

Temperature Dependence of Diffusion of a Disperse Dye in the Multiple Layers of Nylon Fabric

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SYNOPSIS

The apparent diffusion coefficients of a disperse dye in the multiple layers of nylon fabric at 45–75°C are determined as the dyeing model of the textile assembly. The modified pore model is introduced to explain the diffusion behavior in the multiple fabric. The Arrhenius plot of the diffusion coefficient of dye in the spaces or pores of nylon fabric gave a straight line and the activation energy of diffusion was about 9.4 kcal/mol. The temperature dependence of the dye diffusivity in polymer matrix was quantitatively described by a WLF-type relation,

$$\log a_T = - \frac{3.55(T - T_s)}{26.8 + T - T_s}$$

where a_T is a shift factor of diffusion and T_s is the reference temperature.

INTRODUCTION

It has been recently indicated that the rate of sorption of dyes by a textile assembly was influenced by mass-transfer processes in the liquid phase.¹ The diffusional boundary layer model has been applied to such a problem—after having reached the fabric surface by the combination of convective and diffusion processes in the liquid phase, the dye was considered to be immediately sorbed at the surface of the fiber and then to diffuse into the fiber from the surface.

Sibusawa et al.² have studied the rate of dyeing of nonionic dyes on nylon 6 and polyester yarn, and they suggested that the sorption delay due to the diffusional boundary layer was inevitable in dyeing of the fiber assembly even if the dye bath was well stirred. McGregor et al.³ have extended this fundamental treatment to included practical systems in the dyeing of an acid dye on a nylon fabric. In our previous paper,⁴ the concentration distribution of a disperse dye in the multiple layers of nylon fabric was investigated. It was observed that the surface

concentration of dye in the multiple fabric was increased with dyeing time and that the value was smaller than the dye uptake at equilibrium dyeing. In this case, the increase of surface concentration was attributable to the resistance to dye transport across the diffusional boundary layer. The observed diffusion coefficient was reasonably explained by assuming the pore model. In this paper, a further experiment was carried out over the temperature range 45–75°C. The diffusional behavior of the dye in the multiple layers of nylon fabric was discussed in terms of the diffusional boundary layer model and the modified pore model.

THEORETICAL

Diffusional Boundary Layer Model

A theoretical treatment of the diffusional boundary layer model has been presented in detail by McGregor et al.¹ The theoretical equation of the concentration distribution in a slab is given⁴

$$\frac{C_t}{C_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L \cos(\beta_n x / \ell) \exp(-\beta_n^2 D_f t / \ell^2)}{(\beta_n^2 + L^2 + L) \cos \beta_n} \quad (1)$$

where C_t and C_∞ (mol/kg) are the concentration at time t and equilibrium, x (cm) is the distance, D_f (cm^2/s) is the diffusion coefficient in the substrate, ℓ (cm) is the half thickness of the slab, β_n represents the positive roots of $\beta \tan \beta = L$, and L is a boundary layer parameter respectively. As far as nonionic dyes on hydrophobic fibers are concerned, L is fixed by eq. (2)¹

$$L = \frac{D_b \cdot \ell}{D_f \cdot K \cdot \delta_D} \quad (2)$$

where D_b (cm^2/s) is a diffusion coefficient of dye in water, K is a partition coefficient, and δ_D (cm) is a thickness of the diffusional boundary layer.

Modified Pore Model

The textile assembly can be regarded as a porous media. The structure of a porous substrate consists of the interconnected space or pore and polymer matrix. In the dyeing processes, dye molecules diffuse through the water-filled pores with simultaneous adsorption on pore walls and polymer matrix. In the present work, we assume that the dye adsorbed on pore walls is immobilized, i.e., the surface diffusion is ignored. The total concentration of the dye C (mol/kg) is given the sum of mobile dye molecules in the pore solution whose concentration is C_p (mol/dm³) and dye molecules in the polymer matrix whose concentration is C_i (mol/kg)

$$C = PC_p + C_i \quad (3)$$

where P (dm³/kg) is the porosity defined as the pore volume per unit weight of the substrate.

The pore model proposed by Weisz and Zollinger⁵ was taken into account. If the dye in pore solution and in polymer matrix diffuse independently and the diffusion coefficients of both species are D_p and D_i , the one-dimensional diffusion equation is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(\frac{P_e}{\tau} D_p \frac{\partial(PC_p)}{\partial C} \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial C} \frac{\partial C}{\partial x} \right) \quad (4)$$

where P_e is the porosity defined as a fraction of pore volume in the total volume of the substrate, and τ is the tortuosity factor. The left side of eq. (4) may be regarded as the diffusion of the total species, therefore, it can be rewritten as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_{\text{app}} \frac{\partial C}{\partial x} \right) \quad (5)$$

where D_{app} (cm^2/s) is the apparent diffusion coefficient.

If the relationship between the mobile species in the outer bath and the inner pore liquid is assumed

$$C_p = n \cdot C_s \quad (6)$$

where n is the partition coefficient and C_s (mol/dm³) is the dye concentration in the outer bath.

If the adsorption isotherm obeys Henry's law

$$C/P = K \cdot C_s \quad (7)$$

Substituting eqs. (3), (6), and (7) into eq. (5) yields the following equation

$$\begin{aligned} D_{\text{app}} &= \frac{P_e}{\tau} D_p \frac{\partial(PC_p)}{\partial C} + D_i \frac{\partial C_i}{\partial C} \\ &= \left(\frac{P_e}{\tau} D_p - D_i \right) \frac{\partial(PC_p)}{\partial C} + D_i \\ &= \frac{P_e}{\tau} D_p \frac{n}{K} + \left(1 - \frac{n}{K} \right) D_i \end{aligned} \quad (8)$$

If $n \approx 1$ and $K \gg 1$, then

$$D_{\text{app}} = \frac{P_e}{\tau} D_p \frac{1}{K} + D_i \quad (9)$$

EXPERIMENTAL

The fiber used was a nylon 6 taffeta and the fabric density of warp yarn was 42/cm (70 denier, 12 filaments) and that of weft yarn was 32/cm (70 denier, 24 filaments). The dye used was *p*-aminoazobenzene (henceforth *p*AAB). The diffusion coefficient of *p*AAB in water was measured by the capillary method.⁶ Nylon fabric was dyed in the dye bath ($5.1 \times 10^{-5} - 1.5 \times 10^{-4}$ mol/dm³) for 13–20 days to attain the adsorption equilibria. Seven layers of nylon fabric were stacked in a stainless steel holder and the dye bath (1.27×10^{-4} mol/dm³) was magnetically stirred at 0 to 140 rpm; the multiple layers of nylon fabric interposed between a stainless steel circular plate (diameter 65 mm and thickness 4 mm) and a stainless steel ring (inner diameter 35 mm, outer diameter 65 mm, and thickness 4 mm), and settled on three points with bolts and nuts, as shown in Figure 1; one side exposed, through an open window to the solution of the penetrant. The disks (fabric assemblies) were oriented to the direction of

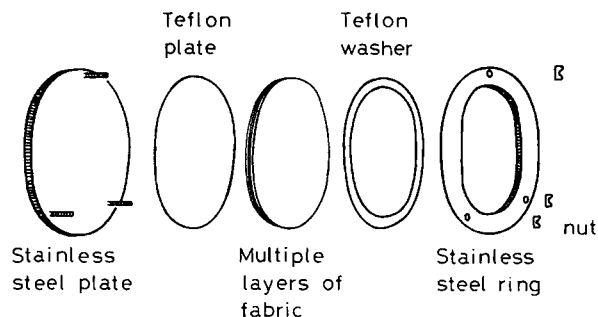


Figure 1 Stainless steel holder.

flow. The apparatus used for dyeing and other procedure was described elsewhere.⁴

RESULTS AND DISCUSSION

In practical dyeing of fiber assemblies, such as yarn packages or fabrics, the dye liquor flow through the spaces between the individual yarns in the fabric and filaments in the yarn. However, the dye liquor did not flow through these spaces provided the impermeable holder was used as shown in Figure 1. Therefore, the multiple layers of fabric can be treated as a slab. Our earlier paper⁴ has demonstrated that such a treatment was actually valid with stirring at 0–140 rpm. Figure 2 shows the concentration distribution curves in the multiple layers of

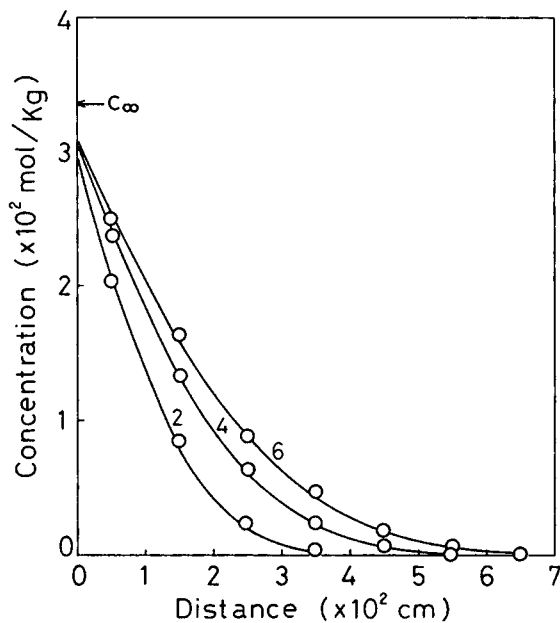


Figure 2 Concentration distribution of pAAB in the multiple layers of nylon fabric at 60°C. Stirring rate is 140 rpm. Figures on curves are time of diffusion (h). (O) Experimental data; (—) theoretical curve.

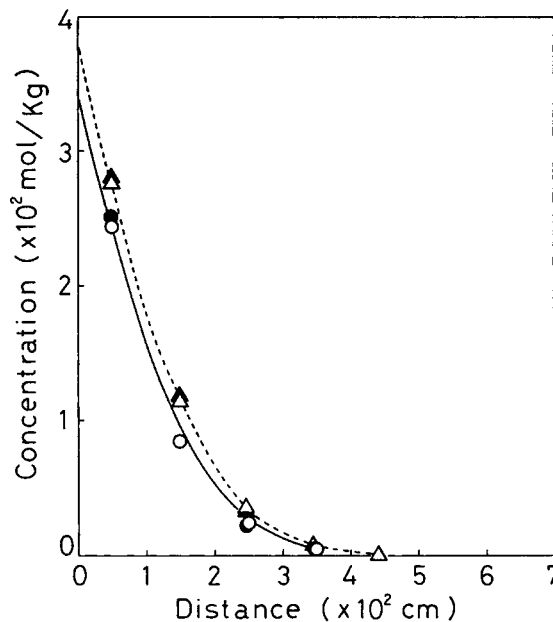


Figure 3 Effect of stirring on concentration distribution of pAAB in the multiple nylon fabric at 50°C for 4 h. (O) 0 rpm; (●) 50 rpm; (Δ) 100 rpm; (▲) 140 rpm.

— : $D_f = 8.19 \times 10^{-9}$, $L = 16$;
 - - - : $D_f = 8.19 \times 10^{-9}$, $L = 30$.

nylon fabric at 60°C at the rate of the stirring 140 rpm. The diffusion coefficient of the dye in the multiple layers of nylon fabric D_f and the boundary parameter L were determined by the curve fitting

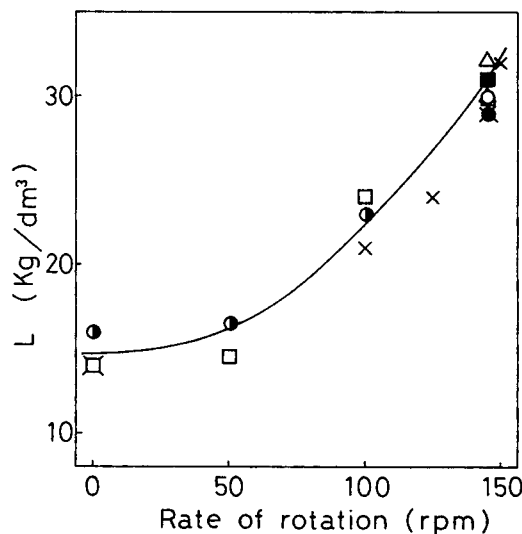


Figure 4 Effect of stirring on L . (x) 40°C; (■) 45°C; (●) 50°C; (Δ) 55°C; (□) 60°C; (●) 65°C; (▲) 70°C; (○) 75°C.

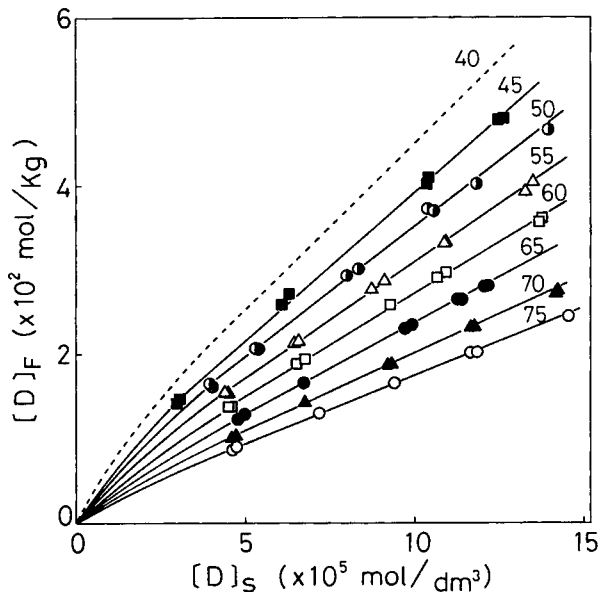


Figure 5 Adsorption isotherms on nylon fabric of pAAB. Figures on curves are temperatures ($^{\circ}\text{C}$).

method using eq. (1). Theoretical curves calculated from eq. (1) using the determined D_f and L are shown with continuous lines in Figures 2 and 3. Figure 3 represents the effect of the rate of stirring on the concentration distribution for the dyeing at 50°C for 4 h. The effect of stirring on the values of L is shown in Figure 4. L was almost independent of temperature. The adsorption isotherms show a linear relation as illustrated in Figure 5, and the apparent partition coefficients K' could be estimated from the slope of the straight line.

Figure 6 shows the relation between the temperature and the values of δ_D calculated from eq. (2) using the estimated apparent partition coefficients.

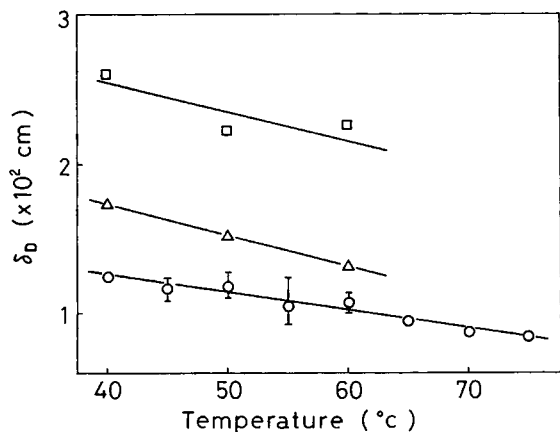


Figure 6 Effect of temperature on δ_D . (\square) 0 rpm; (Δ) 100 rpm; (\circ) 140 rpm.

δ_D tended to decrease as temperature increased. δ_D ranged from 1.2×10^{-2} to 8.4×10^{-3} cm at the rate of stirring 140 rpm. This result appears similar to that observed by Sibusawa et al.²

The plots of $\ln D_f$ and $\ln D_b$ vs. reciprocal temperature are shown in Figure 7. The plot of $\ln D_b$ vs. $1/T$ was found to be linear, and the activation energy obtained for diffusion of pAAB in water was about 3.7 kcal/mol. On the other hand, the plot of $\ln D_f$ vs. $1/T$ is convex downward—the activation energy for diffusion changes with temperature.

The fabric has the spaces or pores between yarns, individual filaments in the yarn and very small pores in the fiber, and polymer matrices. We adopt a simplified model—dye molecules diffuse through these water-filled spaces or pores and polymer matrices. Rattee and Breuer⁷ have suggested that the pore model is not applicable provided the Arrhenius equation does not hold. However, the plot of logarithm of the diffusion coefficient in the pore $\ln D_e$ vs. $1/T$ shows linear relation as discussed below. Therefore, our model represented by eqs. (4) and (7) is valid in this experiment.

The pore model holds several assumptions:

1. The tortuosity factor τ can not be determined experimentally. Then τ is assumed to be equal

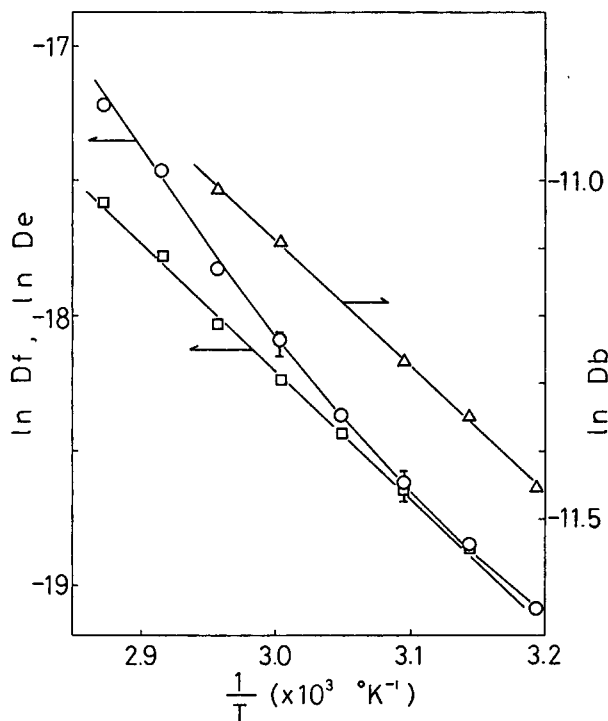


Figure 7 Plots of $\ln D_b$, $\ln D_f$ and $\ln D_e$ vs. $1/T$. (Δ) D_b ; (\circ) D_f ; (\square) D_e .

to $\sqrt{3}^5$ which is obtained in the special case of an isotropic medium.⁸

2. Standing et al.⁹ have showed that the diffusion coefficient of dye in the pore solution D_p was nearly equal to that of bulk solution D_b . However, Hori et al.¹⁰ have pointed out that the diffusivities of diffusing molecules in the pore D_p were smaller than the free diffusion coefficient D_b (cm^2/s) in the bulk solution.
3. The partition coefficient between the mobile species in outer bath and the inner pore liquid is unity.⁵

Therefore, the apparent diffusion coefficient should be compensated for by an appropriate correction factor α . Then, eq. (9) can be rewritten as

$$D_{\text{app}} = \alpha \frac{P_e}{\tau} D_b \frac{1}{K} + D_i \quad (10)$$

It should be noted that eq. (10) needs to fix two variables, α and D_i . If D_i should be negligibly small compared to D_{app} , α can be determined. In regard to the value of D_i , the directly comparable data have not been found. Shibusawa and Iijima¹¹ have found that the diffusion coefficient of *p*AAB in nylon 6 film was $3.53 \times 10^{-10} \text{ cm}^2/\text{s}$ at 40°C . In our earlier paper,⁴ we found that the diffusion coefficient of *p*AAB in the multiple layers of nylon 6 fabric was $5.13 \times 10^{-9} \text{ cm}^2/\text{s}$ at 40°C . The value of the diffusion coefficient in nylon film is about 7% of that obtained by us. The crystallinity of the nylon yarn employed in this paper and that¹¹ of the nylon film which were obtained by density measurement were 27% and 46%, respectively. It is now established that both crystallinity and molecular orientation are significant in strongly affecting the kinetics of dye molecules by substrate. While being drawn, the degree

of crystallinity and orientation is changed. Munden and Palmer¹² have found that there is a marked reduction in the rate of dyeing when nylon 6.6 filaments are drawn. The increase in crystallinity might be expected to decrease the substrate's accessibility, therefore, we presume that the value of D_i for the fabric is smaller than that of the diffusion coefficient in the film as will be demonstrated. Consequently, we can assume that D_i is negligibly small when compared to D_{app} at 40°C . The textile assembly can be regarded as a porous media in which the interconnected space pore exists.¹³ The value of porosity P_e determined was 0.47. Ott and Rys¹⁴ termed the porosity P the "specific pore volume." P was estimated by the porosity P_e and the overall density of the substrate. In this paper, the value of P estimated was $0.785 \text{ dm}^3/\text{kg}$.

If the diffusion based on the segmental motions does not occur, the second term in the right side of eq. (10) can be ignored and eq. (11) can be obtained

$$D_e = \alpha \frac{P_e}{\tau} D_b \frac{1}{K} \quad (11)$$

where D_e denotes the diffusion coefficient of dye in the spaces or pores of fabric. The diffusion coefficients of the dye (D_b , D_{app} , D_e , and D_i) and the apparent partition coefficient (K') at various temperatures are summarized in Table I.

D_i is negligibly small as mentioned above, therefore, the value of α calculated from eq. (11) using the values given in Table I was 0.897 at 40°C . The values of D_e and D_i calculated from eq. (10) using the estimated values and the value of α are given Table I (columns 5 and 6). The plot of $\ln D_e$ vs. $1/T$ shows a linear relation as illustrated in Figure 7. The activation energy for diffusion in the interconnected spaces or pores of the fabric was about

Table I The Diffusion Coefficients of the Dye and the Apparent Partition Coefficients at Various Temperatures

Temp. ($^\circ\text{C}$)	D_b ($\times 10^5 \text{ cm}^2/\text{s}$)	K' (dm^3/kg)	D_{app} ($\times 10^9 \text{ cm}^2/\text{s}$)	D_e ($\times 10^9 \text{ cm}^2/\text{s}$)	D_i ($\times 10^9 \text{ cm}^2/\text{s}$)
40*	1.06	395	5.13	5.13	—
45	1.18	349	6.53	6.46	0.075
50	1.28	306	8.19	7.99	0.202
55	—	273	10.50	9.80	0.735
60	1.53	241	13.90	12.10	1.85
65	1.65	214	18.30	15.30	3.63
70	—	180	26.10	19.00	7.13
75	—	160	33.30	23.20	10.10

* See ref. 4.

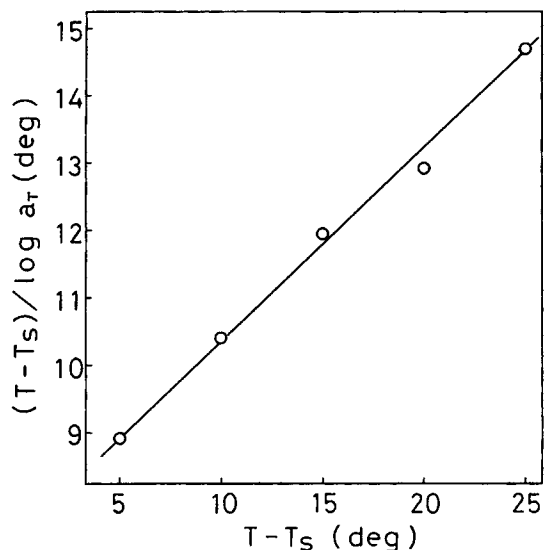


Figure 8 Plot of $(T - T_s) / \log a_T$ vs. $T - T_s$. Solid line is calculated using eq. (12).

9.4 kcal/mol. Iijima et al. have found that the diffusion coefficients of pAAB in nylon 6 film at 60°C were about $2.1 \times 10^{-9} \text{ cm}^2/\text{s}$ ¹¹ and $2.90 \times 10^{-9} \text{ cm}^2/\text{s}$ ¹⁵. The value of D_i estimated at 60°C was $1.85 \times 10^{-9} \text{ cm}^2/\text{s}$. Then D_i was smaller than the diffusion coefficient in the film. Dye diffusion in the polymer matrix is considered to occur because of the thermal motion of polymer segment. The semiempirical WLF equation, describing the variation with temperature of the polymer properties, has been employed for explaining the diffusion in the synthetic fibers¹⁶

$$\log a_T = \log \left(\frac{D_{is}}{D_i} \right) = - \frac{C_1(T - T_s)}{C_2 + T - T_s} \quad (12)$$

where a_T denotes the temperature shift factor of diffusion, D_{is} is the diffusion coefficient in the polymer matrix at reference temperature T_s , and C_1 and C_2 are constants. Shibusawa and Iijima¹¹ have found that the glass transition temperature (T_g) of nylon in water was $\approx 0^\circ\text{C}$. When we select $T_s = 50^\circ\text{C}$ ($= T_g + 50$), the plot of $(T - T_s) / \log a_T$ vs. $T - T_s$ gives a good straight line as illustrated in Figure 8. The values C_1 and C_2 calculated from the slope and intercept are 3.55 and 26.8, respectively. The temperature dependence of the dye diffusivity in polymer matrix obeyed the WLF equation.

CONCLUSIONS

The concentration distribution of a disperse dye in the multiple layers of nylon fabric at 45–75°C is investigated. The estimated values of thickness of diffusional boundary layer ranged from 1.2×10^{-2}

to $8.4 \times 10^{-3} \text{ cm}$ at a stirring rate of 140 rpm. As the diffusion of dye in polymer matrix cannot be ignored at a higher temperature, the modified pore model is introduced. The Arrhenius plot of the diffusion coefficients in the interconnected spaces or pores of the fabric gives a straight line and the activation energy of diffusion is about 9.4 kcal/mol. The temperature dependence of the diffusion coefficient of pAAB in polymer matrix is quantitatively described by a WLF-type relation

$$\log a_T = - \frac{3.55(T - T_s)}{26.8 + T - T_s}$$

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