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Kinetic and thermodynamic studies on red sandalwood

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Red sandalwood (*Pterocarpus santalinus)* has been used as a dye for wool and nylon with and without mordant. Ethanol extract of red sandalwood has been used for carrying out thermodynamic and kinetic studies on wool and nylon. The diffusion coefficients, rate of dye uptake, adsorption isotherms, standard affinity, enthalpy and heat of dyeing have been calculated. It is observed that the red sandalwood dye has higher rate of dyeing and more affinity for nylon than those for wool.

Keywords: Kinetic study, Natural dye, *Pterocarpus santalinus*, Red sandal wood, Thermodynamic study

1 Introduction

Red sandalwood (*Pterocarpus santalinus*) has been, in the past, used as a textile dye. It contains five colouring components ranging from violet to orange in colour. The santalin (C.I. Natural Red 22) and deoxysantalin (C.I. Natural Red 23) have been identified as the main colouring components[1-8] (Fig. 1).

Previous studies have shown that the light fastness of the fabrics dyed with the aqueous as well as the alcoholic extract of the red sandalwood varies between 1 and 2 in most of the cases [9]. However, in a recent study, it has been obsreved that there is a considerable improvement in the fastness properties on mordanting sandalwood dyed wool fabrics with tin, ferrous and copper salts[10].

Since the main colouring components of red sandalwood are sparingly soluble in water and have a non-polar character, they can be dyed on textile fibres as disperse dyes or as disperse/mordant dyes. The present work was, therefore, aimed at studying the thermodynamics and kinetics of dyeing of the alcoholic extracts on nylon and wool fibres to establish the mechanism of dyeing.

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2 Materials and Methods

2.1 Materials

Finely crushed red sandalwood, supplied by Alps Industries Ltd. Ghaziabad, India, was extracted with ethanol at 78°C for 48 h, dried at 50°C under vacuum, pulverized and then used for dyeing.

2.2 Methods

2.2.1 Kinetic Studies

Wool and nylon fibres were scoured for 24 h with acetone and then dyed for the time period varying between 3 min and 240 min at 70° and 90° C in a buffered dye bath set at pH 4. The material - to - liquor ratio was maintained at 1:100. The dye uptake was measured at different time intervals by evaluating the extinction value at 504 nm λ_{max} on Perkin-Elmer Lambda-2 uv/vis spectrophotometer.

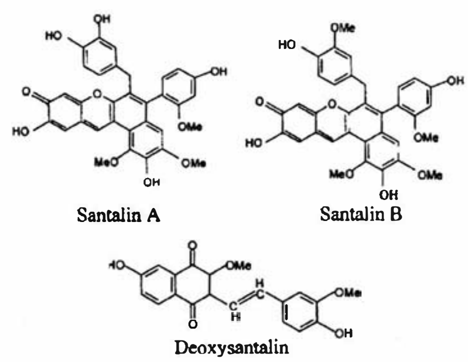

Fig. 1 — Chemical structure of colouring components

2.2.2 Thermodynamic Studies

For thermodynamic study, the wool and nylon fibres were dyed with buffered (pH 4) dye solutions of different concentrations at 70°C and 90°C for 4 h. The material - to - liquor ratio of the dye bath was maintained at 1:100. The dye in the exhausted dye bath was estimated by evaluating the extinction value at 504 nm λ_{max} on Perkin-Elmer Lambda -2 uv/vis spectrophotometer

3 Results and Discussion

3.1 Effect of Treatment Time and Temperature on Dye

The dye was stable at boiling temperature for more than 4 h beyond that the dye decomposed slowly. After 24 h, about 30% of the dye was decomposed. Hence, for kinetic and thermodynamic studies the equilibrium dyeing time was taken as 4 h.

3.2 Kinetic Studies

3.2.1 Rate of Dyeing

The dye uptake curves for wool and nylon dyed with red sandalwood extract are shown in Fig. 2. The half dyeing time ($T_{1/2}$) for wool and nylon were calculated from these curves and are given in the Table 1. The wool has higher $T_{1/2}$ than nylon at both 70°C and 90°C. Since santalin the main colouring component of red sandalwood is a non-polar molecule, it may have higher affinity for the more hydrophobic nylon fibre as compared to less hydrophobic wool. The per cent exhaustion on wool is also lower than that on nylon at both the temperatures. The percentage exhaustion of dye at 90°C is more than that at 70°C for wool, however in the case of nylon fibre the percentage exhaustion at 90°C is less than that at 70°C.There is need for more elaborate further study to critically investigate these points. However, some possible explanation is given below:

The uptake of the dye at different temperatures is dependent on the heat of dyeing. The dyeing could be endothermic or exothermic so that beyond a certain temperature the dye uptake decreases rather than increasing. This has been observed in the case of dyeing of direct dye on cotton. In the present case, the ΔH value (the heat of dyeing) for wool is positive while that for nylon is negative (Table 2).

The main mode of attachment of the dye to the fibre in the present case could be hydrogen bonds or by hydrophobic interactions. Nylon being more hydrophobic absorbs more dye and has higher affinity since both the hydrogen bonding and hydrophobic interactions are operative. On the other hand, in the case of wool the prominent interaction may be via hydrogen bonds and the hydrophobic interactions may be of marginal importance. Hence, the mechanism of adsorption in the two cases may be different.

3.2.2 Diffusion Coefficient

The apparent diffusion coefficient (D_{app}) of red sandalwood on wool and nylon were calculated by

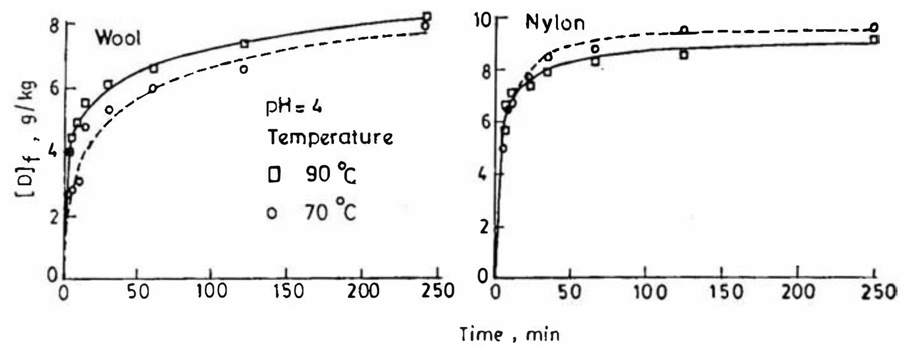

Fig. 2 — Dye uptake of wool and nylon fibres as a function of time

Table 1 — Calculated values of kinetic parameters

Fibre	Fibre radius ×10^{-3} cm	C_t/C_∞ (30 min)		$T_{1/2}$, min		D_{app} (Etters)	
		70° C	90° C	70° C	90° C	70° C	90° C
Nylon	2.88	0.873	0.857	3.89	4.04	5.412	8.123
Wool	1.1	0.664	0.743	15.16	6.16	1.432	1.712

$T_{1/2}$ – Half dyeing time, D_{app} – Apparent diffusion coefficient, C_t – Dye uptake at time t, and C_∞ – Dye uptake at equilibrium

Table 2 — Calculated values of thermodynamic parameters for wool and nylon

$[D]_f$, g/kg		$[D]_s$, g/L		$-\Delta\mu$, kJ/mol				ΔH kJ/mol	ΔS kJ/mol
				With v		Without v			
70°C	90°C	70°C	90°C	70°C	90°C	70°C	90°C		
				Wool					
1.901	2.050	0.009	0.008						
5.100	5.252	0.016	0.015						
6.232	7.619	0.034	0.021	19.17	20.89	16.01	17.49	10.46	86.38
9.320	10.51	0.029	0.024						
13.00	14.01	0.048	0.043						
				Nylon					
8.0180	7.556	0.008	0.011						
18.907	16.68	0.019	0.020						
28.924	24.09	0.028	0.032	27.41	27.57	24.451	24.533	-24.689	7.976
34.185	31.79	0.030	0.062						
41.649	40.53	0.034	0.060						

$[D]_f$ – Conc. of dye in fibre, $[D]_s$ – Conc. of dye in solution, $-\Delta\mu$ – Affinity, ΔH – Heat of dyeing, ΔS – Entropy of dyeing, and v – Internal volume of the fibre

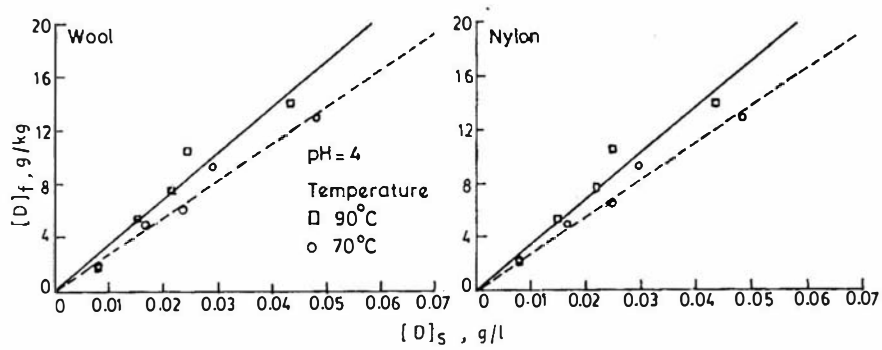

Fig. 3 — Dyeing isotherms for wool and nylon fibres

Etter's equation [11] and are given in the Table 1. From the calculated value of D_{app} and $T_{1/2}$, it can be observed that the dye exhaustion rate on nylon is higher than that on wool at both the temperatures.

Researchers[12-14] have calculated D_{app} for natural dyes dyed on nylon. The reported value of D_{app} for annato is 48.7×10^{-11} cm^2/s; juglone, 2.35×10^{-11} cm^2/s; and chrsophanic acid, 0.71×10^{-11} cm^2/s. These values as well as those of the red sandalwood are almost in the same range as that of synthetic disperse dye Duranol Red 2B (72.5×10^{-11} cm^2/s), further substantiating the hypothesis that these natural dyes are sorbed on nylon as in the case of disperse dyes.

3.3 Thermodynamic Studies

3.3.1 Adsorption Isotherm

The experimental results of dye uptake measurement of red sandalwood extract on wool and nylon at 70° C and 90° C are shown in Table 2 and the isotherms are shown in the Fig. 3. The best-fit isotherms for both wool and nylon are linear isotherms which indicate the partition mechanism of dyeing, corresponding to the Nernst model observed in dyeing of hydrophilic and hydrophobic fibres with non-ionic dyes. The slope of the isotherms increases with the increase in temperature for wool while it decreases with temperature for nylon. Linear isotherms were also obtained by Arshid *et al.*[15] in dyeing of wool with logwood and brazil wood dyes. These observations confirm that the dyeing mechanism of the non-polar natural dyes is similar to that of disperse dyes on synthetic fibres[16].

The slopes and results of statistical analysis for best-fit isotherms are given in Table 3.

3.3.2 Standard Affinity

The standard affinity ($-\Delta\mu$) of dyeing was calculated using the following equation:

Table 3 — Slopes and statistical parameters of isotherms

Parameter	Wool		Nylon	
	70°C	90°C	70°C	90°C
Slope	275.693	339.715	1127.883	589.951
S D	0.728	1.153	2.055	4.641
R	0.990	0.980	0.985	0.964

SD – Standard deviation, and *R* – Correlation coefficient

$$-\Delta\mu \approx RTln\frac{[D]_f}{V[D]_s} = RTlnK_v \quad ..(1)$$

where $[D]_f$ is the concentration of dye in the fibre(g/kg or mol/kg); $[D]_s$, the concentration of dye in the solution (g/L or mol/L); and V, the amount of water (in litres) associated with the fibre which is equal to its moisture regain at 100% humidity. The values of V for wool and nylon were taken as 0.33 and 0.07 litre respectively. The value of V makes K_v, the partition coefficient, dimensionless [17].

The standard affinity values obtained from Eq.(1) for both the fibres at 70°C and 90°C are given in the Table 2. The standard affinity of wool and nylon increases with the increase in temperature; this trend was already evident from the adsorption isotherms. The values of standard affinity at both the temperatures are higher for nylon.

The affinity of many natural dyes on nylon dyed at temperatures varying between 70°C and 100°C has been found in the range of 32.0 - 40 .0 kJmol^{-1}. For synthetic dye Duranol Red 2B, it is 67.4 kJmol^{-1}. An affinity of 27.57 kJmol^{-1} of red sandalwood shows that this dye has slightly lower affinity for nylon as compared to other natural dyes.

3.3.3 Heat of Dyeing

The heat of dyeing (ΔH) is given by the following equation,

$$\Delta H = \frac{T_2\Delta\mu_1 - T_1\Delta\mu_2}{T_2 - T_1} \quad ...(2)$$

The values of heat of dyeing (ΔH), calculated using the Eq. (2), are given in Table 2. For dyeing of wool, the heat of dyeing is positive, i.e. this dyeing process is endothermic and therefore more dye will be adsorbed at equilibrium with the increasing temperature. For dyeing of nylon, the heat of dyeing is negative, i.e. the dyeing process is exothermic and therefore, less dye will be adsorbed at equilibrium with the increasing temperature.

3.3.4 Entropy of Dyeing

The third thermodynamic parameter, entropy of dyeing (ΔS), was calculated by the following equation:

$$\Delta\mu = \Delta H - T\Delta S \quad ...(3)$$

The calculated values of entropy are given in the Table 3. The entropy of dyeing for both the fibres is positive, however, it is higher for wool than that for nylon.

4 Conclusions

The mechanism of dyeing of red sandalwood on wool and nylon seems to be similar to the established mechanism of dyeing of synthetic fibres with disperse dyes.

4.1 The $T_{½}$ values show that the rate of dyeing of red sandalwood is higher on nylon than that on wool. The values of diffusion coefficient are also higher for nylon than that for wool at both 70° C and 90° C.

4.2 The results of thermodynamic studies show that the red sandalwood dye has more affinity for nylon than that for wool. The process of dyeing was found to be endothermic for wool and exothermic for nylon.

4.3 The mechanism of dyeing for both nylon and wool is of partition type like that of disperse dye on hydrophobic fibres.

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