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New Mathematical Model for Determining Time-Dependent Adsorption and Diffusion of Dyes into Fibers Through Dye Sorption Curves in Combination Shades

Part II: Kinetic Data from Dyeing Cotton with a Trichrome Direct Dye System

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ABSTRACT

Time-dependent dye uptake of textile substrates can be described by a new mathematical model that divides the dyeing process into two parts, dye adsorption and dye diffusion. Using this model, the influence of temperature (20–80°C) and NaCl concentration (2.5–10.0 g/L) on the dye uptake of a trichrome dye combination of C.I. Direct Blue 225, C.I. Direct Violet 47, and C.I. Direct Yellow 27 on cotton is determined from sorption curves obtained by UV-VIS spectroscopy. This model can demonstrate differences in temperature dependent dye uptake of the disordered inner and outer surfaces of the substrate and also displacement reactions that occur during dyeing.

Dyeing cellulosic materials with direct dyes is mainly influenced by temperature and dye and salt concentrations. Predictions of the color shades of oligochrome dyeings are mainly based on monochrome dyeing data, often resulting in deviations from the desired hue. This is partly caused by interactions of the different dyes in highly concentrated dye liquors and by displacement reactions on or in the fibers during dyeing [6]. Different models have been suggested for mathematical descriptions of the sorption and diffusion of substances into the polymer matrix during dyeing processes, such as the pore [16], free volume [18] and diffusion/immobilization models [8, 9, 11, 17]. All of these are based on the assumption of a homogeneous matrix and do not distinguish between different accessible regions of the substrate.

Rys [10] investigated selective dye uptake with respect to competitive sorption, but he did not account for structural differences of fibers. The sorption behavior of dyes in mono and oligochrome dyeing processes is often described by the Gouy-Chapman or the Donnan model [6, 7]. The Donnan model considers the standard affinity, the internal volume of the fiber, and the fixed charge of the substrate before dyeing, plus that of the adsorbed dye anions. In the Gouy-Chapman model, the standard affinity, the accessible fiber surface for the dye, and the surface charge density of the substrate have to be deter-

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[1] Excerpts from the dissertation of Horst Duffner.

mined. Both dyeing models are only used to describe dyeing equilibria [6, 7].

In Part I of this series, we presented a new mathematical model [2] that describes dye uptake in the noncrystalline parts of the cellulose matrix as time dependent, divided into fast and slow subprocesses. The fast subprocess describes the adsorption of dye onto the easily accessible outer fiber surface, and the slow subprocess describes diffusion of the dye into the inner disordered regions of the fiber [2]. The inner and outer fiber surfaces of cotton have been investigated using size exclusion chromatography by Bredereck *et al.* [1], who found that generally in the beginning of finishing processes, uptake of textile auxiliaries mainly takes place in the macro- and mesopores with an effective mean pore diameter of $D_p \geq 200$ Å for water swollen cotton fiber. This process is very fast in comparison to the diffusion of chemicals into the micropores located between the elementary fibrils with an effective mean pore diameter of $D_p \approx 30$ Å.

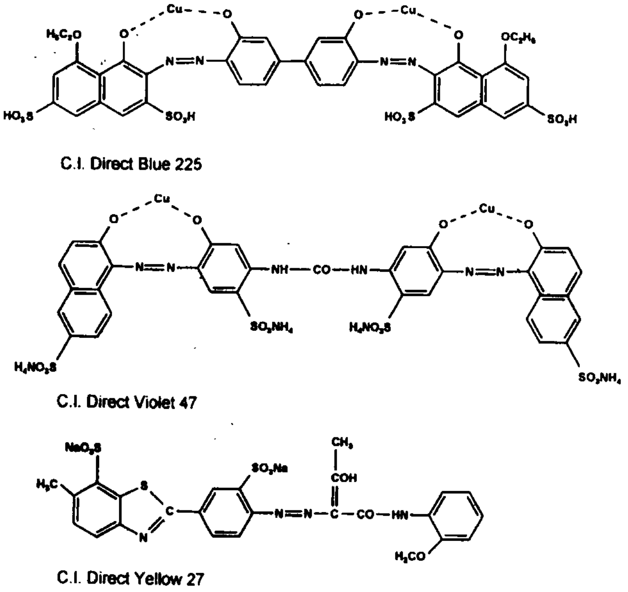
To verify our new mathematical model, we will conduct more far-reaching experiments to correlate the structural features of cotton with the inner and outer surfaces and to find the best fit for fast and slow subprocesses to existing adsorption and diffusion models. In addition, we consider desorption of the dye simultaneously with adsorption at both surfaces. Relating this concept to the dyeing process, it is possible to divide that process into two parts, dye adsorption and dye diffusion with subsequent adsorption. This model has been verified for monochrome dyeing of cotton with direct dyes [2], but it is also transferable to dyeing processes in combination shades. In this paper, we investigate the influence of processing parameters such as dyeing temperature and salt concentration on the dyeing kinetics and hue of a trichrome direct dye system at the inner and outer surfaces of cotton. These investigations are based on dyeing data in previously published work (Denter *et al.* [4]).

Experimental

SUBSTRATE AND DYES

Analogous to the experiments described in Part I of this series [2], we used raw cotton yarn from the Grevener Baumwollspinnerei, Germany. The yarn was pretreated by a boiling-off process at 95°C for 45 minutes with 5 g/L NaOH, 3 g/L Lufibrol KB (BASF, Ludwigshafen, Germany), and 0.75 g/L Leophen U (BASF, Ludwigshafen, Germany) at a liquor ratio of 30:1. Then the material was washed several times with hot and cold demineralized water.

In all dyeing experiments, the three direct dyes were used without further purification in a total concentration (c_0) of 0.5 g/L, achieving a grey hue on cotton. The chemical structures of the dyes are presented in Figure 1. The dye solutions contained 0.23 g/L C.I. Direct Blue 225 (molecular weight of 1056 g/mol, λ_{max} = 590 nm), 0.18 g/L C.I. Direct Violet 47 (molecular weight of 1082 g/mol, λ_{max} = 520 nm), and 0.09 g/L C.I. Direct Yellow 27 (molecular weight of 630 g/mol, λ_{max} = 396 nm), relating to a mixture ratio of 2.5:2:1. All three dyes belong to the SDC-class A, which is characterized by good migration and self-levelling properties (*i.e.*, these dyes are insensitive to small changes in salt concentration and temperature).


C.I. Direct Blue 225

C.I. Direct Violet 47

C.I. Direct Yellow 27

FIGURE 1. Molecular structures of the direct dyes of the trichrome system.

DYEING EQUIPMENT AND CONDITIONS

The dye solution with a constant concentration (c_0) was pumped with a medium pressure chromatographic pump, model Büchi 681, from a reservoir through a column filled with parallel sited cotton yarns with a filling grade of 35%. The dyeing time was 60 minutes. The delivery of the pump through the column with a length of 150 mm and a diameter of 4.9 mm was 5 mL/min. At the end of the column, the absorbance (E) of the dye solution was detected by a UV-/VIS diode array spectrophotometer, Hewlett Packard 8452, at 396, 520, and 590 nm. A schematic drawing of the experimental equipment is shown in Part I [2]. All dyeings occurred within a temperature range of 20–80°C under isothermal conditions.

In order to keep the pH of 9.2 constant, the dye solution was buffered with 1.7 g/L $Na_2B_4O_7$. The dyeing experiments involved the boiled-off cotton yarn conditioned at 20°C and 65% relative humidity.

DETERMINING TIME-DEPENDENT DYE SORPTION

Interpretations of the spectrophotometric data of the eluate after passing the column are based on the calibration of the trichrome dye system prior to dyeing. This is done by varying the concentrations of the dyes within a total liquor concentration of 0.5 g/L by applying the inverse Lambert-Beer law in the form

$$\mathbf{c} = \mathbf{EP} \quad ,$$

where **c** is the concentration matrix, **E** is the extinction matrix, and **P** is the coefficient matrix. **P** can be calculated by multiple linear regression (MLR) after the **P**-matrix method [12]:

$$\mathbf{P} = (\mathbf{E}^T\mathbf{E})^{-1}\mathbf{E}^T\mathbf{c}$$

where $\mathbf{E}^T$ is the transposed matrix of **E**.

The time-dependent dye uptake of the cotton yarn corresponds to the integral of the concentration/time curve obtained by the absorbance in the absorption maximum of each dye [12]:

$$m(t) = \frac{1}{g}\int_{t=0}^{t} (c_0 - c(t))\nu dt \quad ,$$

where $m(t)$ is the standardized total dye uptake (mg/g) referring to 1 g of cotton, c_0 represents the dye concentration at time ($t = 0$) (mg/mL) correlated with the concentration of the eluate in dyeing equilibrium after 60 minutes, $c(t)$ is the dye concentration at time ($t > 0$) (mg/mL), ν is the flow rate of the dye solution (mL/min), and g is the amount of cotton yarn (g) in the dyeing experiment.

According to the mathematical model described in Part I of this series [2], the total dye uptake $m(t)$ of the cotton, dye uptakes $m_s(t)$ and $m_d(t)$ at the outer and inner surfaces of the fibers (see Figure 2), and the velocity constants $k_e = k_s/d_s$ and $k_i = k_d/d_d$ can be computed by this model; k_e is the quotient of the velocity constants of the sorption (k_s) and desorption (d_s) processes at the outer surface, and k_i is the quotient of the velocity constants of the sorption (k_d) and desorption (d_d) processes at the inner surface [2].

COLORIMETRIC MEASUREMENTS

We determined differences in the grey hue of the dyed cotton by colorimetric measurements (Ahiba/Datacolor, Switzerland) with a spectrophotometer 3880. The parameters included a 12 mm aperture, special $d/0°$ geometry, a 10° normal observer, a reference white standard ($BaSO_4$), and daylight D 65. The color differences were determined according to DIN 6174 [5].

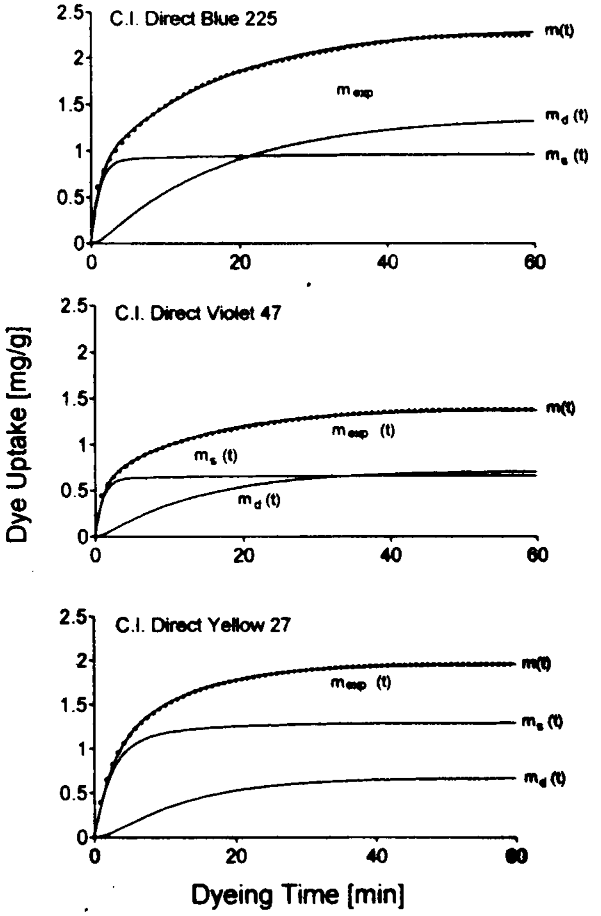


FIGURE 2. Dye-uptake curves of the trichrome direct dyeing system on cotton — calculated data: $m(t)$ total dye uptake, $m_s(t)$ dye uptake of the outer surface, $m_d(t)$ dye uptake of the inner surface, ○ experimental data, total dye uptake.

Results and Discussion

DETERMINING TIME DEPENDENT DYE UPTAKE ON BOTH COTTON SURFACES

We determined the time-dependent dye uptake of cotton for the trichrome system as shown in Figure 2 with measurements at 60°C and 2.5 g/L NaCl-concentration. The figure also shows dye uptake curves simulated by the mathematical model with regard to the sorption of the outer and inner surfaces of cotton based on the velocity constants k_s, k_d, d_s and d_d of the three dyes.

As expected, sorption equilibrium of the three dyes at the outer surface of cotton is achieved within a few minutes, while sorption at the inner surface takes much longer. There are great differences in quantitative dye uptake of the different accessible regions of cotton. Up to a dyeing time of 20 minutes, C.I. Direct Blue 225 is mainly adsorbed by the outer surface of the fiber. Beyond that time, the m_d curve still increases while the m_s values remain constant. After 1 hour, the blue dye is further adsorbed by the inner surface, which means, that dyeing equilibrium is not yet achieved (see also Figure 4). This is also true for C.I. Direct Violet 47. After about 35 minutes the m_d values are similar to m_s but still increase for m_d.

The m_d values C.I. Direct Yellow 27 at the inner surface of the cotton are always lower than those of m_s. This dye molecule has a higher mobility because it is the smallest of the three, and so possibly desorption processes are favored under the dyeing conditions used. Also the displacement reactions of C.I. Direct Yellow 27 by dye molecules with a higher affinity to cotton, such as Direct Violet 47 and Direct Blue 225, could take place. This has to be checked by monochrome dyeing experiments.

DYE SORPTION KINETICS OF TRICHROME DIRECT DYES ON BOTH COTTON SURFACES

The kinetics of dye sorption processes are characterized by $v_x(t)$ and $v_z(t)$, which describe the acceleration or delay of these processes at the different accessible regions of cotton. $v_x(t)$ and $v_z(t)$ are the first derivatives of the dye uptake curves $m(t)$, $m_s(t)$, and $m_d(t)$ obtained from Figure 2. These curves are presented in Figure 3.

The values of $v_x(t)$ and $v_z(t)$ are attributed to superimposed processes at the outer and inner surfaces based on the hypotheses of the sorption model. Therefore, the model only describes the dye uptake of simultaneous processes of sorption and desorption in the different accessible areas of the substrate, but cannot exactly distinguish between them. This is because the solutions of k_e and k_i are the quotients of k_s/d_s and k_d/d_d, respectively [2].

Considering the dyeing velocities $v_x(t)$ and $v_z(t)$ of the adsorption and desorption processes at the outer and inner surfaces of the substrate in Figure 3, it is obvious that after short dyeing times velocity $v_x(t)$ decreases very fast, indicating a rapid covering of the outer surface. The velocity of dyeing $v_z(t)$ in the inner region of the substrate slowly increases up to a maximum value and then decreases asymptotically to zero. Therefore, the values of the initial dyeing rates for the trichrome dyeing process of cotton at 60°C, shown in Table I, exclusively represent dye adsorption at the outer surface of the fiber.

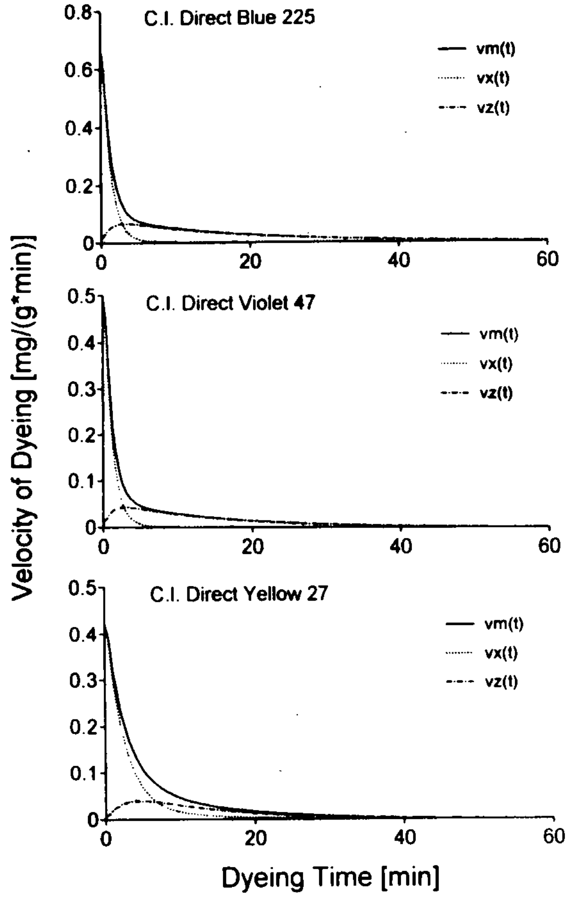


FIGURE 3. Velocity of trichrome direct dyeing of cotton: $v_m(t)$ total sorption, $v_x(t)$ adsorption process, $v_z(t)$ diffusion process.

Generally, if $v_z(t)$ and $v_x(t) = 0$, dyeing equilibrium at both surfaces is reached, which means that dye adsorption and desorption rates are the same order of magnitude. At time $t \leq 5$ minutes the $v_z(t)$ values are very small compared with the $v_x(t)$ values. This can be explained by the much slower diffusion-controlled processes of sorption and desorption in the inner areas of the substrate. The time-dependent velocities of dyeing at the inner surface with C.I. Direct Blue 225, C.I. Direct Violet 47, and C.I. Direct Yellow 27 from Figure 3 are presented in an expanded scope in Figure 4.

After approximately 2.5 minutes, the maximum dyeing velocity value in the inner substrate regions is gained for C.I. Direct Blue 225 and Direct Violet 47. C.I. Direct

TABLE I. Comparison of the temperature for optimum affinity of the monochrome systems (dye manufacturer information) and the trichrome system calculated from experimental values as well as initial dyeing rate.

Dye	Dye manufacturer information	Calculated	Initial dyeing rate, mg/(g · min)]
C.I. Direct Blue 225	50–60°C	60°C	0.420
C.I. Direct Violet 47	80–95°C	≥80°C	0.498
C.I. Direct Yellow 27	40–50°C	50°C	0.669

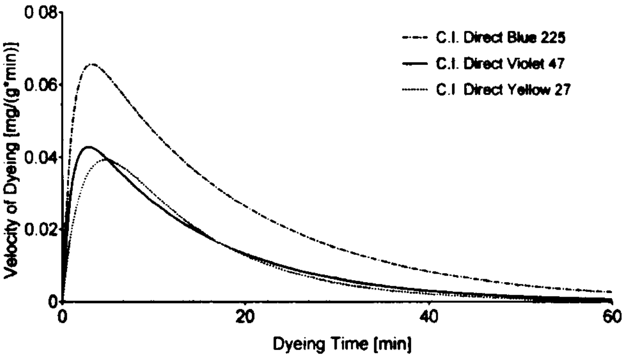


FIGURE 4. Velocity of trichrome direct dyeing $v_z(t)$ in the inner region of cotton (segmental curves of Figure 3).

Yellow 27, the smallest dye molecule of the three, needs twice that time. As mentioned before, this may be related to desorption or displacement reactions during dyeing, but also to the low concentration of the yellow dye in the trichrome dye system. To get more information about this phenomenon, similar molar concentrations of the three dyes should be used. We will discuss this in Part III of this series.

DETERMINING TEMPERATURE DEPENDENT DYE UPTAKE OF BOTH SURFACES

Figures 5 a–c show the equilibrium dye uptake for each dye at the outer and inner surfaces of cotton between 20 and 80°C. The same data are presented in Figures 5 d–f for different amounts of the dyes in the trichrome system adsorbing at the different surfaces of the substrate. No dyeing of cotton was done at temperatures above 80°C because of the high decrease in dye uptake of the blue and yellow dye. NaCl concentration was 2.5 g/L and dyeing time was 1 hour.

As expected, the equilibrium dye uptake of all three dyes depends on the temperature. This is valid for both the inner and outer surfaces. For C.I. Direct Blue 225, dye uptake is maximum at 60°C at both surfaces. At low temperatures, the dye is mainly adsorbed by the outer surface, while above 40°C, dye uptake of the inner surface in relation to the outer surface is higher. For C.I. Direct Violet 47, dye uptake of the outer surface is highest at 70°C, while at the inner surface the values are still increasing. For both dyes, uptake of the outer surface is nearly independent of temperature, but it differs significantly at the inner surface.

There are differences in dye sorption behavior for C.I. Direct Yellow 27. At the outer surface, maximum dye uptake is obtained at 70°C and at the inner surface at 50°C. Dye uptake at both surfaces is highly dependent on temperature. At the inner surface of the fibers, C.I. Direct Yellow 27 seems to be nearly completely displaced by Direct Violet 47 at 70 and 80°C.

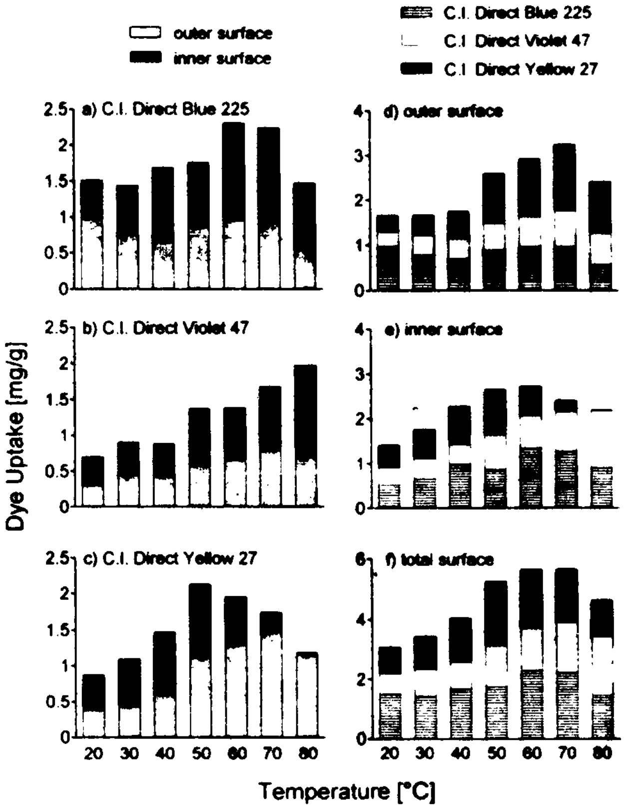


FIGURE 5. Equilibrium trichrome direct dye uptake at the outer (m_s) and inner (m_d) surfaces of cotton at different dyeing temperatures.

Dyeing temperatures relating to the optimum affinity of the trichrome dyeing system correspond with the specifications of the dye manufacturer for monochrome dyeing of cotton. The data are presented in Table I, which also shows the initial dyeing rate of the trichrome dye system on cotton at 60°C.

COLORIMETRIC CHARACTERIZATION OF DYEING RESULTS

The differences in hue obtained at dyeing temperatures between 20 and 80°C can be demonstrated by colorimetric measurements of the color differences of the cotton, as shown in Figure 6. We chose cotton yarn dyed at 50°C as the frame of reference because of the smallest deviations to blue/red or yellow/green of all samples.

Figure 6 demonstrates that at low dyeing temperatures between 20 and 40°C the color looks yellow-greenish, while at temperatures above 50°C the red/blue color is predominant. This corresponds with the dye uptake proportions of all three dyes in the trichrome system, as shown in Figure 5f.

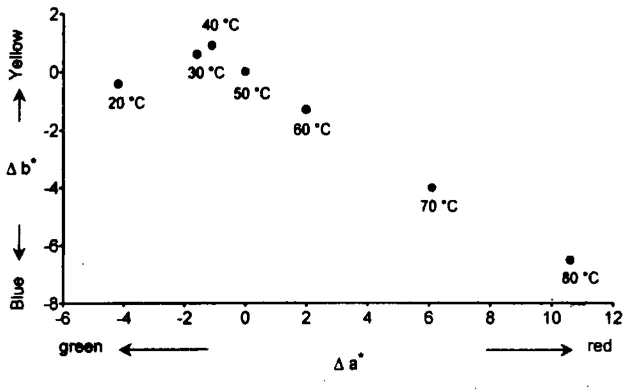


FIGURE 6. Color differences of cotton yarn dyed at different dyeing temperatures in relation to the sample dyed at 50°C.

DETERMINING SALT DEPENDENT DYE UPTAKE OF BOTH SURFACES

Figures 7 a–c show the equilibrium dye uptake of the inner and outer surfaces of cotton depending on salt concentration for each dye of the trichrome experiments. Based on the same data, Figures 7 d–f present the different amounts of each dye at the inner and outer surfaces of cotton for dyeings at 60°C for 1 hour and NaCl concentrations between 2.5 and 10.0 g/L, based on the information of the dye manufacturer for light colors.

The improved dye uptake of the outer surface for all dyes is due to their aggregation with increasing salt concentration. Therefore, at the fiber surface, a multilayer of adsorbed dye molecules can form, from which a constant rate of single dye molecules can dissolve and diffuse into the inner surface of the fibers. Perhaps this is the reason that dye uptake at the inner surface for C.I. Direct Yellow 47 is independent of NaCl concentration. This is also valid for Direct Blue 225 and Direct Violet 47 at salt concentrations ≥ 5.0 g/L (see Figure 7e).

Conclusions

The mathematical model presented in Part I of this series seems to be valid for describing time dependent adsorption and diffusion processes that take place during dyeing in combination shades. We have verified this for a trichrome direct dye system applied to cotton. The first results presented in this paper can only be described under phenomenological aspects. Thus, there are still many questions about dyeing experiments that confirm the differentiation between adsorption and diffusion of dyes onto fiber surfaces and into the inner regions of polymers obtained by the mathematical model. In this context the influence of structural changes in cotton by pretreatment processes such as bleaching, mercerization, and caustification on the dyeing behavior of fibers has to be investigated. Furthermore, displacement and desorption reactions, that occur during dyeing have to be examined for monochrome, bichrome, and trichrome dye combinations at similar and different molar concentrations. Our experiments with dyeing temperature, salt concentration, and dye affinity are still in progress. These investigations, based on the work of Sumner [13–15], are very important, because affinities of dyes to fibers are highly dependent on temperature and change in a systematic way with increasing dye and/or electrolyte concentration [13].

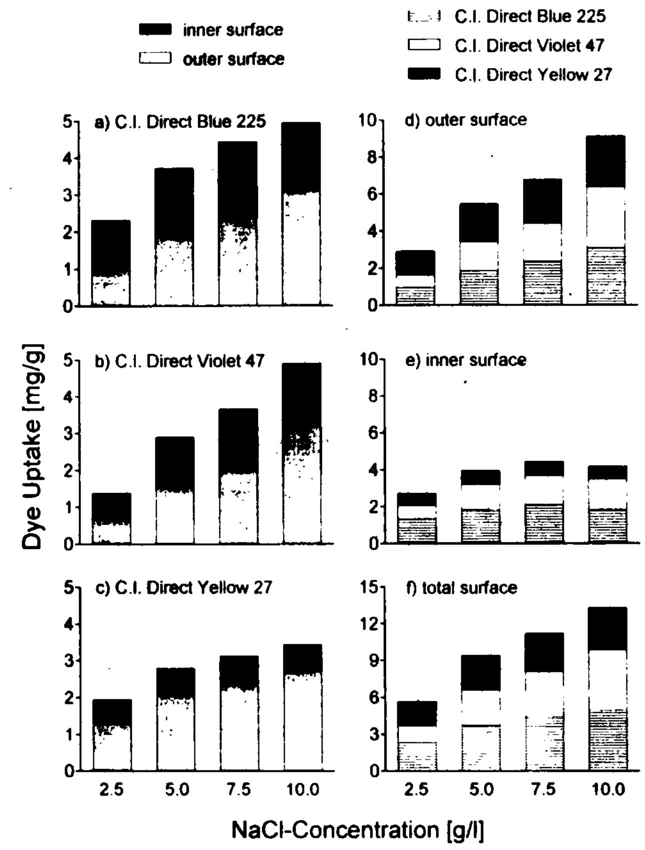


FIGURE 7. Equilibrium trichrome direct dye uptake at the outer (m_s), inner (m_d), and total surfaces of cotton at different salt concentrations.

ACKNOWLEDGMENT

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