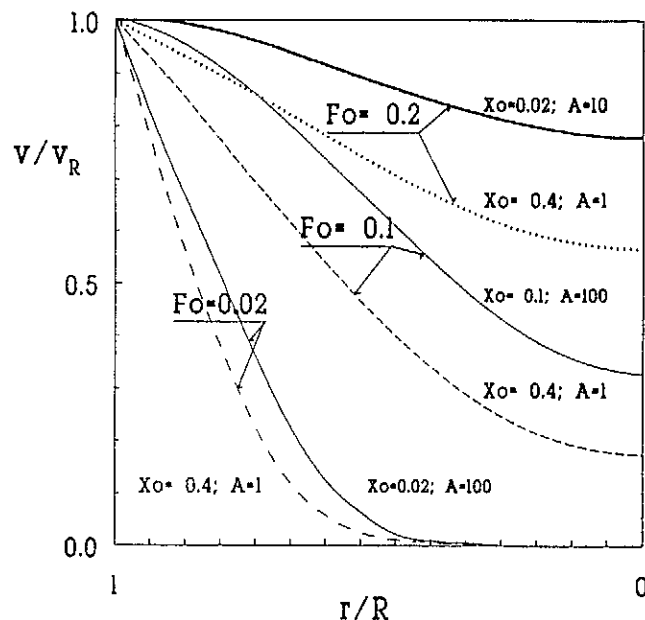


Fig. 9 The effect of criterial parameters  $A$ ,  $Xo$  upon the unit concentration field  $v/v_R = f(\rho)$  in fibre cylinder

## Conclusion

The kinetic course and equilibrium state of transfer of dyestuff from bath to fibre depend on three dimensionless criterial parameters of the dyeing system, viz. the diffusion parameter of Fourier number  $Fo$  and the two affinity parameters  $A$ ,  $Xo$ . The rate of completeness of uptake of dyestuff increase with increasing  $A$  parameter and decrease with increasing  $Xo$  parameter.

The solutions found allow to formulate the properties of dyestuff which affect the rapid and complete exhaustion of bath by a fibre. Beside the diffusion coefficient  $D$ , whose effect is obvious from the definition relation of  $Fo$ , a high value of the partition coefficient  $K$  (which determines the magnitude of the  $A$  parameter) is desirable. Moreover it is desirable to attain the lowest possible value of  $Xo$ . This parameter depends upon the strengths of shade of the dyeing  $p_0$  [the usual percentage of dyeing divided by 100, see Eqs (8,9)]. In particular, for deep shades it is possible to obtain a favourably low  $Xo$  value only with dyestuffs exhibiting a sufficiently high limiting saturation on fibre. In order to compare dyestuffs of various hues, colour strengths and depths, it proved useful in practice to define the parameter  $Xo$  for the case of standard depth of dyeing  $1/1RT$  (ČSN 800 120, IS ISO 105/I):/

Table III The kinetic function of transfer of dyestuff from bath to fibre (exhaustion curves) as a dependence of percentage of bath exhaustion %E upon dimensionless time  $Fo$  for various values of  $A$  and  $Xo$  parameters

$Xo = \rho_0/Z$	$A = 1$		$A = 10$		$A = 100$		$A = 1000$	
	$Fo$	%Ex	$Fo$	%Ex	$Fo$	%Ex	$Fo$	%Ex
$Xo = 0.02$	0.0005	4.73	0.0001	16.70	$5 \times 10^{-6}$	16.52	$1 \times 10^{-6}$	14.36
	0.001	6.56	0.0002	22.38	$2 \times 10^{-5}$	30.48	$2 \times 10^{-6}$	17.16
	0.002	8.87	0.0005	32.11	$5 \times 10^{-5}$	44.53	$5 \times 10^{-6}$	25.21
	0.005	13.53	0.002	50.62	0.0001	57.30	$1 \times 10^{-5}$	33.94
	0.01	18.09	0.005	63.18	0.0002	69.76	$2 \times 10^{-5}$	46.97
	0.02	23.76	0.02	78.47	0.0005	82.58	$5 \times 10^{-5}$	70.82
	0.05	32.64	0.05	85.02	0.001	88.48	0.0001	89.03
	0.1	39.37	0.1	88.23	0.0015	91.00	0.0002	95.95
	0.2	45.50	0.2	90.11	0.002	92.32	0.0003	97.27
	0.3	47.96	0.3	90.58	0.003	93.81	0.0004	97.89
	$Fo \rightarrow \infty$	49.75	$Fo \rightarrow \infty$	90.76	$Fo \rightarrow \infty$	98.99	$Fo \rightarrow \infty$	99.90
$Xo = 0.04$	0.001	6.44	0.0001	14.71	$2 \times 10^{-5}$	19.72	$5 \times 10^{-6}$	13.05
	0.002	8.87	0.0002	19.97	$5 \times 10^{-5}$	30.08	$1 \times 10^{-5}$	17.86
	0.005	13.32	0.0005	29.19	0.0001	40.94	$5 \times 10^{-5}$	38.93
	0.01	17.83	0.001	37.95	0.0002	54.43	0.0001	53.89
	0.02	23.37	0.002	47.73	0.0005	73.75	0.0002	74.99
	0.05	32.03	0.01	70.17	0.001	84.21	0.0003	88.31
	0.1	39.02	0.02	77.52	0.002	90.57	0.0004	92.81
	0.2	45.20	0.05	84.52	0.003	92.80	0.0005	96.05
	0.4	48.76	0.1	87.94	0.005	94.77	0.0006	97.08
	0.5	49.19	0.2	89.93	0.0075	95.72	0.001	98.94
	$Fo \rightarrow \infty$	49.50	$Fo \rightarrow \infty$	90.60	$Fo \rightarrow \infty$	98.97	$Fo \rightarrow \infty$	99.90

$$(Xo)_{RT} = \frac{(\rho_0)_{RT}}{Z} = \frac{(S\%)_{RT}}{100Z} \quad (43)$$

where  $(S\%)_{RT}$  represents the percentage of dyeing for obtaining the standard depth 1/1RT.

From practical point of view it proved useful to define the reciprocal value of this parameter:

$$W = \frac{1}{(Xo)_{RT}} = \frac{Z}{(\rho_0)_{RT}} \quad (44)$$

Table III Continued

$X_o = \rho_0/Z$	$A = 1$		$A = 10$		$A = 100$		$A = 1000$	
	$F_o$	%Ex	$F_o$	%Ex	$F_o$	%Ex	$F_o$	%Ex
$X_o = 0.10$	0.0005	4.41	0.0002	14.88	$5 \times 10^{-3}$	14.36	$2 \times 10^{-3}$	10.06
	0.001	6.12	0.0005	22.52	0.0001	20.12	$5 \times 10^{-3}$	15.79
	0.002	8.47	0.001	30.25	0.0002	28.12	0.0001	22.31
	0.005	12.74	0.005	54.15	0.0004	39.10	0.0002	31.34
	0.01	17.10	0.01	64.98	0.0005	43.33	0.0005	49.16
	0.02	22.55	0.02	74.10	0.001	58.81	0.001	68.80
	0.04	28.90	0.04	81.08	0.002	76.35	0.0015	83.05
	0.05	31.09	0.1	87.00	0.003	84.82	0.002	92.85
	0.1	38.15	0.2	89.31	0.005	91.31	0.0025	97.09
	0.2	44.36	0.5	90.08	0.02	96.98	0.003	98.19
	$F_o \rightarrow \infty$	48.75	$F_o \rightarrow \infty$	90.10	$F_o \rightarrow \infty$	98.90	$F_o \rightarrow \infty$	99.89
$X_o = 0.4$	0.001	4.89	0.0002	6.30	0.0002	7.76	0.0002	7.94
	0.002	6.80	0.0005	9.84	0.0005	0.00	0.0005	12.47
	0.005	10.37	0.001	13.74	0.001	17.12	0.001	17.56
	0.01	14.11	0.002	0.00	0.002	24.02	0.002	24.69
	0.02	18.87	0.005	29.14	0.005	37.34	0.003	30.10
	0.05	26.77	0.01	0.00	0.01	51.64	0.005	38.52
	0.1	33.56	0.02	51.72	0.02	0.00	0.01	53.69
	0.2	39.97	0.05	68.94	0.03	82.29	0.02	74.17
	0.3	42.75	0.1	79.03	0.05	93.49	0.03	88.90
0.5	44.58	0.2	0.00	0.1	97.32	0.05	99.30	
	$F_o \rightarrow \infty$	45.05	$F_o \rightarrow \infty$	86.72	$F_o \rightarrow \infty$	98.38	$F_o \rightarrow \infty$	99.83

Thus the quantity  $W$  gives the level of the saturation limit of dyestuff on substrate in multiples of the standard depth  $1/1RT$ . Particularly, the dyestuffs used for illustration of the model exhibit the limit saturation  $W$  of the values of 3.59 and 10.31 multiples (for the dyestuffs B-Me and B-Et, respectively) of the standard depth  $1/1RT$ . The magnitude of parameter  $W$  depends not only on the dyestuff but also on the properties of the fibre dyed. Therefore, in practice always the same reference fibrous materials is used for testing and mutual comparison of dyestuffs.

The basic trends of influence of the parameters  $F_o$ ,  $A$ ,  $X_o$  (or  $W$ ) upon the rate and completeness of transfer of dyestuff from bath to fibre, which were calculated for the isothermal case of dyeing, make themselves felt analogously also in the case of a nonisothermal dyeing process. Here also it is true that the dyestuffs with more favourable characteristics of the parameters  $F_o$ ,  $A$ ,  $X_o$  (or  $W$ ) show a more rapid and complete uptake by fibre, which can be seen in Fig. 6 for the dyestuffs B-Me and B-Et. In a nonisothermal case the character

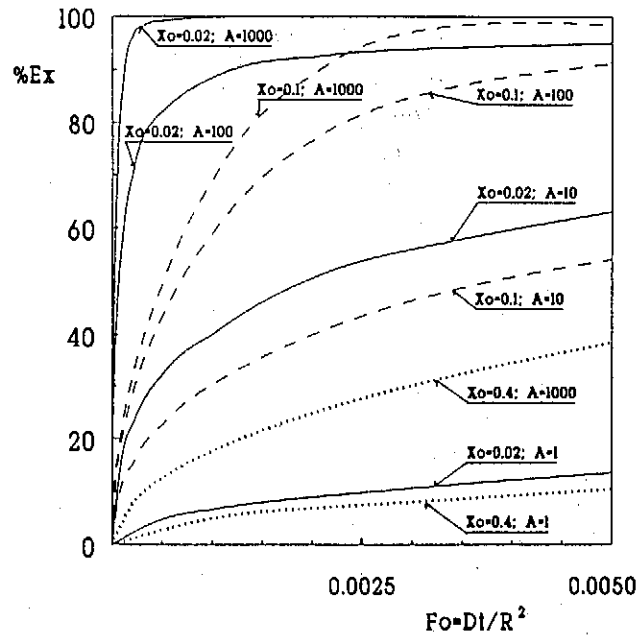


Fig.10 The kinetic transfer function of dyestuff from bath to fibre (exhaustion curve) obtained by numerical simulation - the graph represents the dependence of percentage of bath exhaustion %  $Ex$  upon the dimensionless time  $Fo$  for various parametrical values of  $A$  and  $X_0$  criteria (for more details see Table II)

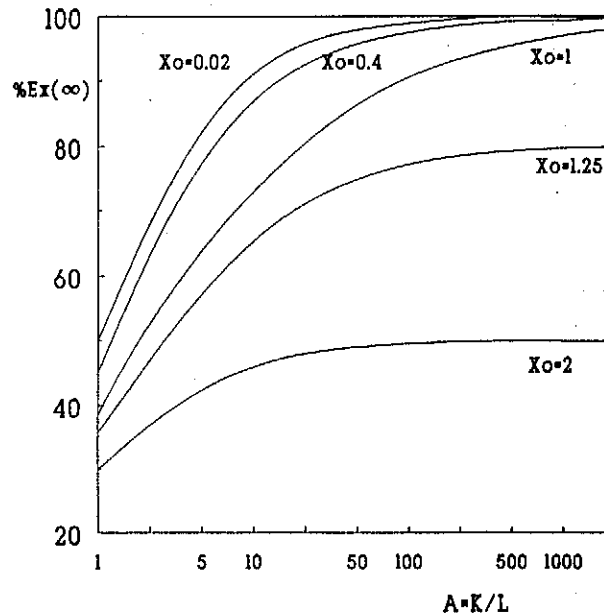


Fig.11 Dependence of equilibrium exhaustion of bath %  $Ex(\infty)$  upon the parameters  $A$ ,  $X_0$

of kinetic function of dyeing will change in the region of low temperatures where due to decreased diffusion coefficient (and affecting of other parameters too) the time scale is expanded (cf. Figs 5 and 6).

The system suggested for monitoring the criterial parameters of dyeing system and the therewith connected properties of dyestuff for use in the optimized and rapid dyeing processes in the technological classes of disperse and reactive dyes.

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