THE THIRD STAGE OF THE DIFFUSION PROCESS OF FISETIN MOLECULE IN THE FIBROIN FIBER

**Abstract:** The previous article stated that the diffusion of the dye continues until it reaches an equilibrium concentration in the entire volume of the fiber. This period was mentally divided into three stages: 1) adsorption of fisetin molecules on the surface of fibroin fibers; 2) moment when fisetin molecules reach the center of the fibroin fiber. Since the first stage occurs almost instantaneously, it is almost impossible to separate this stage from the second stage during which the actual dyeing occurs. We combined the first and second stages of diffusion and devoted a previous article to them. The third stage begins after the completion of the second and continues until the equilibrium concentration is restored in the entire volume of the fiber. This article is focused on the third stage of diffusion of flavonoid fisetin molecules in the fibroin fiber. This article also uses a three-dimensional physical model of the diffusion of dyes in the fiber. We established mathematical relations that describe the kinetics of dye diffusion at the third stage of the dyeing process.

**Keywords:** dye solution temperature; electrolyte concentration in the solution; diffusion kinetic parameters; physical model of distribution; kinetic characteristic of diffusion.

**Results and discussion (continuation of [1])**

By using the three-dimensional model and carrying out simple mathematical calculations, it can be shown that at the moment when the dye reaches the center of the fiber, the concentration of penetrating dye molecules is equal to \( \frac{2}{3} C_\infty \). The model uses figure with volumes equal to \( 2\pi r_0^2 / 3 \) (Fig. 6) to express the concentration. As one can see during the third stage, the remaining volume with concentration: \( C_{t_{III}} \) is equal to \( \pi r_0^2 / 3 \), and in this volume the maximum concentration should be equal to one third of the concentration of the dye at the fiber edges: \( C_\infty \), which is equal to \( C_\infty / 3 \). Consequently, the dye diffusion intensity in the fiber at the third stage of the process is determined by the first Fick's law, the difference in concentration potentials at the edges and in the center of the fiber, can be composed as the following equation:

\[
\frac{1}{r_0} \frac{dQ_{III}}{dt} = -D \frac{3}{r_0} (C_\infty - C_{t_{III}}) Sm dt, \tag{21}
\]

where \( dQ_{III} \) is mass quantity of fiber transported over time \( dt \), inside the fibers at the third stage of diffusion; \( C_{t_{III}} \) is the concentration of dye molecules penetrating during an arbitrary period of time \( t \), that has passed since the beginning of the third stage; \( D \) is the diffusion coefficient; \( S \) is the active area of the fiber.
In order to make sure that $S$, which is used in the formula (21), and determines area of the active fiber, is equal to $S = 2\pi r_0$, we shall take note of three-dimensional model of fiber (Fig.6) In this model, the height of fibroin fiber shown as a transparent cylinder, equals to one. Taking this into account, the formula (21) can be written as:

$$dQ_{III} = D\frac{1}{r_0} \frac{C_\infty - C_{i,III}}{2\pi r_0 m_o dt} = 2\pi D\left(\frac{1}{3} C_\infty - C_{i,III}\right) m_o dt.$$  \hspace{1cm} (21 a)

Figure 6 shows that the mass quantity of the transported dye at the third stage of diffusion can be expressed by the following formulas:

$$Q_{III} = \frac{1}{3} \pi r_0^2 m_o C_{i,III}.$$ \hspace{1cm} (22)

By differentiating (22) with respect to $C_{i,III}$, the following equation is obtained:

$$dQ_{III} = \frac{1}{3} \pi r_0^2 m_o dC_{i,III}.$$ \hspace{1cm} (22 a)

By comparing (21a) and (22a) with respect to $dQ_{III}$, the following equation is obtained:

$$\frac{1}{3} C_\infty - C_{i,III} = 6\frac{D}{r_0^2} dt.$$ \hspace{1cm} (23)

By integrating right-hand side of (23) to $C_{i,III}$, and left-hand side to $dt$, we obtain the following:

$$-\ln\left(\frac{1}{3} C_\infty - C_{i,III}\right) = 6\frac{D}{r_0^2} t + c_j.$$ \hspace{1cm} (24)

By accepting the end of the second stage and beginning of the third stage as check time, we determine the value of the integration constant $- c_j$. The third stage of the diffusion process begins at $t_{III} = 0$. At that moment $C_{i,III}$ is equal to 0. Considering that (24):

$$c_j = -\ln\left(\frac{1}{3} C_\infty\right).$$

By adding $c_j$ to (24), we obtain the following equation:

$$-\ln\left(\frac{1}{3} C_\infty - C_{i,III}\right) = 6\frac{D}{r_0^2} t - \ln\left(\frac{1}{3} C_\infty\right).$$ \hspace{1cm} (25)

or

$$\frac{C_{i,III}}{C_\infty} = \frac{1}{3} \left[1 - \exp\left(-\frac{6D}{r_0^2} t\right)\right].$$ \hspace{1cm} (26)

(26) is the kinetic equation for the concentration of dye molecule that penetrates the fiber at the third stage of the diffusion process.

The kinetic dependence of the relative concentration of fisetin molecules in the fibroin fiber at the third stage of the diffusion process, which is shown in (Figure 7), was constructed based on this equation.

The kinetic equation for the diffusion of dye molecules into fibers (26) at the third stage of the process is especially significant due to the fact that by applying these equations at a given temperature and concentration of the dye, the diffusion coefficient $D$ can be determined. The results of our measurements were used to determine $D$.

As shown in Figure 1 (in previous article), molecules of fisetin dye that penetrate fibroin fibers introduced into the dye solution at boiling point (373 K) have the maximum concentration equal to
\( C_{\text{max}} \approx 0.56 \text{g/kg} \). This concentration is established in 30 minutes. The comparison shows that the concentration of penetrating dye molecules in the fiber in the second and third stages of diffusion is equal to \( C_{\text{II}} : C_{\text{III}} = 2:1 \). Using this dependence and knowing that \( C = C_{\text{II}} + C_{\text{III}} \), we can construct the following equations:

\[
C_{\text{max}} \approx 0.37 \text{g/kg} \quad \text{and} \quad C_{\text{max}} \approx 0.19 \text{g/kg}.
\]

We used 4g of fisetin to prepare an aqueous solution of the fisetin dye for each 100g of fibroin. Consequently: \( C_o = 40 \text{g/kg} \).

To calculate average value of \( D \), we use the ratios of the volumes of the second and third stages equal to 2:1, consequently, the ratios between the time of fiber dyeing at the second and third stages is also 2:1. Therefore, by inserting the values of the duration of the second stage: \( t_{\text{II}} = 20 \text{minutes} \) and the duration of the third stage: \( t_{\text{III}} = 10 \text{minutes} \), the cross-sectional area of the natural silk fiber is \( \approx 370 \text{ \mu m}^2 \) and by accepting the shape of the fiber as a cylinder, we obtain the value for the radius of the cylinder \( r_0 = 10.8 \cdot 10^{-6} \text{m} \).

To calculate \( D \) by (25), we use the following values:

\[
D = \frac{r_0^2}{6t} \ln \left( \frac{C_o}{C_{\text{max}}} - C_{\text{III}} \right) = \frac{118 \cdot 10^{-12}}{6 \cdot 600} \ln \left( \frac{40}{40 - 0.19} \right) \frac{m^2}{s} = 1.56 \cdot 10^{-12} \frac{m^2}{s} = 1.56 \cdot 10^{-12} \frac{cm^2}{s}.
\]

We use Nernst-Einstein equation that established relationship between mobility, diffusion, and temperature of the medium to calculate the mobility of the fisetin dye molecule in the fibroin+water medium [3]:

\[
D = \frac{u k T}{s},
\]

where \( u \) is the mobility of molecules, \( k \) is the Boltzmann factor, \( T \) is the temperature of the medium. Consequently:

![Figure 7](image-url)
\[
\frac{u}{kT} = \frac{D}{1.38 \times 10^{-23} \cdot 373} \frac{m^2}{s} \cdot \frac{1}{\frac{J}{K}} = 3.03 \cdot 10^4 m/(N\cdot s).
\]

Consequently, the mobility of fisetin molecules in the fibroin+water medium at the temperature of 373 K is 3.03 \cdot 10^4 m/(N\cdot s).

Due to the fact that in dye-fiber system, the relativity properties of diffusion and sorption determine the color formation rate [3] and correspond to the slow diffusion of the fisetin dye molecules into natural silk fiber \(D = 1.56 \cdot 10^{-16} m^2/s\) and high-speed sorption \((u = 3.03\cdot10^4 m/(N\cdot s))\) demonstrate affinity between the fisetin dye and the fibroin protein.

As kinetic and thermodynamic parameters, there is a very complex relationship between the diffusion rate and the affinity between the dye and the fiber [4]. Textile materials have a specific requirement for the fiber and dye diffusion and sorption processes must simultaneously be active during interaction. Color cannot be formed if any of those conditions is not met.

Electrostatic forces are undoubtedly affect the diffusion process. It is generally believed that a moderately high concentration of a medium high concentration of low-molecular electrolyte, such as NaCl, will remove any such effects and it is confirmed by the fact that \(D\) at moderately high ionic forces, becomes virtually non-affected by the total charge [5]. However, the added electrolyte, apparently, will have minor effect if it (the added electrolyte) initially has the universally identical concentration [6].

Another important point is that, on the one hand, we are trying to create dyes with increased affinity for the fiber, since this provides high dyeing fastness to wet treatments, on the other hand, the increased dye affinity for the fiber reduces the diffusion rate, and, consequently, speed of dyeing process. This contradiction can be overcome in real conditions by building the technological process to ensure a decrease in the affinity of the dye at the time of the fiber entering the dye solution and to create conditions for the manifestation of this affinity after the diffusion is completed. Temperature changes, solvation of dye with auxiliary substances of hydrophilic solvents, etc. are used for these purposes.

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