

# Disperse Dyeing of Polyester Fibers: Kinetic and Equilibrium Study

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Received 3 January 2001; accepted 3 July 2001

**ABSTRACT:** The effect of temperature on the dyeing rate constant  $k$ , diffusion coefficient  $D$ , time of half-dyeing  $t_{1/2}$  was evaluated for the dyeing of polyester fibers with two disperse dyes, an azo and an anthraquinone dye. Activation energies of diffusion  $E$  were calculated. The polyester dyeing equilibrium was also studied and the partition coefficient  $K$  and standard affinity  $\Delta\mu^\circ$  at various temperatures were determined for the anthraquinone dye. Standard enthalpy  $\Delta H^\circ$  and standard entropy  $\Delta S^\circ$  of dyeing were also obtained. The same equilibrium parameters were not obtained for the azo dye because of its dyeing behavior. A similar kinetic and equilibrium study was made for the pure azo and anthraquinone compounds free from the dispersing agents present in the commercial dyes and the results are discussed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2785–2790, 2002; DOI 10.1002/app.10254

**Key words:** disperse dyes; polyester fibers; kinetic and equilibrium parameters

## INTRODUCTION

Polyester fibers can be dyed to useful depths only by dyes with low solubilities in water. Disperse dyes are the most important dyes used in dyeing polyester fibers. Because of their high crystallinity and orientation these fibers can be dyed with a satisfactory rate of dyeing, either at temperatures in the region of 130°C or at lower temperatures in the presence of an accelerating agent.

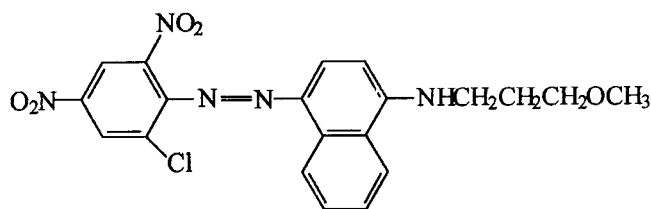
Thermodynamics and kinetics of dyeing have been extensively studied by many researchers (indicatively<sup>1–10</sup>). There are also references on the dyeing characteristics of both natural<sup>11–14</sup> and synthetic fibers.<sup>15–22</sup> The dyeing behavior of polyester fibers modified<sup>23</sup> or not was also studied in the presence of a carrier or at high temperature, both with single disperse dyes<sup>24–31</sup> or combinations<sup>32–34</sup> of dyes.

In this study we report the results of an investigation into the quantitative evaluation of the dyeing behavior, both kinetic and thermodynamic, of two disperse dyes **1** and **2** on polyester fibers.

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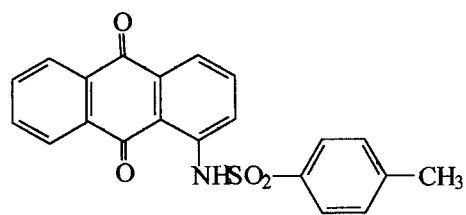
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*Journal of Applied Polymer Science*, Vol. 83, 2785–2790 (2002)  
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**1**

Disperse Blue 321

(MW = 443.5)

**2**

Disperse Red 86

(MW = 377)

We studied the effect of temperature as a dominant factor on the kinetic and equilibrium parameters of dyes **1** and **2** in the dyeing of polyester. Structural differences between the two dyes are correlated with differences in the diffusion of the dyes in the fiber.

To investigate the effect of dispersing agents on the dyeing of polyester with the two dyes the study was repeated for the pure compounds **1** and **2** free from the dispersing agents present in the commercial dyes.

## EXPERIMENTAL

### Materials

Bleached polyester fabric (PET 167dtex, 130 filaments, 225 g/m<sup>2</sup>, fiber diameter 30 μ) was used.

Viosperse Blue RFS (C.I. Disperse Blue 321, **1**; Viochrom S.A., Greece) and Viosperse Brilliant Pink 2GLFS (C.I. Disperse Red 86, **2**; Viochrom S.A.), 40 and 36%, respectively, in pure dye were used for the dyeings.

Laboratory-grade chemicals were used in the study.

The amounts of dyes quoted in this study correspond to 100% of pure material.

### Methods

#### Dyeing

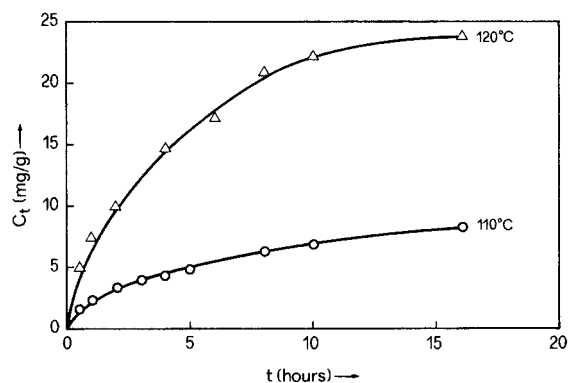
Dyeings were carried out in a Rotadyer dyeing apparatus (John Jeffreys Ltd., Rochdale, Banbury, UK) at temperatures of 110, 120, 130°C and for various time intervals using a liquor ratio of 1 : 20 at pH 4.6. The samples were then washed with running water and squeezed.

### Determination of Dye Absorbed on the Fiber

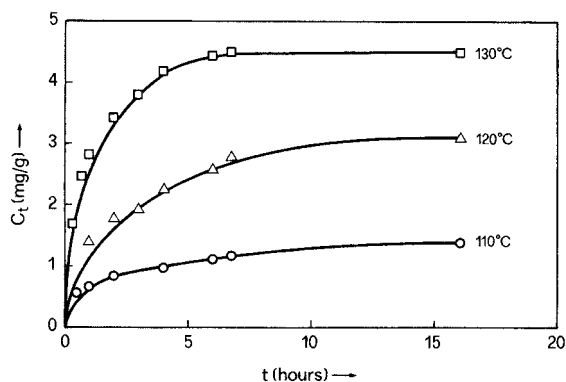
This was obtained by extracting the absorbed dye with chlorobenzene and measuring the dye concentration of the chlorobenzene solutions using a Shimadzu UV-2101 PC spectrophotometer (Shimadzu, Japan) at 513.5 and 598.5 nm ( $\lambda_{\max}$  of C.I. Disperse Red 86 and C.I. Disperse Blue 321, respectively, in chlorobenzene). All the determinations were made in duplicate, and the figures given are the mean values of the two readings.

## RESULTS AND DISCUSSION

The rate of dyeing curves for dyes **1** and **2** at temperatures of 110, 120, and 130°C are given in Figures 1 and 2, respectively. The time of half dyeing  $t_{1/2}$  was estimated for each isotherm and the corresponding values are given in Table I. Time of half dyeing estimations provided an indirect measure of the rate of diffusion of the dyes into the fiber.



**Figure 1** Rate of dyeing curves for Disperse Blue 321 at 110 and 120°C (initial amount of dye 40 mg/g fiber).



**Figure 2** Rate of dyeing curves for Disperse Red 86 at 110, 120, and 130°C (initial amount of dye 40 mg/g fiber).

By plotting  $c_t$  (dye absorbed on the fiber at time  $t$ ) versus square root of time, the rate of dyeing constants  $k$  were obtained at the above temperatures (Fig. 3) according to the rate law expressed in eq. (1):

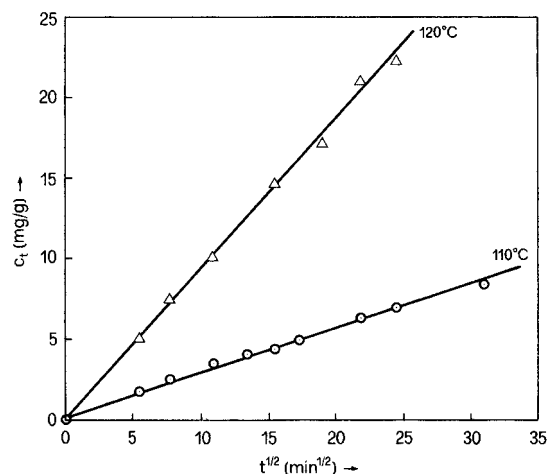
$$c_t = k \sqrt{t} \quad (1)$$

The  $k$  values for both dyes **1** and **2** at the temperatures studied are given in Table I. It was concluded that the dyeing rate constants  $k$  increase with increasing temperature, as was expected.

The diffusion coefficient values  $D$  for the two dyes in polyester fiber at the same temperatures were calculated using eq. (2):

$$D = \frac{\pi r^2}{16t} \left( \frac{C_t}{C_\infty} \right)^2 \quad (2)$$

where  $r$  is the radius of the fiber ( $15 \times 10^{-3}$  mm),  $c_t$  is the dye uptake at time  $t$ , and  $c_\infty$  is the equilibrium dye uptake (in the present study taken as the dye uptake after 16 h).



**Figure 3** Variation in uptake of Disperse Blue 321 with square root of time.

librium dye uptake (in the present study taken as the dye uptake after 16 h).

Plots of  $c_t/c_\infty$  versus square root of time were linear and diffusion coefficients  $D$  were obtained from their slopes (Fig. 4).

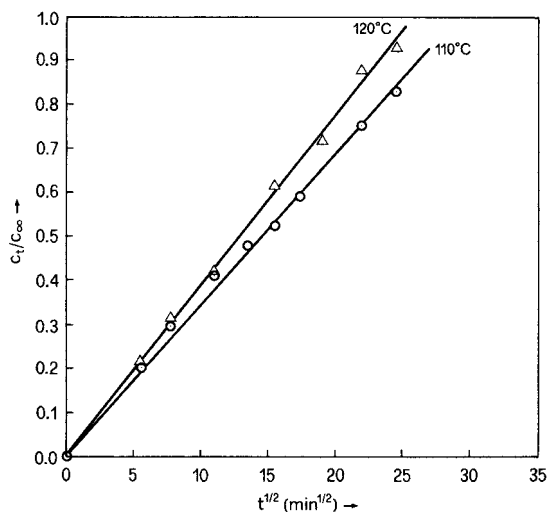
Given that the diffusion coefficient is proportional to the square of  $c_t$ , it increases with increasing temperature (Table I). The diffusion increases because the segmental mobility of the polyester increases with temperature above the glass-transition temperature.

Diffusion is obviously a function of the ease of penetration of the dye molecules through non-crystalline regions of the fiber. Differences in behavior between the two dyes indicate that dyeing is a function of the dye structure as well.

In the simplest approximation the diffusion coefficient is inversely proportional to the molecular volume to the power 0.6 and therefore smaller molecules have a higher diffusion coefficient.<sup>35</sup>

**Table I** Dyeing Rate Constants  $k$ , Diffusion Coefficients  $D$ , Times of Half Dyeing  $t_{1/2}$ , Activation Energies of Diffusion  $E$  for Dyes **1** and **2** and Partition Coefficient  $K$ , Standard Affinity  $\Delta\mu^\circ$ , Standard Enthalpy  $\Delta H^\circ$ , and Standard Entropy  $\Delta S^\circ$  for Dye **2** at Different Temperatures (depth of dyeing 4% o.w.f., pH 4.6)

Dye	$T$ (°C)	$t_{1/2}$ (min)	$k$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	$D \times 10^6$ (mm <sup>2</sup> /min)	$E$ (kJ/mol)	$K$	$-\Delta\mu^\circ$ (cal/mol)	$\Delta H^\circ$ (cal/mol)	$\Delta S^\circ$ (cal/mol <sup>-1</sup> K <sup>-1</sup> )
<b>1</b>	110	205.0	0.285	0.052	22.8				
	120	154.0	0.955	0.063					
<b>2</b>	110	100.8	0.076	0.077	90.3	8.62	1639.4	-1620	-20.4
	120	78.6	0.160	0.114					
	130	32.4	0.352	0.326					



**Figure 4** Variation of  $c_t/c_\infty$  with square root of time for Disperse Blue 321.

However, because no dye molecule is spherical it seems likely that molecular shape will also play a role, frequently the most important, and dye **2** with the anthraquinoid structure is at an advantage over the highly substituted azo dye **1**.

On the other hand, eq. (2) shows that the diffusion coefficient as a function of the fiber dimension is inversely proportional to the square of  $c_\infty$  (dye absorbed on the fiber at equilibrium). Thus lower  $D$  values are obtained for the azo dye **1** (high dye uptake,<sup>36</sup> almost quantitative absorption on the fiber at time  $t_\infty$ ) compared to values obtained for the anthraquinoid dye **2** (low to medium uptake<sup>37</sup>).

The linear isotherm

$$K = c_{f,\infty}/c_{s,\infty} \quad (3)$$

where  $c_{f,\infty}$  and  $c_{s,\infty}$  are the equilibrium concentrations of dye on the fiber and in the dyebath, respectively, is preferred for describing the equilibrium in terms of constants depending on temperature. The partition coefficients  $K$  of dye **2** at temperatures of 110, 120, and 130°C were thus obtained and are given in Table I.

Contrary to expectations the absorption isotherms of dye **1** obtained experimentally were not typical for disperse dyeing of hydrophobic fibers but of a type rarely found,<sup>38</sup> as a result of its high affinity and rate of absorption on the polyester fiber [Figs. 5(a) and 5(b)].

By treating  $K$  as an equilibrium constant, the standard affinity  $\Delta\mu^\circ$ , the standard enthalpy  $\Delta H^\circ$ ,

and the standard entropy  $\Delta S^\circ$  of dyeing with **2** were obtained (Table I) according to eqs. (4) and (5):

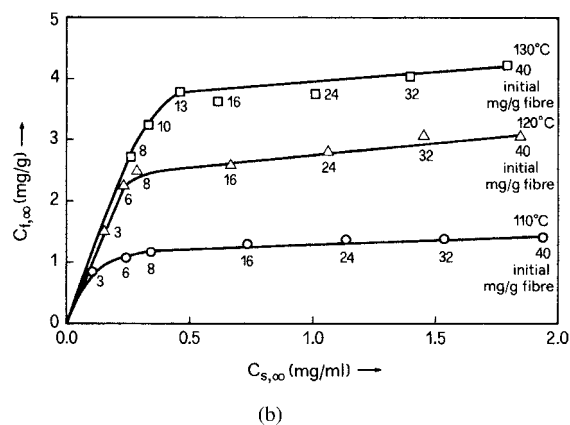
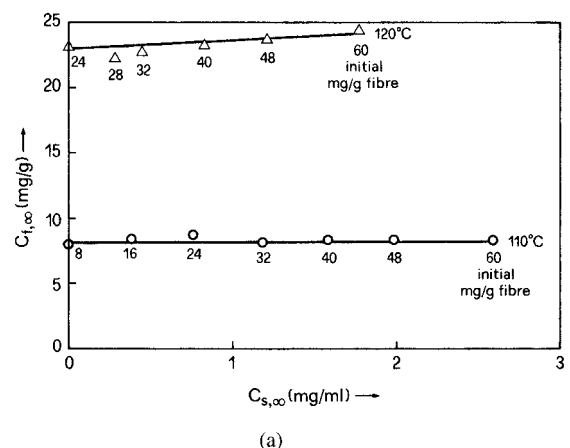
$$-\Delta\mu^\circ = RT \ln K \quad (4)$$

$$\Delta\mu^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

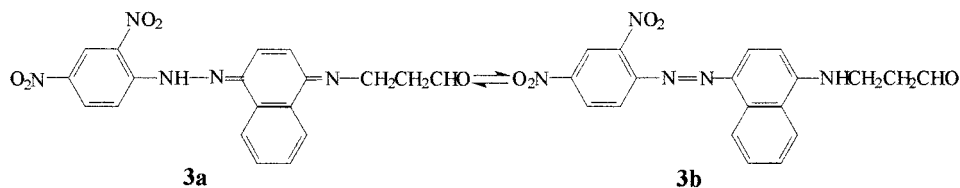
The least-squares method gives the  $\Delta H^\circ$  and  $\Delta S^\circ$  values as the intercept and the slope of the regression curves, respectively.

It can be noted that  $K$  values increase with increasing temperature. Negative values of both  $\Delta\mu^\circ$  and  $\Delta H^\circ$  indicate that the dyeing process of polyester with dye **2** is an exothermic process.

A similar study was also made with the pure azocompounds **1a** and **2a**, free from the dispersing agents present in the corresponding commercial dyes.



**Figure 5** (a) Absorption isotherms of Disperse Blue 321 at 110 and 120°C ( $t_\infty = 16$  h). (b) Absorption isotherms of Disperse Red 86 at 110, 120, and 130°C ( $t_\infty = 16$  h).



Scheme 1 Degradation product of compound 1.

In this preliminary investigation compounds **1a** and **2a** were applied in depths of dyeing of 1, 2, and 2.5% on the weight of the fiber (o.w.f.) from an acetone solution, which was added to the appropriate amount of buffer solution. The solvent was removed by gentle heating before the dyeing procedure. A depth of dyeing higher than 2.5% o.w.f. could not be applied in the case of **1a** and **2a** because of the absence of dispersing agents.

Dispersing agents used in the manufacture and application of insoluble dyes in a dispersion form not only have a solubilizing effect but also influence the diffusion of the dyes into the polyester.<sup>39,40</sup> Thus the results of this preliminary study could not be correlated with the corresponding results of the commercial dyes **1** and **2** (depth of dyeing 4% o.w.f.).

In this preliminary study significantly higher  $D$  values were obtained for **1a** and **2a** compared to those of **1** and **2**, because of the fact that an excess of either **1a** or **2a** was determined as diffused dye, although it was only superficially absorbed on the fiber as a result of the absence of dispersing agents. This result was microscopically confirmed. Thus kinetic and thermodynamic parameters of the two compounds **1a** and **1b** are not given.

At temperatures of 110 and 120°C and after 18 h ( $t_{\infty}$ ) green shades were observed on the polyester fabrics dyed with **1a**. This could be attributed to reductive degradation of the compound **1a**. The same degradation was observed in similar compounds<sup>41</sup> with strong electron acceptor groups in the diazo component, when heated in aqueous dispersions. On the other hand commercial dye **1** diffused in polyester fiber did not show such degradation. Thus it could be assumed that in the case of diffusion interactions between all constituents present in both phases, the solvent and the amorphous region of polyester occupied by the dye protect it, as it were, whereas the superficially adsorbed dye or the dye dispersed in water is left unprotected.

An attempt was made to isolate and identify the degradation product, which appeared bluish

green in polar solvents (water, methanol, acetone) and yellow in nonpolar solvents (toluene, chlorobenzene). According to the fragments in mass spectra of the degradation product, the following structure was tentatively assigned to it (**Scheme 1**). An equilibrium exists between the two forms **3a** and **3b**, which is confirmed by the color change from yellow (nonpolar solvents) to bluish green (polar solvents).

## CONCLUSIONS

The kinetic parameters rate of dyeing constant  $k$ , time of half-dyeing  $t_{1/2}$ , and diffusion coefficient  $D$  were investigated for the dyeing of polyester fibers at temperatures of 110, 120, and 130°C with a disperse azo and a disperse anthraquinone dye. It was found that the above parameters increase with increasing temperature. Activation energies of diffusion  $E$  were also found.

The equilibrium of polyester dyeing with the anthraquinone dye was also studied and the partition coefficient  $K$  and standard affinity  $\Delta\mu^{\circ}$  at the three temperatures mentioned above, standard enthalpy  $\Delta H^{\circ}$ , and standard entropy  $\Delta S^{\circ}$  of dyeing were obtained. It was noted that the absorption isotherms of the azo dye obtained experimentally were not typical of those for disperse dyeing of hydrophobic fibers, but of a type rarely found because of the high affinity and rate of absorption on the polyester fiber.

An attempt was also made to quantitatively evaluate the effect of the dispersing agents present in the commercial dyes on the dyeing behavior of the corresponding compounds. Thus a similar study was made with the pure azo and anthraquinone compounds. The results could not be compared to the corresponding results for the commercial dyes because of experimental difficulties.

The authors thank Dr. L. Kyriazis, Viochrom S.A., Greece, for the provision of the dyes.

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