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Thermodynamic parameters of disperse dyeing on several polyester fibers having different molecular structures

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Abstract

Dyeing properties of the easy dyeable polyester (EDP) and the polytrimethylene terephthalate (PTT) were investigated in terms of their thermodynamic and kinetic factors, such as standard affinity ($-\Delta\mu^0$), enthalpy change (ΔH^0), entropy change (ΔS^0), diffusion coefficient (D_T) and activation energy of the diffusion (E_D). The results were compared with corresponding properties of the PET (polyethylene terephthalate). The $-\Delta\mu^0$ of the EDP and the PTT showed a little higher value than that of the PET. PET displayed the highest negative values of the ΔH^0 and the ΔS^0, while PTT showed the lowest negative values of them. For all three polyester types, as the temperature increased, the D_T increased. PTT had the highest D_T at every temperature and PET showed the lowest values of the D_T. The E_D of the EDP and the PTT was lower than that of the PET.

Keywords: Thermodynamic parameters; Diffusion; Polyester; Polytrimethylene terephthalate; Easy dyeable polyester; Disperse dye

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1. Introduction

Polyethylene terephthalate (PET) fiber, which is a type of polyester fiber, is the most widely used synthetic fiber due to its good physical and chemical properties. It is also well known that PET fiber is dyed using disperse dyes at high temperatures of 120–130 °C, owing to its hydrophobic nature and highly compact molecular structure [1].

In recent trend that synthetic fibers are blended with natural fibers to combine advantages of both substrates, the damage of the natural fibers during dyeing process has been considered as very serious problem due to higher dyeing temperatures, especially being mixed with PET [2]. In this context, the demand of new polyester fibers which can be dyed at low temperature has been increasing. Thereby two polyester fibers are recently introduced with a practical success. One is easy dyeable polyester (EDP) fiber and the other is polytrimethylene terephthalate (PTT) fiber. EDP is manufactured by polymerizing terephthalic acid with the mixtures of polyethylene glycol and normal ethylene glycol. In the case of polyethylene glycol, the degree of polymerization is 500–1000. This approach for EDP fiber is to relax the compact structure of the fiber molecules, to improve its hydrophilicity and finally to reduce its dyeing temperature [3]. In addition, PTT is produced by polymerizing terephthalic acid with 1,3-propandiol instead of ethylene glycol to increase mobility and flexibility of the polymer molecular chains and to make it easy for disperse dye to penetrate into the fiber substrates [4]. Consequently, the easy dyeable characteristics were achieved by both types of polyesters.

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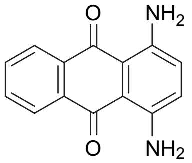
In this study, dyeability of the EDP and PTT was investigated in terms of their thermodynamic and kinetic properties, such as standard affinity, enthalpy change, entropy change, diffusion coefficient and activation energy of the diffusion. These findings were compared with the corresponding results of conventional PET.

2. Experimental

2.1. Materials

Three polyester fabrics, namely EDY, PTT and PET, were used. Scouring was carried out using 2 g/l of nonionic surfactant at 60 °C for 30 min. The liquor ratio was 100:1. The fabrics were then washed completely in cold distilled water and dried in the open air. A disperse dye, C. I. Disperse Violet 1 (1,4-diaminoanthraquinone), was purchased from Aldrich Chemical Co. and was used without further purification.



C. I. Disperse Violet 1

2.2. Adsorption isotherm

Three polyester fabrics (0.01 g) were dyed in solutions containing 0.0010, 0.0015, 0.0020, 0.0025 and 0.0030 g/l of the dye at the various temperatures of 100, 110, 120 and 130 °C until equilibrium adsorption was obtained. The liquor ratio was 10,000:1 which could be considered as a concept of the infinite liquor ratio.

2.3. Partition coefficient and standard affinity

The partition coefficient (K) of the dye between the fiber ($[D]_f$) and the dyeing solution ($[D]_s$) was obtained from the adsorption isotherm. The standard affinity ($-\Delta\mu^0$) of the dye was calculated using Eq. (1).

$$-\Delta\mu^0 = -\left(\mu_f^0 - \mu_s^0\right) = \mathrm{R}T\ln\frac{[D]_f}{[D]_s} = \mathrm{R}T\ln K \tag{1}$$

$-\Delta\mu^0$, standard affinity (cal/mol); μ_f^0, standard chemical potentials of dye in the fiber; μ_s^0, standard chemical potentials of dye in the solution; R, gas constant (1.9872 cal/mol K); T, absolute temperature (K); $[D]_f$, dye concentration in the fiber (mol/kg); $[D]_s$, dye concentration in the solution (mol/L); and K, partition coefficient.

2.4. Enthalpy change

The enthalpy change was obtained from the empirical plot that shows the relationship between $\Delta\mu^0/T$ and $1/T$ using Eq. (2)

$$\Delta H^0 = \frac{\delta(\Delta\mu^0/T)}{\delta(1/T)} \qquad \frac{\Delta H^0}{T} = \frac{-\Delta\mu^0}{T} + C \tag{2}$$

ΔH^0, heat of dyeing (cal/mol); $-\Delta\mu^0$, standard affinity (cal/mol); T, absolute temperature (K); and C, integral constant.

2.5. Entropy change

The entropy change was calculated using Eq. (3)

$$-\Delta\mu^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

$-\Delta\mu^0$, standard affinity (cal/mol); ΔH^0, heat of dyeing (cal/mol); ΔS^0, change in entropy (cal/mol K); and T, absolute temperature (K).

2.6. Dyeing rate

For dyeing rate, the polyester fabrics (0.01 g) were dyed in a solution containing 0.01 g/l of the dye at the temperatures of 90, 110 and 130 °C. The liquor ratio was 10,000:1.

2.7. Diffusion coefficient

According to Eq. (4), the diffusion coefficient was calculated from the plot that shows the relationship between C_t/C_{eq} and $t^{1/2}$ in the initial stage of dyeing

$$\frac{C_t}{C_{eq}} = 4\sqrt{\frac{Dt}{\pi r^2}} \tag{4}$$

C_t, dye exhaustion at a time (t) (mol/kg); C_{eq}, dye exhaustion in the equilibrium (mol/kg); D, diffusion coefficient (cm^2/min); and r, radius of fiber (cm).

2.8. Activation energy of the diffusion

Using Eq. (5), the activation energy of the diffusion was calculated from the relationship between $\ln D_T$ and $1/T$

$$\ln D_T = \ln D_0 - \frac{E}{\mathrm{R}T} \tag{5}$$

D_T, diffusion coefficient at a temperature T (cm^2/min); D_0, constant; E, activation energy; R, gas constant (1.9872 cal/mol K); and T, absolute temperature (K).

2.9. Adsorption amount of the dye on to fiber

At the end of dyeing, the samples were completely washed with cold acetone and dried in a vacuum oven. The dried samples were weighed and then dyes were extracted using *N,N*-dimethylformamide at 95 °C until the samples became colorless. The dye concentration in the extracts was measured using spectrophotometer and the extent of dye adsorption was calculated.

3. Results and discussion

3.1. Standard affinity

The most basic thermodynamic parameter is the standard affinity ($-\Delta\mu^0$) of the dye in dyeing solution towards fiber substrate. This parameter was defined as a difference between the chemical potential of the dye in the fiber and the chemical potential of the dye in the dyeing solution. This value is the measure of the tendency of the dye to move from its standard state of the solution to its standard state of the fiber [5]. In order to calculate the standard affinity of C. I. Disperse Violet 1 towards EDP, PTT and PET, the isotherm data of dye adsorption were obtained at several different temperatures of 100–130 °C.

Fig. 1 shows the adsorption isotherms of C. I. Disperse Violet 1 on PET and the linear relationship between the dye concentration and the adsorption amount of the dye on PET. This relationship obeys the Nernst's adsorption model which commonly represents the dyeing mechanism between disperse dye and PET [6]. Herein, the slopes of the straight lines in the isotherms are the partition coefficients (K) of the dye between the dyeing solution and the fiber substrate.

From Eq. (1), the standard affinity could be calculated and the corresponding values for EDP, PTT and PET are shown in Table 1. As shown in Table 1, the standard affinities of EDP and PTT are a little higher than those of PET. This finding explains that the dye has higher tendency to move from the dyeing solution to EDP and PTT substrates than to PET substrate. As the temperature increases, the standard affinity decreases in all fibers. This observation can be explained that because the adsorption of dyes towards fiber is well known as an exothermic reaction process, resulting higher dyeing temperature gives a negative effect on the thermodynamic adsorption [7]. However, in the practical aspect, since the dyeings are commonly carried out within the limited time using excess amounts of dyes, higher adsorptions are obtained at higher application temperatures.

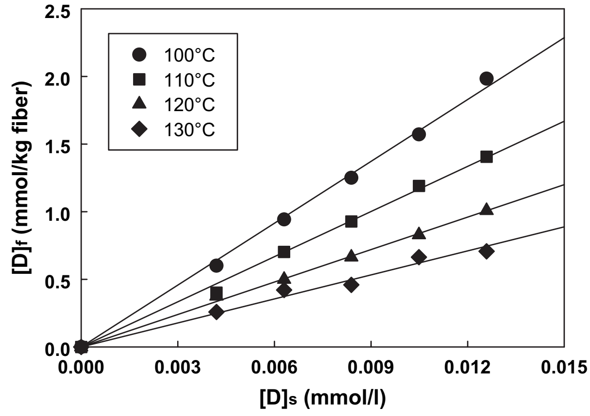


Fig. 1. Adsorption isotherm of C. I. Disperse Violet 1 on PET.

Table 1
The partition coefficient (K) and the standard affinity ($-\Delta\mu^0$) of C. I. Disperse Violet 1 on PTT, EDP and PET

Temperature (°C)	PTT		EDP		PET	
	K	$-\Delta\mu^0$ (cal/mol)	K	$-\Delta\mu^0$ (cal/mol)	K	$-\Delta\mu^0$ (cal/mol)
100	171.0	3811	175.1	3830	152.4	3726
110	128.8	3699	127.3	3690	118.8	3636
120	95.7	3562	97.0	3570	82.1	3443
130	71.1	3416	69.9	3400	59.2	3268

3.2. Enthalpy and entropy change

As mentioned earlier, the dye adsorption is an exothermic reaction process. The amount of exothermic energy depends on the dyeing conditions, such as fibers, dyes, dyeing media and etc. In addition, the enthalpy change (ΔH^0) is considered as the measure of the adsorption strength of dyes. Meanwhile, the entropy change (ΔS^0) in dyeing represents the entropy difference of the dye molecules within the fiber [7]. The entropy change shows negative values in most dyeing process, because adsorbed dyes become more restrained within fiber molecules than dyeing solution. Therefore, the value of the entropy change could be regarded as the measure of immobility of dyes within the fibers. Fig. 2 shows the relationship between $\Delta\mu^0/T$ and $1/T$ on enthalpy change (ΔH^0). As expected from Eq. (2), they show linear relationship. From the slopes of the straight lines, the enthalpy change can be calculated.

Meanwhile, from Fig. 3 and Eq. (3) showing the linear relationship between $\Delta\mu^0$ and T, the entropy change can be also obtained. The enthalpy and the entropy change obtained are summarized in Table 2. According to Table 2, PET showed higher negative values of ΔH^0 (−9562) and ΔS^0 (−15.66), while PTT showed lower negative values of them.

The enthalpy change means the amount of the released thermal energy when dye molecules are adsorbed into polymer chains. The negatively larger value represents that the dye molecules were more strongly embedded within the polymer molecules. In this

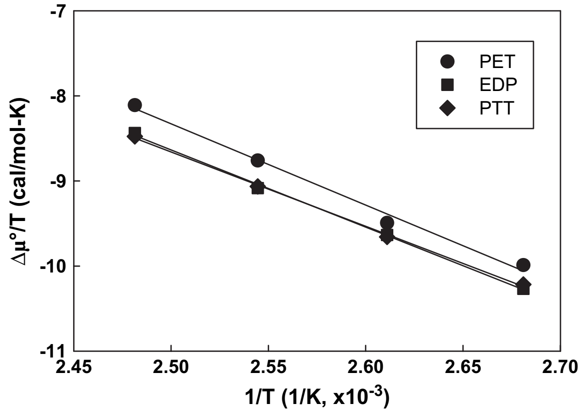


Fig. 2. Relationship between $\Delta\mu^0/T$ and $1/T$ on enthalpy change.

context, it is proposed from Table 2 that PTT and EDP being consisted of more flexible units of polymer chains had less strongly held the dye molecules within the substrate than PET.

The entropy change shows the extent of the reduced freedom of dye molecules after the completion of dyeings [7]. The negatively larger value of the entropy change represents the phenomenon that the mobility of the dye molecules significantly decreased after dyeing. In Table 2, the entropy change of PET showed the largest negative value among the three polyester types. This observation suggests that the dye molecules within PET became the most immobilized state.

Considering that the different internal structures of the three polyesters resulted from the different chemical compositions, it might be more reasonable that the PTT should have larger negative values of ΔH^0 and ΔS^0 than those of EDP, because EDP has more flexible polyethylene glycol unit than 1,3-propandiol unit of PTT. As mentioned earlier, EDP is manufactured by polymerizing terephthalic acid with the mixtures of polyethylene glycol and normal ethylene glycol. The polyethylene glycol unit is hydrophilic and its characteristic increases hydrophilicity of EDP substrate as well as flexibility. However, EDP still has regular ethylene glycol units which are condensed with terephthalic acid to be like conventional PET. During dyeing of EDP, disperse dye molecules could be adsorbed onto the normal ethylene glycol polyester parts, showing higher affinity rather than onto the polyethylene glycol parts. Because the polyethylene glycol units of EDP are very hydrophilic, the hydrophobic disperse dyes could not be adsorbed onto the polyethylene glycol units but could be adsorbed onto ethylene glycol units. This is the reason that EDP has larger negative values of ΔH^0 and ΔS^0 than those of PTT. In the case of PTT, this substrate has one more methylene group in its repeat units throughout the polymer chains and this characteristic gives higher flexibility compared with PET.

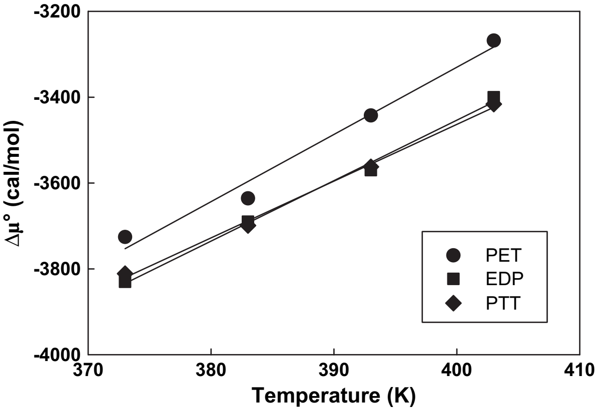


Fig. 3. Relationship between $\Delta\mu^0$ and T on entropy change.

Table 2
The enthalpy change (ΔH^0) and the entropy change (ΔS^0) of C. I. Disperse Violet 1 on PTT, EDP and PET

Parameters	PTT	EDP	PET
ΔH^0 (cal/mol)	−8735	−9080	−9562
ΔS^0 (cal/mol K)	−13.22	−14.10	−15.66

3.3. Dyeing rate and diffusion coefficient

It is generally agreed that dyeing process involves three continuous steps. The first step is the diffusion of dye through the aqueous dyebath on to the fiber. The second step is the adsorption of dye into the outer layer of the fiber. And the last step is the diffusion of dye into the fiber inside from the adsorbed surface. The second step, the actual adsorption process, is generally assumed to be much more rapid than either of the other diffusion steps. Of the two diffusion steps, the diffusion into the inner layer is much slower than the movement of dye through the aqueous solution due to the physical obstruction of dye diffusion presented by the network of fiber molecules [8].

For the dye molecule to diffuse into the fiber, it is expected that the free volume could be formed within the substrate. This free volume is regarded as the void being temporarily formed within the polymers by the thermal movement of molecular chains and the dye molecules penetrate into this empty space [9]. Under the same temperature, the thermal movement of molecular chains is directly related to the hardness and the stiffness of the polymer substrate, which can be determined by its chemical compositions. In other words, the fast dye diffusion can be achieved from softer and more flexible polymer substrate. Since the polymer chains of EDP and PTT are more flexible than that of PET, the diffusion of dye molecules into these polymers could be faster than into PET.

To compare the diffusion of C. I. Disperse Violet 1 on the three types of polyester fibers, the dyeing rate was

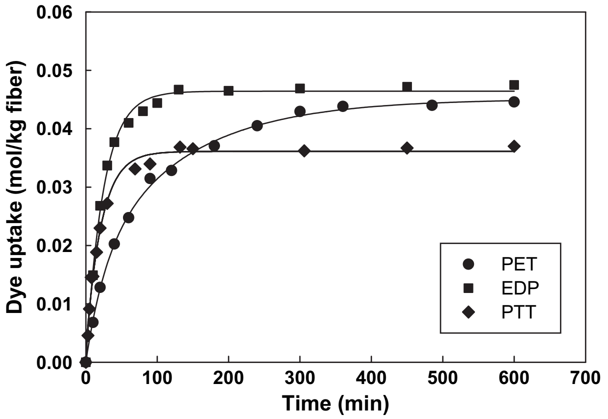


Fig. 4. Dyeing rate of C. I. Disperse Violet 1 on PTT, EDP and PET at 110 °C.

obtained at 90, 110 and 130 °C. Fig. 4 shows the dyeing rate of C. I. Disperse Violet 1 on the three polyester fibers at 110 °C. The result shows that the dyeing rate of the EDP and PTT was much faster than that of PET.

According to Eq. (4), the C_t/C_{eq} should be linearly proportional to the $t^{1/2}$ and the diffusion coefficient (D_T) could be obtained from the slop of the relationship. Fig. 5 shows the relationship between C_t/C_{eq} and $t^{1/2}$ on the three polyester fibers at 110 °C. In addition, the diffusion coefficients (D_T) of the three polyester fibers are presented in Table 3. For all polyester fibers, as the temperature increased, the diffusion coefficients also increased. This finding represents that the mobility of the polymer chains greatly increased with increasing temperature. PTT showed the highest diffusion coefficient at every temperature and PET had the lowest values.

3.4. Activation energy of the diffusion

The activation energy of the diffusion can be calculated using Eq. (5) that is known as the Arrhenius equation. This parameter describes the dependence of the diffusion coefficient on the dyeing temperature and also represents the energy barrier that a dye molecule should overcome to diffuse into the polymer molecules [10]. The activation energy of the diffusion can be obtained from the slope in the linear relationship between $\ln D_t$ and $1/T$ shown in Fig. 6. The calculated activation energy is presented in Table 4.

Table 3
The diffusion coefficient (D_T) of C. I. Disperse Violet 1 on PTT, EDP and PET

Temperature (°C)	D_T (cm^2/min)		
	PTT	EDP	PET
90	1.09×10^{-9}	0.87×10^{-9}	0.02×10^{-9}
110	1.17×10^{-8}	3.21×10^{-9}	0.72×10^{-9}
130	3.57×10^{-8}	1.42×10^{-8}	1.25×10^{-8}

The activation energy of EDP and PTT was lower than that of PET. The result can be proposed that during dyeing process the relaxation of the polymer chains of PTT and EDP was less affected by the temperature than the case of PET. However, more discussion has to be made about characteristics between the EDP and PTT. In Table 3, PTT had higher diffusion coefficients than EDP. Nonetheless, the activation energy showed higher value in PTT than in EDP. This result could be explained in that EDP is more hydrophilic fiber than PTT, because EDP contains more hydrophilic polyethylene glycol units in its structures. Therefore, in water EDP could be swollen more easily than PTT and it makes possible for the dye molecule having low kinetic energy to diffuse into the polymer chains of EDP.

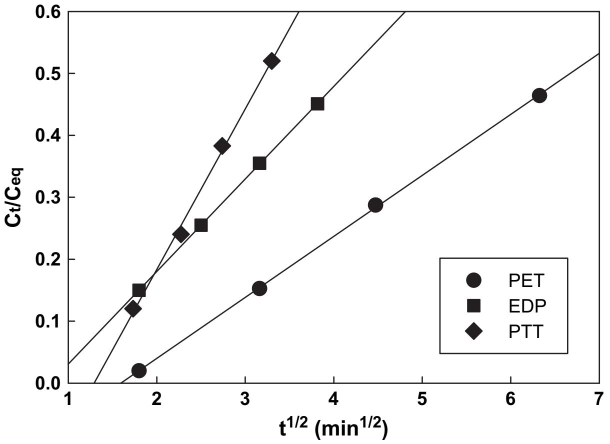


Fig. 5. Relationship between C_t/C_{eq} and $t^{1/2}$ on diffusion coefficient.

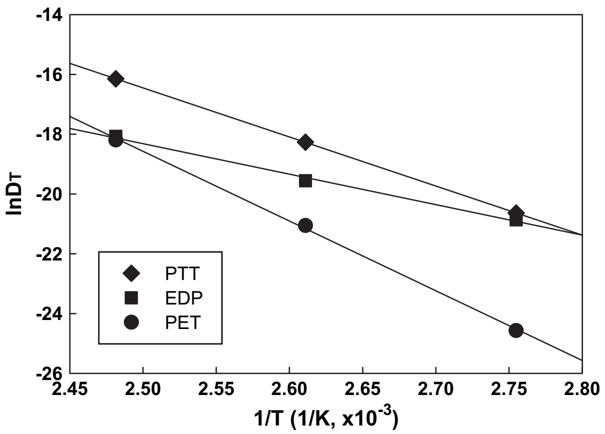


Fig. 6. Relationship between $\ln D_T$ and $1/T$ on activation energy.

4. Conclusions

Dyeing properties of the EDP and the PTT were investigated on their thermodynamic and kinetic characteristics compared with those of the PET. The obtained properties were discussed in terms of the

Table 4
The activation energy of the diffusion (E_D) for C. I. Disperse Violet 1 on PTT, EDP and PET

Parameter	PTT	EDP	PET
E_D (kcal/mol)	32.63	20.26	46.35

relationship between the chemical structures of polyesters and the dye adsorption.

The standard affinities of EDP and PTT were a little higher than those of PET. In the case of enthalpy change and entropy change, PET showed higher negative values of ΔH^0 and ΔS^0, while PTT showed lower negative values of them. For all of the three polyester fibers, as the temperature increased, the diffusion coefficients also increased. PTT had the highest diffusion coefficient at every temperature and PET showed the lowest values. The activation energy of EDP and PTT was lower than that of PET.

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