

# The Kinetics and Thermodynamics of Nylon 6 Fiber Dyeing with Hydrogen Peroxide-Glyoxal Redox System

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**ABSTRACT:** Investigations were focused on the kinetics and thermodynamics of nylon 6 fiber dyeing with the hydrogen peroxide-glyoxal redox system. We tried to understand thoroughly the difference between the new redox and the conventional dyeing system, since the mechanism of redox dyeing is a combination of free radical and ionic dyeing, whereas the conventional system is only ionic. The study consisted of measuring the dyeing transition temperature ( $T_D$ ), diffusion coefficient ( $D_T$ ), activation energies of diffusion, dyeing affinity, and the dyeing enthalpy and entropy. From the experimental results, the dyeing transition temperature ( $T_D$ ) in the redox system is lower than that in the conventional system. But the diffusion coefficient ( $D_T$ ) in the redox dyeing is larger than that in the conventional dyeing. The dyeing affinity of the free radical dyeing type (redox) is lower than that of the ionic type (conventional). Moreover, from the analysis of thermodynamics of dyeing, the enthalpy is found to be positive (endothermal reaction) in the redox system, but it is negative (exothermal reaction) in the conventional one. The entropy is also found to behave similarly, i.e. positive in the redox system, but negative in the conventional dyeing. Finally, the dyeing saturation value in the redox dyeing system is found to be higher than that in conventional dyeing. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 2105–2114, 2000

**Key words:** nylon 6; dyeing; redox system

## INTRODUCTION

Many investigators have reported on the dyeing of nylon 6 fiber with low temperature methods. There are: the use of surface active agent,<sup>1–3</sup> the use of modifying dyestuff,<sup>4</sup> the use of solvent to assist dyeing,<sup>5</sup> the use of formic acid,<sup>6</sup> and the redox dyeing method.<sup>7–13</sup> The redox dyeing method is considered to be the most attractive among them. The method is not only capable of dyeing at a low temperature, about 70°C, but also it is easy to obtain high dye-uptake, high dye fastness, and high dyeing fabric quality. This is attributed to the system generating a free radical to form a covalent bond between the fiber and the dyestuff in dyeing.

Although the redox dyeing system exhibits good dyeing properties, and it is able to dye at a low temperature, its mechanism is not yet fully understood. Therefore, we analyzed the thermodynamics and kinetics of nylon 6 fiber dyeing with the redox system and compared it with conventional acid dyeing in this paper.

## THEORY

### Diffusion Coefficient and its Activation Energy in an Infinite Bath

Analysis of dyeing kinetics is considered to be an important route to understand the mechanism of redox dyeing. According to the simple equation derived from Inoue,<sup>14–17</sup> the diffusion coefficient of nylon 6 fiber dyeing in an infinite bath can be described as:

$$-\ln(1 - (C_t/C_\infty)) = A - (Dt/r^2) + B$$

(as  $C_t/C_\infty > 0.5$ ), (1)

where  $A = 5.85$ ,  $B = 0.346$ , and the rate constant  $k = 5.85 (D/r^2)$ . Thus, it can be rewritten as

$$1/(1 - (C_t/C_\infty)) = 13.9(Dt/r^2) + 1.13$$

(as  $0.16 < C_t/C_\infty < 0.66$ ), (2)

where  $C_t$ ,  $C_\infty$  are the dye-uptake at time  $t$  and equilibrium, respectively,  $r$  is the radius of fiber ( $\mu\text{m}$ ), and  $t$  is the dyeing time (sec).

To evaluate the diffusion coefficient ( $D$ ), based on equation (1) or (2), the diffusion coefficient ( $D$ ) can be obtained from the slope of the plot of  $-\ln(1 - (C_t/C_\infty))$  or  $1/(1 - (C_t/C_\infty))$  against time  $t$ .

Furthermore, in the case of evaluating the diffusion coefficient in free radical dyeing by redox (the redox dyeing is a combination of free radical and cationic dyeing), one can use the equation of Crank and Wilson<sup>17,18</sup> from Fick's second equation,<sup>14-16</sup> since the dyeing rate of free radical dyeing is much more rapid with respect to conventional ionic dyeing. Thus, the equation is expressed as:

$$C_t/C_\infty = 4\sqrt{Dt/\pi r^2}, \quad (3)$$

where  $C_t$  and  $C_\infty$  are the dye-uptake (mg/g) in the free radical dyeing at time  $t$  and equilibrium, respectively. According to equation (3), a straight line of the plot of  $C_t/C_\infty$  v.s.  $\sqrt{t}$  can be obtained and the diffusion coefficient ( $D$ ) can be evaluated from the slope.

Moreover, according to Arrhenius equation, the activation energies ( $E$ ) of diffusion can be obtained from the slope of a plot of  $\ln D$  v.s.  $1/T$ , i.e.,

$$\ln D_T = \ln D_0 - E/RT, \quad (4)$$

where  $D$  is the diffusion coefficient at temperature  $T$  ( $\text{cm}^2/\text{sec}$ );  $D_0$  is a constant; and  $T$  is the absolute temperature ( $^\circ\text{K}$ ).

### Affinity of Acid Dye to Nylon 6 Fiber

As the fiber is dyeing in the dyebath, the dye molecule is moving toward the fiber. This means that the dyestuff has an affinity toward fiber. From the viewpoint of thermodynamics, the affini-

ty of a dye to a fiber can be described as the chemical potential difference of a dye between the phase of fiber and solution. In the dyeing system, the chemical potential in the phase of solution and fiber is;

$$\mu_S = \mu_S^0 + RT \ln a_S, \quad (5)$$

$$\mu_F = \mu_F^0 + RT \ln a_F. \quad (6)$$

At equilibrium,  $\mu_S = \mu_F$ , then

$$-(\mu_F^0 - \mu_S^0) = -\Delta\mu^0 = RT \ln a_F - RT \ln a_S, \quad (7)$$

where  $\Delta\mu^0$  is the difference of a standard chemical potential between two phases; that is the affinity of a dye molecule to the fiber.

Vickerstaff has derived the affinity of dye to fiber according to the different types of dyeing mechanism.<sup>21</sup> It is dependent on the absorption type of a dye molecule to the fiber and also the dissociation state of a dye in the dyebath. For an ionic dyeing of nylon 6 in a redox system, the system can be described as of the type Vickerstaff stated "dyestuff is absorbed in the specific site and dissociated in both phases of fiber and dyebath," therefore the affinity is;

$$a_F = [\theta_D/(1 - \theta_D)][\theta_{Na}/(1 - \theta_{Na})], \quad (8)$$

$$a_S = [\text{Na}]_S[\text{D}]_S, \quad (9)$$

where  $\theta_D$  is the absorption fraction of dye ion (negative) in the total sites,  $\theta_N$  is the absorption fraction of sodium ion in the total sites, and  $[\text{D}]_S$  and  $[\text{Na}]_S$  are the equilibrium concentrations of dyestuff and sodium ion in solution, respectively. If an infinite dyebath is used, the equilibrium concentrations of  $[\text{D}]_S$  and  $[\text{Na}]_S$  are considered to be constants, i.e., the concentrations of  $[\text{D}]_S$  and  $[\text{Na}]_S$  kept constant before and after dyeing.<sup>19,22</sup> Then, in combination of equations (7), (8), and (9), the affinity between fiber and dyestuff is:

$$-\Delta\mu^0 = RT \ln[\theta_D/(1 - \theta_D)][\theta_{Na}/(1 - \theta_{Na})] - RT \ln[\text{Na}]_S[\text{D}]_S, \quad (10)$$

or

$$-(\mu_D^0 + \mu_{Na}^0)/2.303RT = \log[\theta_D/(1 - \theta_D)] + \log[\theta_{Na}/(1 - \theta_{Na})] - \log[\text{D}]_S - \log[\text{Na}]_S. \quad (11)$$

### Dyeing Affinity of Nylon 6 Fiber in the Free Radical Dyeing of Redox System

Since the diffusing rate of a dye molecule to a fiber is much faster in radical dyeing of a redox system, as compared to that in conventional ionic dyeing, the dyeing mechanism can be stated as the third type of Vickerstaff's dyeing mechanism, i.e., the dyestuff is absorbed in the specific site and there is no dissociation in both phases of fiber and dyebath. The activity of dye free radical  $a_F$  in the fiber is:

$$a_F = n/(N - n), \quad (12)$$

where  $N$  is the total number of sites in the fiber, and  $n$  is the number of sites of fiber which are occupied by the dye free radical. Also, the activity of the dye free radical in the dye solution  $a_S$  is:

$$a_S = [D]_S. \quad (13)$$

Let  $\theta_D = n/N$ , then

$$a_F = \theta_D/(1 - \theta_D), \quad (14)$$

where  $\theta_D$  is the absorption fraction of dye free radical occupied in the total sites of fiber.

From equation (7)  $-\Delta\mu^0 = RT \ln a_F - RT \ln a_S$ . Equations (13) and (14) add into  $-\Delta\mu_0$ , then the affinity of dye free radical in the redox dyeing is

$$-\Delta\mu^0 = RT \ln[\theta_D/1 - \theta_D] - RT \ln[D]_S, \quad (15)$$

where  $\theta_D = [D]_S/[S]_{F,R}$ ,  $[D]_R$  is the equilibrium dye-uptake of free radical, and  $[S]_{F,R}$  is the saturation value of dye free radical in the redox system.

### Dyeing Enthalpy and Entropy

We can use the Clausius-Clapeyron equation to calculate the dyeing enthalpy ( $\Delta H^0$ ), i.e.,

$$\Delta H^0 = d(\Delta\mu^0/T)/d(1/T). \quad (16)$$

Based on equation (16), if we plot  $\Delta\mu^0/T$  v.s.  $1/T$ , the value of  $\Delta H^0$  can be obtained from the slope. In case where the slope is a constant, it indicates that  $\Delta H^0$  is not influenced by the temperature. As the temperature is fixed, integrating equation (16) gives:

$$\Delta H^0/T = \Delta\mu^0/T + C, \quad (17)$$

where  $C$  is the integration constant.

If integrating equation (16) from  $T_1$  to  $T_2$ , it is then expressed as

$$\Delta H^0 = (T_2\Delta\mu_1^0 - T_1\Delta\mu_2^0)/(T_2 - T_1), \quad (18)$$

where  $\Delta\mu_1^0$ ,  $\Delta\mu_2^0$  are the affinity at  $T_1$  and  $T_2$ , respectively. Moreover, since it is difficult to get  $\Delta S^0$  from the experimental measurement, the entropy,  $\Delta S^0$  can be calculated from the following equation.

$$\mu^0 = \Delta H^0 - T\Delta S^0. \quad (19)$$

Or, it can be rewritten as;

$$\Delta S^0 = (\Delta H^0 - \Delta\mu^0)/T. \quad (20)$$

### Isothermal Absorption of Acid Dye in Nylon 6 in the Conventional Dyeing System

According to Langmuir's absorption equation, it hypothesizes that: (1). the fiber has specific sites that are able to absorb dye molecules during dyeing, (2). each site can only absorb one molecule, and (3) the dye molecules absorbed in the fiber exhibit no interaction with each other. When nylon 6 fiber is dyed with an acid dye, the end groups ( $-\text{NH}_2$ ) can be regarded as specific sites for dyeing. Thus, the conventional dyeing system will obey the Langmuir equation and both the saturation value of dye in fiber  $[S]_F$  and the rate constant  $k$  can be evaluated.

If  $[D]_F$ ,  $[D]_S$  are the equilibrium concentrations of dyestuff in fiber and dyebath, respectively, the absorption rate of dye molecule to the specific sites is described as follows according to Langmuir's absorption;

$$d[D]_F/dt = k_1[D]_S([S]_F - [D]_F). \quad (21)$$

Also, the desorption rate of dye from the specific site is given by:

$$-d[D]_F/dt = k_2[D]_F. \quad (22)$$

At  $t = \infty$  (equilibrium), the absorption rate is equal to the desorption rate, thus

$$d[D]_F/dt = -d[D]_F/dt, \quad (23)$$

i.e.,

$$k_1[D]_S([S]_F - [D]_F) = k_2[D]_F, \quad (24)$$

or

$$\begin{aligned} (k_2/k_1)[D]_F &= [D]_S([S]_F - [D]_F) \\ &= [D]_S[S]_F - [D]_F[D]_S, \end{aligned} \quad (25)$$

or

$$[D]_S[D]_F = [D]_S[S]_F - (k_2/k_1)[D]_F.$$

Let  $k' = 1/k = (k_2/k_1)$ , then

$$[D]_S[D]_F = [D]_S[S]_F - k'[D]_F \quad (26)$$

or

$$[D]_F = [S]_F - k'[D]_F/[D]_S. \quad (27)$$

Therefore, using a plot of  $[D]_F$  v.s.  $([D]_F/[D]_S)$  by equation (27), we can obtain the value of  $k'$  from the slope of the curve and also get the saturation value of acid dye in fiber,  $[S]_{F,R}$  from the intercept.

### Isothermal Absorption of Acid Dye in Nylon 6 in the Redox System

If  $[D]_F$ ,  $[D]_S$  are the equilibrium concentrations of dyestuff in the fiber and dyebath, respectively and obey the Langmuir's absorption equation, then the absorption rate of a dye molecule to the specific sites of fiber is given as:

$$d[D]_{F,R}/dt = k_{1,R}[D]_S([S]_{F,R} - [D]_{F,R}), \quad (28)$$

where  $k_{1,R}$  is the absorption rate of dye in the redox system; and  $[S]_{F,R}$  is the saturation value of dye in the fiber. If the desorption rate of dye molecule from the specific sites of fiber is only proportional to ionic part of dye absorption (since the redox dyeing system is a combination of ionic and free radical dyeing), the desorption rate of dyestuff is given as;

$$-d[D]_F/dt = k_{2,R}[D]_F, \quad (29)$$

where  $k_{2,R}$  is the desorption rate constant in the redox dyeing system.

As  $t = \infty$  (equilibrium), the absorption rate is equal to desorption rate.

$$d[D]_{F,R}/dt = -d[D]_F/dt \quad (30)$$

or

$$k_{1,R}[D]_S([S]_{F,R} - [D]_{F,R}) = k_{2,R}[D]_F \quad (31)$$

or

$$\begin{aligned} (k_{2,R}/k_{1,R})[D]_F &= [D]_S([S]_{F,R} - [D]_{F,R}) \\ &= [D]_S[S]_{F,R} - [D]_S[D]_{F,R}. \end{aligned} \quad (32)$$

Equation (32) can be rearranged as  $[D]_S[D]_{F,R} = [D]_S[S]_{F,R} - k_{2,R}/k_{1,R}[D]_F$ .

Let  $k_R = k_{1,R}/k_{2,R}$  ( $k_R$  is the dyeing rate constant in the redox system) and  $k'_R = 1/k_R$ , then

$$[D]_S[D]_{F,R} = [D]_S[S]_{F,R} - k'_R[D]_F \quad (33)$$

or

$$[D]_{F,R} = [S]_{F,R} - k'_R[D]_F/[D]_S. \quad (34)$$

Therefore from a plot of  $[D]_{F,R}$  v.s.  $([D]_F/[D]_S)$  by equation (34), we can get the value of  $K'_R$  from the slope of the curve and also get the saturation value of dye in fiber by the redox system,  $[S]_{F,R}$  from the intercept.

## EXPERIMENTAL

### Materials

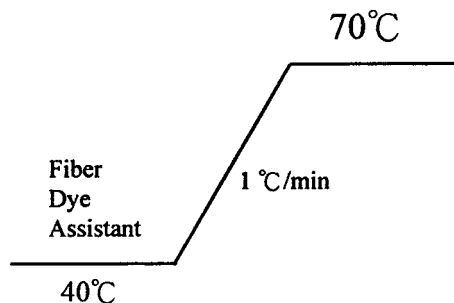
The nylon 6 fiber was first extracted by  $\text{CCl}_{4(\text{aq})}$ , at room temperature for 15 min, twice, then using warm water with a non-ionic surface active agent (1 g/L) and sodium carbonate (1 g/L), it was treated at 60°C for 150 min, and finally washed with water until the pH of washing water was kept constant. The purpose was to remove the oil and impurity from fiber. Moreover, in order to avoid an unstable structure of fiber, the fiber was treated by boiled water before dyeing at 95°C for 2 h.

Chemicals hydrogen peroxide (35%) and glyoxal (40%), which were used as an oxidant and reductant agent, respectively, were employed without further purification. Dyestuff of Supracen Red B (C. I. Acid Red 42), which was provided by Bayer Corporation, was purified until the high-

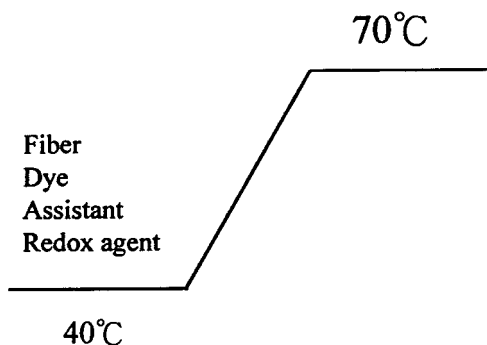
est absorption wavelength was kept at the same extinction coefficient.

### Methods and Conditions of Dyeing

Two dyeing methods were used in the dyeing, i.e., the conventional and the redox dyeing as illustrated by the following dyeing schemes:



(a) Conventional dyeing method:  
Dye=0.6 g/L; Na<sub>2</sub>SO<sub>4</sub>=2 g/L;  
PH=3; bath ratio=1 : 1600.



(b) Redox dyeing method:  
Dye=0.6 g/L; oxidant =x mole/L;  
reductant = y mole/L; PH=3;  
bath ratio=1 : 1600.

The redox dyeing method is described as follows: the dye bath was first prepared with 0.15M oxidant agent of hydrogen peroxide (excess of molar ratio), 0.10M reductant agent of glyoxal, and dye at various concentrations (0.1, 0.3, 0.6, 0.8, and 1.2 g/L) to form a dye solution with a dye bath

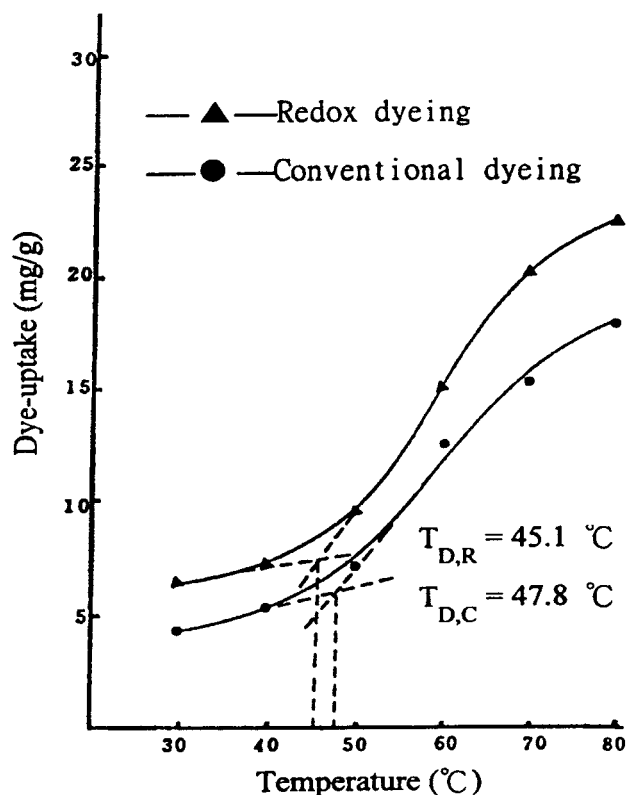


Figure 1 Evaluation of  $T_d$  from dye-uptake and temperature relationship.

ratio of 1 : 1600 and at PH = 3, then increasing the dyeing temperature to a desired value (30, 40, 50, 60, 70, or 80°C), maintaining that temperature for a definite time (1, 2, 3, 4, 5, 15, 30, 45, 50, 60, 75, 90, 105, 120, 135, 150, 165, or 180 min, and also 40, or 60 h). After dyeing, the fiber was washed in distilled water at 70°C, and rewashed in methanol/water (50/50) solution for several times, until the washed solution was clear. Finally, the fiber was washed in distilled water and dried at room temperature.

### Measuring Dyeing Properties

The dye-uptake of fiber was evaluated by dissolving the fiber in formic acid and measuring the

Table I Dyeing Transition Temperature in Conventional and Redox Systems

Dyeing Transition Temperature	Conventional Dyeing	Redox Dyeing
$T_D(\text{ } ^\circ\text{C})$	47.8	45.1

\* Dyeing with C.I. Acid Red 42

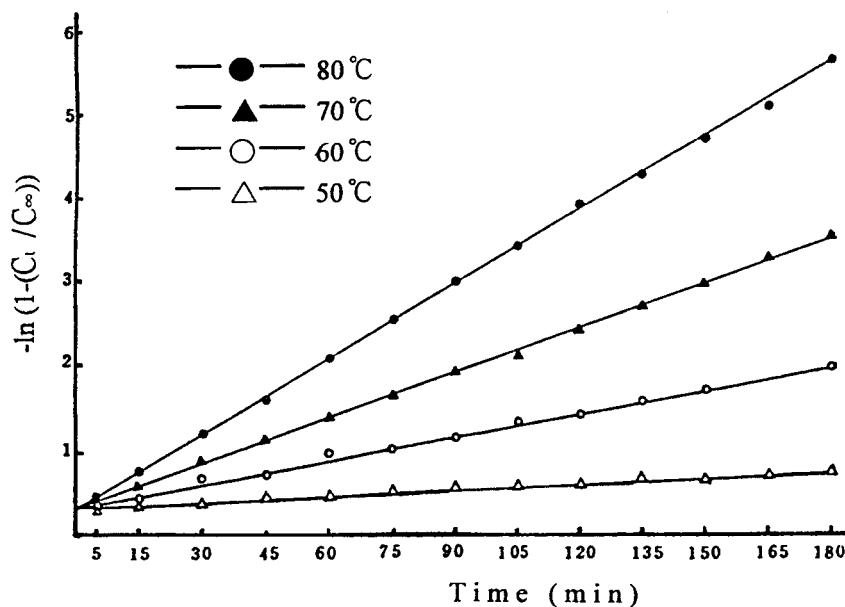


Figure 2 The relationship of  $-\ln(1 - (C_t/C_\infty))$  versus time in conventional dyeing.

solution by a Simadzu Seisakusho UV-300 spectrophotometer (Japan) at 25°C. The range of wavelength was 195–850 nm.

## RESULTS AND DISCUSSION

### Dyeing Transition Temperature

The dyeing transition temperature,  $T_D$ , which is similar to the glass transition temperature ( $T_g$ ) of

a polymer, is related to its diffusion rate. In order to have a sufficient diffusion rate of dyeing, the dyeing temperature is required to be higher than  $T_D$ . The experimental results, as seen in Figure 1 and Table I, demonstrate that the  $T_D$  in the redox system (45.1°C) is lower than that in the conventional system (47.8°C). The reason is believed to be that, in the presence of hydrogen peroxide and glyoxal in the redox system, formic acid is generated and it swells the fiber. Consequently, it in-

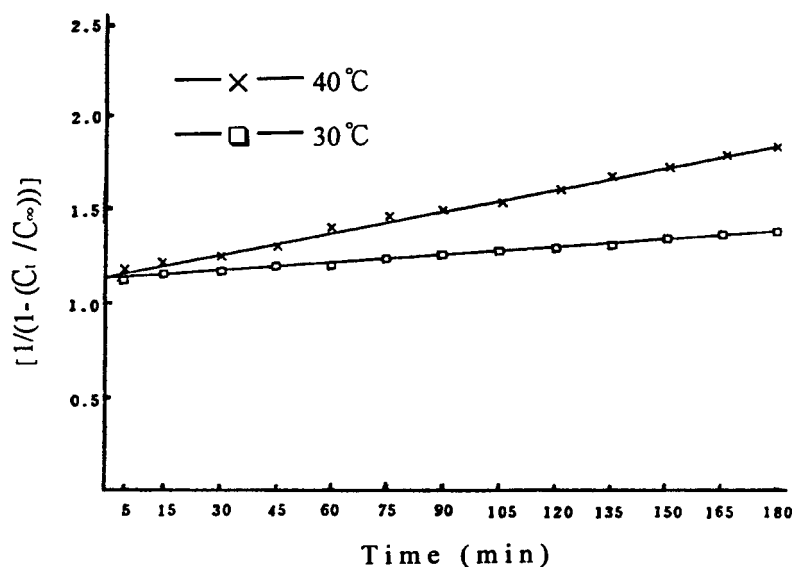


Figure 3 The relationship of  $[1/(1 - (C_t/C_\infty))]$  versus time in conventional dyeing.

**Table II Dyeing Diffusion Constant in Redox and Conventional Dyeing**

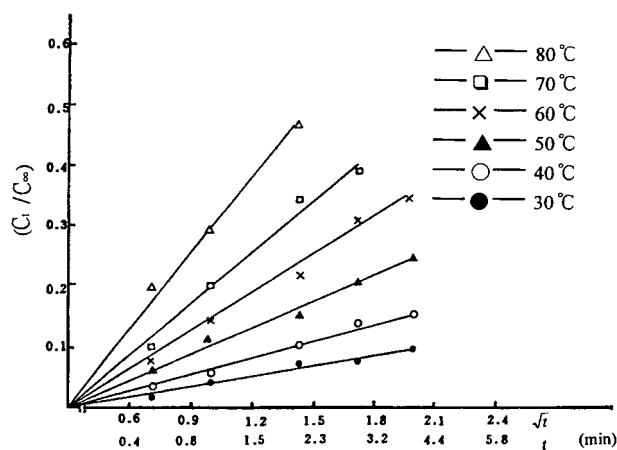
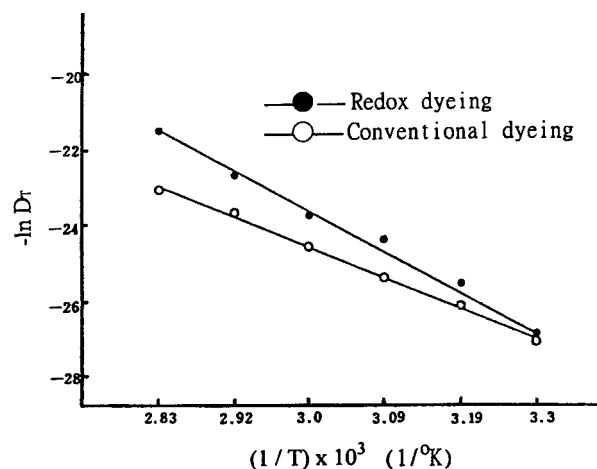
Dyeing Temperature	Conventional Dyeing ( $\text{m}^2/\text{min}$ )	Redox Dyeing ( $\text{m}^2/\text{min}$ )
30	$1.76 \times 10^{-12}$	$9.02 \times 10^{-12}$
40	$5.29 \times 10^{-12}$	$2.79 \times 10^{-11}$
50	$7.48 \times 10^{-12}$	$6.77 \times 10^{-11}$
60	$2.88 \times 10^{-11}$	$7.28 \times 10^{-11}$
70	$5.75 \times 10^{-11}$	$1.41 \times 10^{-10}$
80	$9.17 \times 10^{-11}$	$2.93 \times 10^{-10}$

creases the free volume of fiber and lowers the dyeing transition temperature. Thus, it requires a lower temperature to dye the fiber in the redox system.

Also in Figure 1, it is shown that the dye-uptake in the redox system is more than that in the conventional dyeing system. It was explained earlier that the redox system is a combination of conventional ionic and free radical dyeing. The fiber can provide more dyeing sites, which can absorb more dye molecules in the redox dyeing.

#### Diffusion Coefficients of Conventional and Free Radical Dyeing

Diffusion is considered to be by an irregular path of the dye molecule moving toward the fiber. The driving force comes from the difference in dye concentration or chemical potential of dye in dye bath. Since the dyeing rate is related to the diffusion rate, we will use the diffusion coefficient to estimate the dyeing rate. In this paper, the measurement of diffu-


**Figure 4** The relationship of  $(C_t/C_\infty)$  versus  $\sqrt{t}$  in redox dyeing.

**Figure 5** The relationship of  $-\ln D_T$  versus reciprocal temperature in conventional and redox dyeing.

sion coefficient ( $D_T$ ) is dependent on the dyeing system. In the conventional ionic dyeing system, equation (1) or (2) of an infinite dye-bath is used to evaluate the diffusion coefficient. The results are seen in Figures 2 and 3, and Table II.

For the free radical dyeing of the redox system, the diffusion of dye free radical into fiber is much faster than that in conventional acid dyeing, i.e., the dyeing time is short. Thus, the equation (3) of Crank and Wilson can be used to calculate the diffusion coefficient. Figure 4 and Table II show the experimental results.

As seen in Table II, it is found that the diffusion coefficient of the redox system is higher than that in the conventional acid dyeing, as we expected.

Using the Arrhenius equation of  $k = D_0 \exp(-E/RT)$ , we plotted  $\ln D_T$  v.s.  $1/T$ . The activation energies of diffusion can be obtained from the slope. The results are shown in Figure 5 and Table III. As seen in the table, the activation energies in free radical dyeing are lower than those in conventional ionic dyeing. The results also explain the results of low temperature dyeing in the redox system.

**Table III Diffusion Activation Energies in Conventional and Redox Dyeing**

Diffusion Activation Energy	Conventional Dyeing	Redox Dyeing
E (kcal/mole)	16.9	14.7

**Table IV Thermodynamic Parameters in the Conventional System**

Dyeing Temperature (°K)	$(1/T) \times 10^{-3}$ (°K <sup>-1</sup> )	$-\Delta\mu^0$ (Kcal/mole)	$-\Delta\mu^0/T$ (Kcal/mole °K)	$H^0$ (Kcal/mole)	$S^0$ (e.u.)
303	3.30	8.38	27.7	-8.316	-1.393
313	3.19	8.38	26.7	-8.316	-1.381
323	3.09	8.37	25.8	-8.316	-1.378
333	3.00	8.35	25.1	-8.316	-1.398
343	2.92	8.34	24.4	-8.316	-1.390
353	2.83	8.32	23.6	-8.316	-1.404

### Dyeing Affinity, Enthalpy, and Entropy of Conventional and Free Radical Dyeing

Since the dyestuff is a sodium salt with single-sulfuric acid group, the affinity ( $-\Delta\mu^0$ ), by the equation (35), can be expressed as;

$$-\Delta\mu^0 = RT \ln[\theta_D/(1 - \theta_D)][\theta_{Na}/(1 - \theta_{Na})] - RT \ln[Na]_s[D]_s. \quad (35)$$

Since the nylon 6 fiber contains 63 m mol/kg of carboxylic acid end groups and 54 m mol/kg of amine end groups, so  $\theta_{Na} = [(63 - 54)/63] \theta_D = 1/7 \theta_D = 0.143 \theta_D$ . We can get the affinity by equation (35). The results are shown in Table IV.

For the dyeing affinity of the free radical in the redox system the diffusion rate of dye free radical is much faster than that in conventional ionic dyeing. Its dyeing mechanism is stated as "dyestuff is absorbed in the specific sites and not dissociated in both phases of fiber and dyebath" as described by Vickerstaff,<sup>21</sup> and the affinity is expressed as;

$$-\Delta\mu^0 = RT \ln[\theta_D/(1 - \theta_D)] - RT \ln[D]_s, \quad (36)$$

where  $\theta_D = ([D]_F/[S]_{F,R})$ ;  $[D]_R$  is the equilibrium dye-uptake of dye free radical in fiber; and  $[S]_{F,R}$  is the saturation value of dye in the free radical dyeing.

Since the nylon fiber contains carboxylic acid content of 63 m mol/kg and amine group content of 54 m mol/kg, so let  $\theta_{Na} = [(63 - 54)/63] \theta_D = 1/7 \theta_D = 0.143 \theta_D$ . From equation (36), we can get the affinity of free radical dyeing. The results are shown in Table V. From the experimental results, it is found that conventional ionic acid dyeing exhibits higher affinity than that in free radical dyeing. It is explained that the positive charge of nylon fiber can absorb more of the negative charge of dye anion by ionic bonding in conventional acid dyeing. Thus, it exhibits a higher affinity.

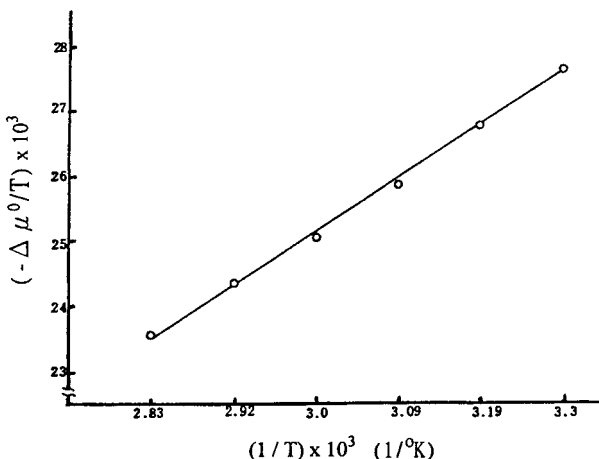
For obtaining the dyeing enthalpy and entropy, the enthalpy,  $\Delta H^0$  can be measured by plotting  $-\Delta\mu^0/T$  v.s.  $1/T$  and the entropy,  $\Delta S$  can be calculated by using  $-\Delta\mu^0 = \Delta H^0 - T\Delta S$ . The results are shown in Figures 6 and 7, and Tables IV and V.

As seen in Tables IV and V, the dyeing enthalpy is found to be negative (exothermic reac-

**Table V Thermodynamic Parameters in the Redox System**

Dyeing Temperature (°K)	$(1/T) \times 10^{-3}$ (°K <sup>-1</sup> )	$-\Delta\mu^0$ (Kcal/mole)	$-\Delta\mu^0/T$ (Kcal/mole °K)	$H^0$ (Kcal/mole)	$S^0$ (e.u.)
303	3.30	2.56	8.46	3.829	21.09
313	3.19	2.76	8.82	3.829	21.03
323	3.09	2.91	8.98	3.829	20.81
333	3.00	3.19	9.57	3.829	21.09
343	2.92	3.40	9.91	3.829	21.09
353	2.83	3.47	9.81	3.829	20.64





**Figure 6** The relationship of  $(-\Delta\mu^0/T) \times 10^3$  versus reciprocal temperature in conventional dyeing.

tion) for conventional acid dyeing, but it is positive (endothermic reaction) for redox dyeing. This indicates that the equilibrium dye-uptake is decreased with an increase of temperature in conventional ionic dyeing. Nevertheless, since the formation of the dye free radical is an endothermic reaction (the dyeing enthalpy is positive), the dye-uptake is increased with an increase of the dyeing temperature in the free radical system.

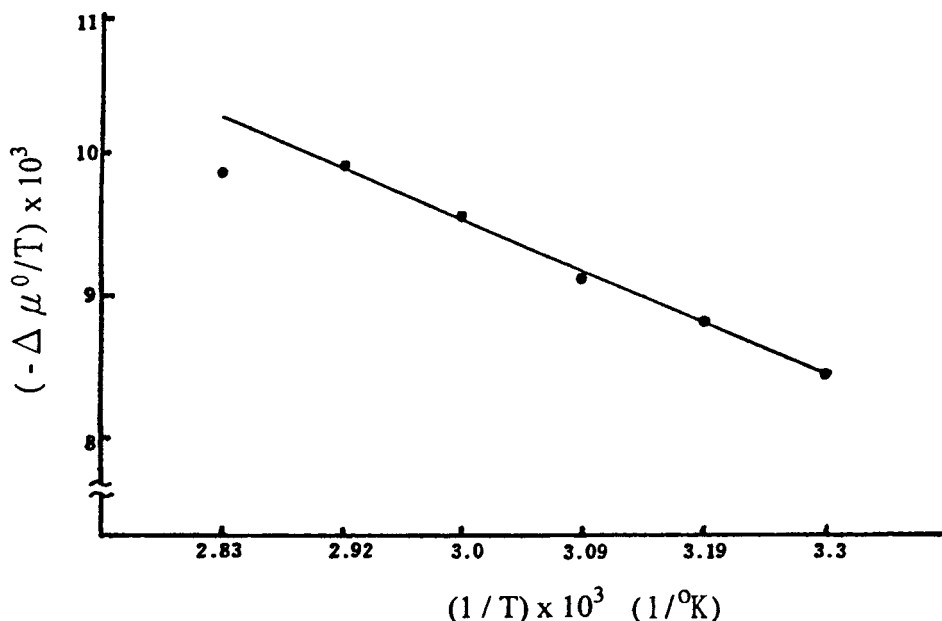
Moreover, the dyeing entropy is negative in conventional dyeing, i.e., the degree of randomness is getting higher. This implies that the size of absorbed dye anion is bigger in the dyed fiber

by conventional acid dyeing. However, for the redox dyeing system, most free radical molecules can form restrained covalent bonds with fiber. Thus, the degree of randomness is smaller. In other words, the dye molecule is combined more compactly in the fiber during the free radical dyeing, so the dyeing entropy is positive.

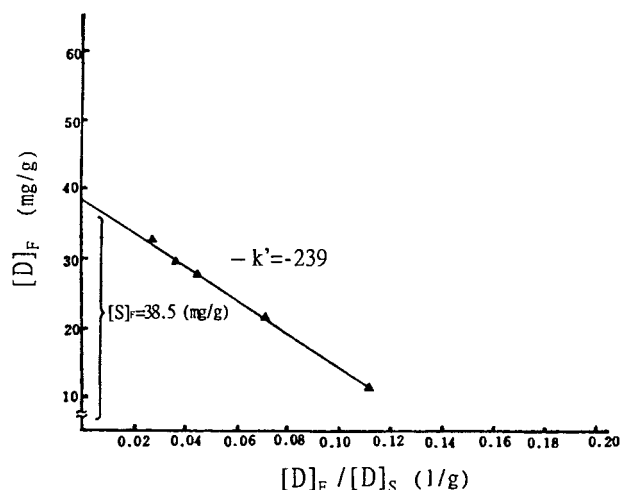
#### Saturation Concentration in Conventional and Redox Dyeing

According to Langmuir's isothermal absorption equation, we can plot of  $[D]_F$  v.s.  $[D]_F/[S]_{F,R}$ , and the saturation value,  $[S]_F$  in conventional acid dyeing can be evaluated by extrapolation. The results are shown in Figure 8. Similarly, the saturation value in redox dyeing can also be obtained by plotting  $[D]_F$  v.s.  $[D]_F/[S]_{F,R}$ . The results are shown in Figure 9.

As seen in Figures 8 and 9, it is found that the saturation value in the redox dyeing system is higher than that in conventional dyeing. This indicates that the dye free radical can react with the end group ( $-\text{NH}_2$ ) of nylon 6 fiber besides the conventional dye anion. Thus, the fiber will form both ionic and covalent bonds. Moreover, it is also found that the dyeing rate of  $k'$  value in conventional acid dyeing (from the slope of the figure) is higher than that in redox dyeing. It demonstrates that the desorption rate of dyestuff in conventional dyeing is faster than that in redox dyeing as the system reaches equilibrium.



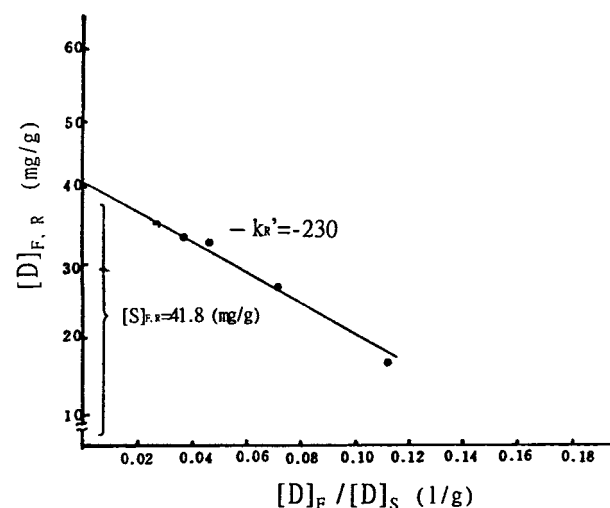
**Figure 7** The relationship of  $(-\Delta\mu^0/T) \times 10^3$  versus reciprocal temperature in free radical dyeing.



**Figure 8** The relationship of  $[D]_F$  versus  $[D]_F/[D]_S$  in conventional dyeing.

## CONCLUSION

In this paper, we evaluate the dyeing transition temperature ( $T_D$ ), diffusion coefficient ( $D_T$ ), activation energies of diffusion, dyeing affinity, and the dyeing enthalpy and entropy in the hydrogen peroxide-glyoxal redox system in order to understand thoroughly the dyeing mechanism between redox and conventional dyeing. From the experimental results, the dyeing transition temperature ( $T_D$ ) in the redox system is found to be lower than that in the conventional system. However, the diffusion coefficient ( $D_T$ ) of the redox dyeing system is larger than that of the conventional system. These results may come from the formation of formic acid by the



**Figure 9** The relationship of  $[D]_{F,R}$  versus  $[D]_F/[D]_S$  in redox dyeing.

oxidant and reductant, which swells the fiber during the redox dyeing. Moreover, the dyeing affinity of the free radical dyeing type (redox) is lower than that in the ionic dyeing type (conventional); the enthalpy is found to be positive (endothermic reaction) in the redox system, but negative (exothermic reaction) in the conventional system; and the entropies also exhibit a similar tendency, i.e. positive in the redox system, but negative in the conventional system. This indicates that the dye molecule is combined more compactly in the fiber, forming more stable covalent bonding in the radical dyeing. Finally, the dyeing saturation value in the redox dyeing system is found to be higher than that in the conventional system. It demonstrates that the redox dyeing system results in deeper shade than does conventional dyeing due to its combination of the radical and ionic dyeing mechanisms.

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