KINETIC AND THERMODYNAMIC STUDIES OF C.I. ACID RED 37 ON POLYAMIDE AND PROTEIN FIBRES

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ABSTRACT

Kinetic and thermodynamic studies were conducted with C.I. Acid Red (AR 37) on three substrates, polyamide fibre (nylon 6) and protein fibre (silk and wool) at various temperatures. All the three substrates showed good exhaustion percentages. Specific dyeing rate constant k, diffusion coefficient D, standard affinity $\Delta\mu°$, activation energy of diffusion $\Delta F_D°$, enthalpy change $\Delta H°$, and entropy change $\Delta S°$ have been calculated and have been discussed. For all three fibres, as the temperature increased, the diffusion coefficient increased. Nylon had the highest D at every temperature and wool showed the lowest value of D. The activation energy of diffusion $\Delta F_D°$ of both nylon and silk was lower than that of wool.

1. INTRODUCTION

It is undesirable to proceed directly to practical dyeing without at least surveying a general knowledge of the dyes and fibres which make up the dyeing system and account for the nature of the dye-fibre interactions.

Nylon is a polyamide fibre and is considered as one of the most important synthetic fibres. All polyamide fibres have terminal amino groups-NH₂, terminal carboxyl groups-COOH and amido groups -NH- along the chain which is simplified as H₂N-NH-COOH [**Bhattacharya, *et al.*, (1998)**]. These positively charged groups in polyamide can take up anions by the formation of salt- like linkage. The advantages of

polyamides over natural and other synthetic fibres are of a relative low specific gravity, high strength and good durability [**Aspland *et al.*, (1993)**].

Silk is a protein fiber composed of different alpha amino acids orienting to form a long chain polymer [**Shukla, et al., (1996)**]. The chemistry of silk in some aspects parallels that of wool. Unlike wool, silk contains no sulphur and the only amino and carboxylic acid groups come as end groups. It has been called the queen of fibres, its natural luster, handle and draping properties being superior to those of many other textile fibres [**Shukla, et al., (1995)**].

Wool is a member of a group of proteins known as keratin, it contains three main types of reactive groups, peptide bonds, the side chains of amino acid residues and disulphide crosslinks. Some of the most interesting properties of wool depend on its crosslinks which can form hydrogen bonds between two amide groups on adjacent polymer chains; ionic bonds between acidic and basic groups on adjacent chains and chemical crosslinks such as the disulphide link. The chemical reactions involving these groups have been studied extensively [**Popescue *et l.*, (2001) and Yang *et al.*, (1997)**].

Nylon, silk and wool were characterized by the presence of weakly basic amino groups and weakly acidic carboxylic acid groups which give rise to ionic properties of these polyamide and protein fibres and cause their dyeing properties to differ so markedly from those of the cellulosic fibres [**Jutao *et al.*, (1977) and Riva *et al.*, (2002)**].

Acid dyes used principally for the dyeing of polyamides and protein fibres [**Moore, (1999); Burkinshaw *et al.*, (2001) and Dhara *et al.*, (1988)**]. Dye anions are able to displace counter ions of ammonium groups in the fibre because they are supported by numerous secondary bonds (ion-exchange mechanism) [**Kamel *et al.*, (2001)**]. The dye uptake depends upon the diffusion of the dye molecule inside the fibre structure and also to the formation of the ionic bond between the amino end group of the fibre and sulphonated group of the acid dye molecule [**Kuhnel *et al.*, (1991)**].

In this study, dyeability of wool, silk and nylon were investigated in terms of their kinetic and thermodynamic properties, such as specific dyeing rate constant (k), diffusion coefficient (D), activation energy of the diffusion ΔF_D°, standard affinity ($\Delta\mu^\circ$), enthalpy and entropy (ΔH°) changes (ΔS°).

2. EXPERIMENTAL

2.1 Materials

Three fabrics, namely, nylon 6, silk and wool were used. Scouring was carried out using 2g./l. of nonionic surfactant at 60°C for 30 min., then the fabrics was thoroughly washed with water and air dried at room temperature.

An acid dye, C.I. Acid Red 37, (AR 37) was obtained from Aldrich Chemical Co. and was used without further purification. All other chemicals used were laboratory grade reagents.
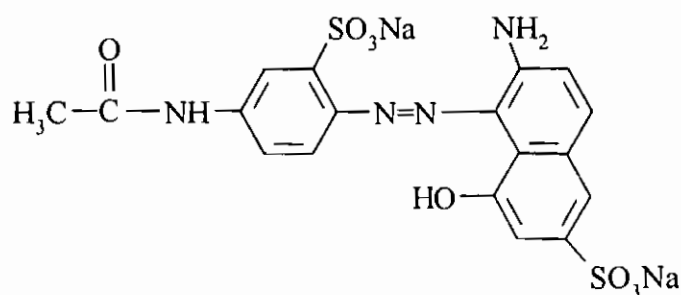
C.I. Acid Red 37 (AR 37)

2.2. Dyeing method

Nylon 6, silk and wool were dyed using C.I. Acid Red 37 [2% o.w.f., Liquor ratio 1:100]. The pH of the dye bath was adjusted to 4.0 by the addition of acetic acid.

Dyeing was performed at various temperatures 55, 65, 75 and 85°C and for different time intervals (10-280 min.) with occasional stirring. The original bath and the used ones were measured spectrophoto-metrically using Spekol 11 spectrophotometer in order to calculate the amount of exhausted dye at $\lambda_{max.} = 513$ nm.

3. RESULTS AND DISCUSSION

It is generally agreed that dyeing process involves three continuous steps. The first step is the diffusion of the dye through the aqueous dye bath on the fibre. The second step is the adsorption of the dye into the outer layer of the fibre and the last step is the diffusion of dye into the fibre inside from the adsorbed surface. The second step is the actual adsorption process and it is generally assumed to be much more

rapid than either of the other diffusion steps. Through the two diffusion steps, the diffusion into the inner layer is much slower than that of the movement of the dye through the aqueous solution and this may be due to the physical obstruction of the dye diffusion presented by the network of the fibre molecules [**Vickerstaff, (1954)**].

3.1. Kinetic Characterization
Exhaustion (E) and fixation (F)

To compare the diffusion of C.I. Acid Red 37 on the three types of the fibres under investigation, the percentage rate of exhaustion (E) and the percentage rate of fixation (F) of the dye on the fibre were measured spectrophotometrically and were calculated according to the following equations [**Yeung *et al.*, (1999)**]:

$$E = \frac{A_o - A_t}{A_o} \times 100 \tag{1}$$

$$F = \frac{A_o - A_t - A_w}{A_o} \times 100 \tag{2}$$

where A_o and A_t are the absorbance values of the dye originally present in the dyebath and that the of residual dye in the dyebath at specific time, respectively. A_w is the absorbance corresponding to the unfixed dye removed from the fibre by stripping at the boiler for 15 min in (1:1) DMF water solution [**Asquith *et al.*, (1979)**].

Figure 1 shows the variation of the percentage rate of exhaustion and fixation with time for C.I. Acid Red 37 on nylon, silk and wool at 85°C. The result shows that the exhaustion percentage by a particular fibre depends on the force of attraction between the dye and fibre i.e. the strike rate as well as, fibre structure. Nylon and silk recorded highest exhaustion percentage due to their finest diameter than wool [**Gupta *et al.*, (1994)**]. Furthermore, the hydrogen bonds in nylon can easily be disrupted by the polar molecules of water, this characteristics gives a higher exhaustion compared with silk and wool [**Bruce *et al.*, (2000)**]. Similar results were obtained at 55,65 and 75°C.
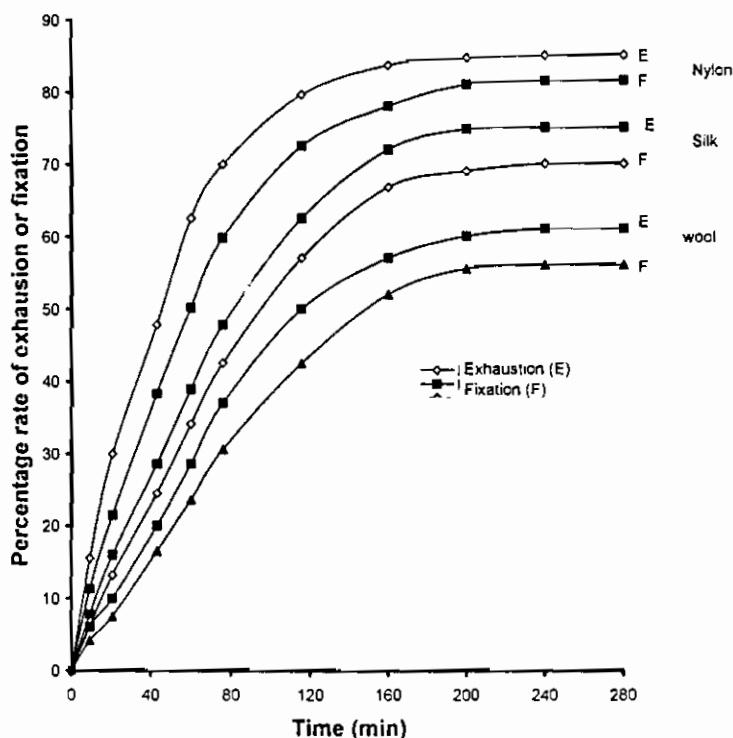
Fig. (1): Percentage rate of exhaustion (E) and fixation (F) of C.I. AR 37 by nylon, silk and wool as a function of time. at 85°C.

Specific dyeing rate constant (k)

The specific dyeing rate constant (*k*) can be estimated using the following equation (Johnson, 1994).

$$k = 0.5 \, C_\infty \left(\frac{d}{t_{1/2}} \right)^{1/2} \tag{3}$$

The values of half dyeing time ($t_{1/2}$ min) were calculated from the plots in Figure 1 and were used in calculating the specific dyeing rate constant. (d) is the fibre diameter and C_∞ is the percentage of dye adsorbed on the fibre at equilibrium conditions.

Table (1) contains the values of half dyeing time ($t_{1/2}$), and the specific dyeing rate constant (*k*) calculated for nylon, silk and wool. It can be observed that for nylon, the half dyeing time was found to be shorter and the specific dyeing rate constant was shown to be greater than those for silk and wool. Also ($t_{1/2}$) was decreased and (*k*) was increased in

each of the three cases by rising the temperature. Thus, the dyeing rate of nylon and silk was much faster than that of the wool.

Table (1): Time of half dyeing ($t_{1/2}$) and specific dyeing rate constant (k) of (AR 37) on nylon, silk and wool.

Temp. °C	Nylon		Silk		Wool	
	$t_{1/2}$ (min)	$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^2$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^2$ (min^{-1})
55	98.00	5.42	140.00	3.39	177.00	1.67
65	92.00	6.24	134.00	4.08	172.00	1.88
75	85.00	6.98	127.00	4.53	166.00	2.06
85	80.00	8.50	120.00	5.30	160.00	2.20

Apparent diffusion coefficient (D)

According to equation (4), the apparent diffusion coefficient was calculated **[Brody, (1966)]**.

$$D = \frac{\pi r^2}{16 t}\left(\frac{C_t}{C_\infty}\right)^2 \tag{4}$$

Where C_t is the dye exhaustion at time t, C_∞ is the dye exhaustion at equilibrium; D is the diffusion coefficient; and r is the radius of the fibre.

The diffusion coefficient data D, of the three fibres are presented in Table (2). For all fibres, as the temperature was increased, the diffusion coefficients were also increased. This finding represents that the mobility of fibre greatly increased with increasing temperature **[Tae et al., (2005)]**. Nylon showed the highest diffusion coefficient at every temperature and wool had the lowest values.

Table (2): Diffusion coefficient (D) of (AR 37) on nylon, silk and wool at different temperatures.

Temp. °C	$D\,(cm^2\,min^{-1})$		
	Nylon	Silk	Wool
55	1.11×10^{-10}	5.36×10^{-11}	6.02×10^{-12}
65	1.34×10^{-10}	6.32×10^{-11}	8.52×10^{-12}
75	1.59×10^{-10}	7.54×10^{-11}	9.60×10^{-12}
85	2.34×10^{-10}	9.03×10^{-11}	12.26×10^{-12}

3.2. Thermodynamic Characterization :

Activation energy of diffusion (E_D^o)

The activation energy of diffusion can be calculated using Arrhenius equation.

$$\ln D = D_o - \frac{E_D^o}{RT} \qquad (5)$$

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 fibre substrate [Tae *et al.*, (2005)]. The activation energy of the diffusion can be obtained from the slope of the linear relationship between ln D and 1/T

The calculated activation energy (E_D^o) is presented in Table 3. The activation energy of nylon and silk was lower than that of wool. This result can be proposed that the resistance of the fibre to the dye diffusion was controlled by the fibre structure.

Table (3): The activation energy of the diffusion E_D^o of (AR 37) on nylon, silk and wool.

Parameter	Nylon	Silk	Wool
E_D^o (kcal/ mol)	4.99	5.28	6.60

Partition coefficient (K) and standard affinity ($-\Delta\mu^o$)

The partition coefficient *(K)* of the dye between the fibre (D_f) and the dyeing solution (D_s) was estimated from the following equation [Bendak *et al.*, (1998)].

$$K = \frac{\text{Concentration of the dye in the fibres (mg./kg. fibres)}}{\text{Concentration of the dye in the solution (mg./l.)}}$$

(6)

The most basic thermodynamic parameter is the standard affinity $(-\Delta\mu^\circ)$ of the dye in the dyeing solution towards the fibres substrate. This parameter was defined as a difference between the chemical potential of the dye in the fibre (μ_f°) and that in the dyeing solution (μ_s°). This value is a measure of the tendency of the dye to move from its standard state in the solution to its standard state on the fibre.

The standard affinity $-\Delta\mu^\circ$ of the dye was calculated using equation:

$$-\Delta\mu^\circ = -(\mu_f^\circ - \mu_s^\circ) = RT \ln \frac{D_f}{D_c} = RT \ln (K)$$

(7)

Where $(-\Delta\mu^o)$ is the standard affinity (cal/mol), (R) is the gas constant and (T) is the absolute temperature.

The corresponding values of the standard affinity of the three substrates, nylon, silk and wool are shown in Table 4.

Table (4): The partition coefficient (K) and the standard affinity $(-\Delta\mu^o)$ of (AR 37) on nylon , silk and wool.

Temp (°C)	Nylon		Silk		Wool	
	K	$-\Delta\mu^o$ (cal/mol)	K	$-\Delta\mu^o$ (cal/mol)	K	$-\Delta\mu^o$ (cal/mol)
55	737.50	4288.42	637.50	4208.71	526.00	4110.03
65	571.80	4248.86	538.50	4193.79	421.00	4084.82
75	493.70	4273.37	418.70	4159.84	259.00	3867.55
85	400.0	4246.99	250.00	3913.83	155.00	3574.98

As shown in Table 4, the standard affinities of nylon and silk are higher than those of wool. This finding explains that the dye has a higher tendency to move from the dyeing solution to the nylon and the silk substrates than to the wool substrate. As the temperature was increased, the standard affinity was decreased in all fibres. This observation explained that the adsorption of the dye towards the fibre was well known as an exothermic reaction process [Trotman, (1984)].

Enthalpy ($\Delta H°$) and entropy change($\Delta S°$)

As mentioned earlier, the dye adsorption is an exothermic reaction process. The amount of exothermic energy depends on the dyeing conditions, such as fibres, dyes, dyeing media and etc. The enthalpy change means the amount of the released thermal energy when the dye molecules adsorbed into fibre. The enthalpy change was obtained from the empirical plot that shows the relationship between $\Delta\mu_o/T$ and $1/T$ using the next equation:

$$\frac{\Delta H°}{T} = \frac{-\Delta\mu°}{T} + C \tag{8}$$

Where, $(\Delta H°)$ is the enthalpy of dyeing (cal/mol); $(\Delta\mu°)$ is the standard affinity (cal/mol); (T) absolute temperature (°K); and (C) is constant. From the slopes of the straight lines, the enthalpy changes can be calculated [**Kongkachuichay** *et al.,* **(2002)**].

The negatively larger value of enthalpy as shown in (Table 5) represents that the dye molecules were more strongly embedded within fibre, whereas the entropy change shows the extent of the reduced freedom of the dye molecules after the completion of dyeing [**Trotman** *et al.,* **(1984)**]. The negative value of entropy change represents the phenomenon that the mobility of the dye molecules was significantly decreased after dyeing. The entropy changes ($\Delta S°$) was calculated using equation (9):

$$-\Delta\mu'' = \Delta H'' - T\Delta S'' \tag{9}$$

In Table 5, the entropy change of wool showed the largest negative value among the three fibres. This observation suggests that the dye molecules within wool became the most immobilized state.

Table (5): The enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$) of (AR 37) on nylon, silk and wool.

Parameter	Nylon	Silk	Wool
$\Delta H°$ cal/mol	– 8660.66	– 10000.0	– 12142.80
$\Delta S°$ cal/mol K	– 16.05	– 31.25	– 41.97

CONCLUSION

In this work, the dyeing behaviour using acid dye (AR 37) and the three fiber substrates (nylon, silk and wool) were examined. The percentage rate of exhaustion was generally increased with increasing temperature. This behaviour could be attributable to the greater diffusional power of the acid dye molecules within the substrates. Dyeing properties in terms of time of half dyeing ($t_{1/2}$). specific dyeing rate constant (k), diffusion coefficient(D), activation energy of diffusion (E_D^o), standard affinity ($-\Delta\mu^o$), enthalpy change (ΔH^o) and the entropy change (ΔS^o), were also investigated. It was noted that the dyeing process is an exothermic in nature. The standard affinities of nylon and silk were a little higher than those of wool. Wool showed higher negative values of ΔH^o and ΔS^o, while nylon showed lower negative values. For all the three fibres as the temperature was increased the diffusion coefficients were also increased. Nylon had the highest diffusion coefficient and the lower activation energy at every temperature than those of silk and wool, respectively.

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دراسات حركية وثرموديناميكية للصبغة الحامضية الحمراء ٣٧
على ألياف البولى أميد والياف البروتين

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فى هذا البحث تم دراسة السلوك الحركى والثيرموديناميكى للصبغة الحامضية الحمراء ٣٧ على ثلاث ألياف وهى النايلون (بولى أميد) والحرير والصوف (ألياف البروتين) عند درجات حرارة مختلفة. وتبين من الدراسة أن نسبة النفاذية جيدة للألياف الثلاثة قيد الدراسة. كما تم تعيين وحساب كل من معدل ثابت الصباغة النوعى ، معامل الانتشار، القابلية القيلسية ، وطاقة تنشيط عملية الانتشار، والتغيير فى الانثالبى وأيضاً التغيير فى الانتروبى

وأوضحت الدراسة أن معامل الانتشار يزداد بزيادة درجة الحرارة. وأن معامل انتشار النايلون أعلى من معامل إنتشار كل من الحرير والصوف. وأن طاقة تنشيط عملية الانتشار للصبغة على كل من النايلون والحرير أقل منها على ألياف الصوف .