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Low-Temperature Dyeing of Protein and Polyamide Fibres using a Redox System

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ABSTRACT

*Dyeing investigations were performed on wool, silk and polyamide-6 fibres with acid dyes having various A-values (ratio of organic to inorganic character) in the presence of a thiourea/hydrogen peroxide redox system and in aqueous and water/*n*-propanol (9:1). An increase in colour intensity of the substrates dyed in presence of the redox system, as well as rapid exhaustion of the dyebath, were observed. Wool gave the highest relative colour intensity, followed by silk and then polyamide-6. Colour intensity was relatively improved in the case of the water/propanol dyeing medium compared to a purely aqueous medium.*

Both the time of half-dyeing and the specific dyeing rate constant decreased with increase in the A *values of the dyes. Addition of* n*-propanol to the bath preferentially lowered the time of half-dyeing, especially in the presence of the redox system.*

A tendency was also observed for the affinity and heat of dyeing of the substrates with acid dyes to increase with increasing A *values of the dyes.*

The presence of n*-propanol during dyeing gave a decrease in entropy due to the increased availability of the fibre structures to dyes of relatively high* A *value.*

1 INTRODUCTION

Improved technological aspects in the dyeing of textile fibres can be partially fulfilled by preservation of the quality of the dyed fibres and by attainment

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of maximum dye absorption and the re-use of the dyeing baths. Several successful trials have been carried out to meet the demands of energy conservation and higher production rates[1,2] as well as increasing the dye fibre interaction.[3] The creation of a covalent link between anionic or cationic dyes and fibres has been effected by application of γ-irradiation, which in turn results in the production of fast dyeings.[4] Redox systems have been used in the covalent fixation of dye moieties on protein fibres as well as on polyamide[5-13] and polyester fibres.[14] It has been pointed out that the dye uptake on some protein and synthetic fibres takes place to a greater extent when dyeing is carried out at a lower temperature than the boil in the presence of such redox systems.[11,15]

This present work deals with a study of the possibility of using an accelerating system in dyeing wool, silk and polyamide fibres with acid dyes at low temperature. A kinetic evaluation of the dyeing process is also attempted.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Substrates

Characteristics and preparations of the textile substrates used in this study are as follows.

(a) Plainly woven Merino wool fabric 286 g m^{-2}, soaped, washed thoroughly and dried.
(b) Natural silk, 1/1 weave, 52·5 g m^{-2}, degummed in boiling aqueous carbonate solution (1 g litre^{-1}) containing 0·5 g litre^{-1} neutral soap for 5 h, bleached at 75°C for 30 min with sodium hydrosulphite solution followed by acid rinse, washing and air drying.
(c) Polyamide-6 fabric, 210 denier/35 filament yarn, density 1·14 g ml^{-1}; soaped at 70°C for 1 h, washed and air dried.

2.1.2 Dyes

Commercial acid dyes, CI Acid Blue 23, CI Acid Orange 7, CI Acid Red 85 and CI Acid Blue 3, were used.

2.1.3 Chemicals

The oxidant used was hydrogen peroxide and the reductant was thiourea. Acetic acid, dimethylformamide, sodium carbonate, sodium hydrosulphite, hydrochloric acid and *n*-propanol were laboratory-grade chemicals.

2.2 Dyeing procedures

Substrates (1 g) were exhaust-dyed in 100 ml of dye solution at a starting acidity of pH 4, adjusted with acetic acid. A closed-circulating dyeing liquor in a Turbomat apparatus (Ahiba, Switzerland) was utilized. Dyeing time, temperature, dye moiety and redox system concentration as well as dyeing medium were changed according to the prescribed experimental conditions. At the end of the dyeing, the dyed samples were rinsed with cold water, scoured at 65°C for 0·5 h in soap solution (4 g litre^{-1}), then rinsed and finally dried under ambient conditions.

2.3 Dye extraction

The dyed samples were completely extracted with hot dimethylformamide/water mixture (1:1). The amount of the extracted dye was determined spectrophotometrically.

2.4 Testing

Colour intensity, expressed as K/S values of the dyed samples, was determined by applying the Kubelka–Munk equation:[16]

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

where R is the decimal fraction of the reflectance of the dyed sample, R_0 is the decimal fraction of the reflectance of the undyed sample, K is the absorption coefficient and S is the scattering coefficient.

2.4 Time of half-dyeing and specific dyeing rate constant

Fibre substrate samples (5 g) were dyed at 70°C and 90°C using 2% acid dye solution (o.w.f., on weight of fibres) for various time intervals (5 min to 6 h) to establish an equilibrium. Samples were removed from the dyebath immediately after the predetermined time. The remaining dye in the bath was spectrophotometrically estimated. For each dyeing temperature, the percentage exhaustion versus dyeing time was plotted. Time of half-dyeing ($t_{1/2}$, min) was determined from the resulting curve. The specific dye rate constant (K') was calculated according to:

$$K' = 0{\cdot}5C_\infty(dt_{1/2})^{1/2}$$

where C_∞ is the percentage dye absorbed on the sample at equilibrium

conditions between the sample and the dyebath divided by the weight of the sample and d (cm) is the fibre diameter.[17]

2.6 Affinity and heat of dyeing[17]

A 5% dyeing was carried out on two 0·5 g samples at 70°C and 90°C for 2 h using a liquor ratio of 80:1. At the end of the dyeing time the samples were immediately removed and rinsed in several changes of cold distilled water. One of the dyed samples was treated in 80 ml of distilled water for 2 h at 80°C. The other sample was similarly treated but for 4 h at 60°C. Samples were then squeezed and transferred to a 50-ml flask half-filled with water and left overnight. The volume of the flask was made up with water. The absorbance of the solution was determined spectrophotometrically. Calculation of the affinity ($-\Delta\mu^{\ominus}$) and the heat of dyeing ($\Delta H^{\ominus}$) were determined by first calculating the partition coefficient of the dye (k):

$$k = \frac{\text{Concn of dye in fibres (mg kg}^{-1}\text{ fibres)}}{\text{Concn of dye in solution (mg litre}^{-1}\text{)}}$$

$$-\Delta\mu^{\ominus} = 2{\cdot}3RT\log k \text{ (cal mol}^{-1}\text{)}$$

$$\Delta H^{\ominus} = \left[\frac{\Delta\mu_1^{\ominus}}{T_1} - \frac{\Delta\mu_2^{\ominus}}{T_2}\right] \Big/ \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

2.7 Entropy[18]

The entropy change $\Delta S^{\ominus}$ was calculated from the equation:

$$\Delta\mu^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

where T is the absolute temperature.

3 RESULTS AND DISCUSSION

A study was carried out on the effect of dyeing protein as well as polyamide fibres with acid dyes of various A values. Dyeing was performed in aqueous and aqueous/organic solvent media in the presence and absence of a thiourea–hydrogen peroxide redox system. Attempts were made to improve the dyeing process by obtaining maximum exhaustion and by carrying out the dyeing below the boiling temperature with preservation of both fibre and dyeing qualities.

3.1 Redox system

Substrates were introduced to the aqueous solutions of the acid dyes containing a constant amount of thiourea (0·05 M) and adjusted to pH 4 with acetic acid. Various amounts of H_2O_2 (0·01–0·04 M) were added to the dyeing solution. Dyeings were carried out at 75°C. Figure 1 shows the relationship between the acquired colour intensity, expressed as K/S values, and the

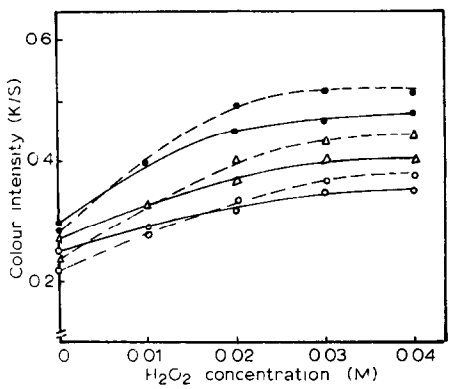

Fig. 1. Relationship between colour intensity of the dyed substrates and the concentration of H_2O_2 present in the dyeing medium. Dyeing: 2% o.w.f., 75°C, pH 4, 1 h, liq. ratio 100:1; thiourea 0·05 M. ——, CI Acid Blue 23; – – –, CI Acid Red 85; ●, wool; △, silk; ○, polyamide-6 fabric.

concentration of H_2O_2 present in the dyeing medium. The figure indicates an increase in colour intensity of the dyed substrates with increasing H_2O_2 concentration up to ~0·03 M. The presence of further H_2O_2 does not significantly affect the colour intensity and this may be due to the possibility of partial oxidation of the dye molecules in the solutions and/or some lack of thiourea as a reducing component in the redox system.

Figure 2 presents the relative colour intensity expressed as (K/S for dyed sample in presence of redox system)/(K/S of control dyed sample in absence of redox system) versus the time of dyeing at 75°C. It can be generally observed that incorporation of the redox system in the dyeing medium enhanced significantly the colour intensity of the dyed substrates. Rapid exhaustion of the dyebath was also noticed in the presence of the redox system. Wool showed the highest relative colour intensity, followed by silk and then polyamide.

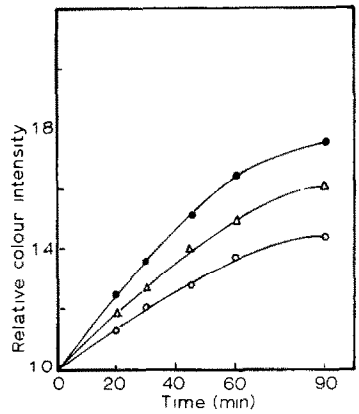

Fig. 2. Relationship between the relative colour intensity of the dyed substrates and the time of dyeing at 75°C in the presence of H_2O_2 (0·03 M)/thiourea (0·05 M) redox system. Dyeing: CI Acid Blue 3, 1% o.w.f., pH 4, liq. ratio 100:1. ●, Wool; △, silk; ○, polyamide-6.

3.2 Dyeing media

Dyeings were carried out using various acid dyes from a water/*n*-propanol medium (9:1) in the presence and absence of the redox system. Figure 3 shows the influence of introducing a small proportion of *n*-propanol to the aqueous dyebath in enhancing relatively the imparted colour intensity in the presence of the thiourea–H_2O_2 redox system. The colour intensity was found to be relatively improved compared with the use of a purely aqueous

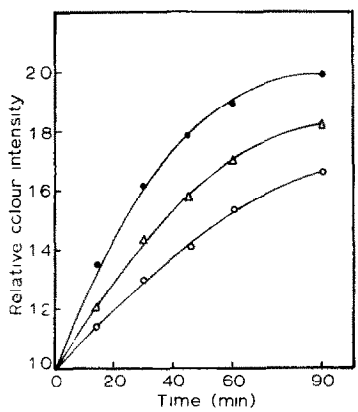

Fig. 3. Relationship between the relative colour intensity of dyed substrates and the time of dyeing at 75°C in water/*n*-propanol (9:1) medium and in presence of H_2O_2 (0·03 M)/thiourea (0·05 M) redox system. Dyeing: CI Acid Blue 3, 1% o.w.f., pH 4, liq. ratio 100:1. ●, wool; △, silk; ○, polyamide-6 fabric.

dyeing medium and this may be ascribed to the polarity of the solvent medium. Ionic interaction between dye molecules and substrates has an interesting role in solvent mixtures with high dielectric constants, whilst a dipolar interaction prevails in solvents of low dielectric constant (cf. Refs 5, 19–22).

3.3 Physicochemical investigations

A physicochemical investigation was carried out on the dyeing behaviour of wool, silk and polyamide with some acid of different chemical structures, and having an increasing *A* value. Dyeings were carried out in aqueous medium as well as in the water/*n*-propanol mixture (9:1) and in the absence and presence of the thiourea–H_2O_2 redox system.

3.3.1 Time of half-dyeing

Wool, silk and polyamide-6 fibres were dyed at 80°C with various acid dyestuffs without and with incorporation of *n*-propanol. Figure 4 shows the relationship between the time of half-dyeing ($t_{1/2}$, min) and the *A* values of the dyes. It is apparent that $t_{1/2}$ decreases with increase in the *A* value of the dye. Addition of *n*-propanol to the aqueous dyeing medium lowered the $t_{1/2}$ values and this would indicate that as the *A* value of the dye increases, there is a greater diffusion into the substrates during dyeing in the presence of the thiourea–H_2O_2 redox system, as indirectly shown by the $t_{1/2}$ values. The presence of small amounts of *n*-propanol in the vicinity of the fibres may cause some disorder in the fibre structure and consequently improve the dye-uptake characteristics, even at temperatures lower than the boiling point.

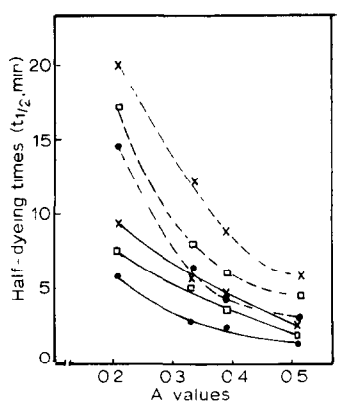

Fig. 4. Relationship between half-dyeing time of dyed substrates and the *A* value of the acid dyes. Dyeing: 3% o.w.f., 80°C, pH 4, liq. ratio 100:1, H_2O_2 (0·03 M)/thiourea (0·05 M). – – –, Aqueous medium; ——, water/propanol (9:1) mixture medium; ●, wool; □, silk; ×, polyamide-6.

3.3.2 Specific dyeing rate constant

Table 1 presents the values for the specific dyeing rate constant (K') of wool, silk and polyamide dyed at 80°C in the presence of the redox system under the aforementioned conditions. Changes in K' values were observed after addition of *n*-propanol to the medium, K' values decreasing with increase in the A value of the dye. The relatively high $t_{1/2}$ values, as well as the corresponding K' values, for dyes of low A values (CI Acid Blue 23), may show together the influence of the interrelating characteristics of the dye molecules such as size, shape, configuration, mobilization in the fibre phase and most importantly polar interactions. Polar interactions could make a contribution to the inorganic character, and non-polar interactions could make contributions to the organic character,[24] and thus dyes with low A values largely form ionic bonds with protein fibres during dyeing. On the other hand, non-polar interactions may predominate between acid dyes of high A values and the same substrates during dyeing. Moreover, the volume of the induced voids in the substrate structures also plays an important role in increasing the dye diffusion (cf. Ref. 25).

3.3.3 Affinity and heat of dyeing

Dyeing of the substrates was allowed to proceed to a practically perfect equilibrium so that the fibres were uniformly penetrated by the dye molecules and their adsorption and desorption took place at the same rate. The partition coefficient of the dye between the fibres and the liquor was estimated to provide calculations of the affinities[26] and consequently the heat of dyeing.[27] It was noted that the affinity and heat of dyeing were negative values, indicating that the dye–fibre interaction was exothermic.

TABLE 1

Specific Dyeing Rate Constant (K') for Wool, Silk and Polyamide-6 Dyed with Various Acid Dyes[a]

Dye	A^b	*Specific dyeing rate constant, K'*					
		Aqueous medium			*Water/propanol medium*		
		Wool	*Silk*	*Polyamide*	*Wool*	*Silk*	*Polyamide*
CI Acid Blue 23	0·211	0·50	0·58	0·65	0·42	0·50	0·56
CI Acid Orange 7	0·333	0·41	0·50	0·60	0·36	0·43	0·52
CI Acid Red 85	0·388	0·28	0·37	0·46	0·20	0·30	0·41
CI Acid Blue 3	0·511	0·22	0·30	0·40	0·18	0·27	0·37

[a] Dyeing at 80°C, 3% o.w.f., pH 4, liq. ratio 100:1, H_2O_2 (0·03 M)/thiourea (0·05 M).
[b] Ref. 23.

TABLE 2

Affinities and Heats of Dyeing of Wool, Silk and Polyamide-6 Dyed with Various Acid Dyes in the Presence of Redox System and in H_2O/Propanol (9:1) Mixture as Dyeing Medium[a]

Dye	A^b	*Affinity*, $-\Delta\mu^\circ$ ($kJ\,mol^{-1}$)						*Heat of dyeing*, $-\Delta H^\circ$ ($kJ\,mol^{-1}$)		
		Wool		*Silk*		*Polyamide*		*Wool*	*Silk*	*Polyamide*
		70°C	*90°C*	*70°C*	*90°C*	*70°C*	*90°C*			
CI Acid Blue 23	0·211	31·3	29·6	34	32·2	38	36·3	60·5	64·9	67·2
CI Acid Orange 7	0·333	28·6	27·0	32	28·1	35·4	33·7	56·1	62·0	64·6
CI Acid Red 85	0·388	26	22·9	29	27·2	32·8	31·0	54·0	60·0	63·0
CI Acid Blue 3	0·511	19·1	17·4	23	21·3	27·2	25·5	48·3	52·2	59·8

[a] Dyeing 5% o.w.f., pH 4, liq. ratio 80:1, H_2O_2 (0·03 M)/thiourea (0·05 M).
[b] Ref. 23.

Table 2 shows a tendency for the affinity of the dye molecules to substrates to increase with increasing A values at both the dyeing temperatures indicated. The heat of dyeing increased with increase in the A values of the dye. This could be anticipated since the greater disorder obtained in the fine structure of the substrates in the presence of *n*-propanol results in more free volume accessible to dye molecules within the fibre structure, as well as enhancing van der Waals attractions between the substrates and the dye molecules.

3.3.4 Entropy change

The values of the entropy change ($-\Delta S^\circ$) of the dyed substrates under investigation were also calculated. These values ranged, for all substrates, between 85 and 95 kJ mol^{-1} K^{-1} for the lowest A value to the highest A value respectively. It is suggested that the presence of a small amount of *n*-propanol in the vicinity of the substrate in the dyebath could decrease the degree of randomness due to the increased availability of the fibre structure to dyestuffs of relatively high A values.

REFERENCES

1. Anon., *International Wool Secretariat Technical Information Sheet No. 6* (1966).
2. Abdel-Fattah, S., Bendak, A. & Shakra, S., *Kolor. Ert.*, **20** (1978) 215.

3. Bakker, P. & Johnson, J., *J. Soc. Dyers Col.*, **89** (1973) 203.
4. Tikhomolova, M., Stephantsova, A., Celler, B., Shalamova, A., Tairova, G. & Kunzaetsova, L., *Tekh. Tekstil Prom.*, No. 2 (1971) 93.
5. Bendak, A. & Ali, J. H., *Ann. Chim.*, **75** (1985) 523.
6. Ibrahim, N. A., Haggag, K. & Hebeish, A., *Angew. Makromol. Chem.*, **131** (1985) 15.
7. Shenai, V. A. & Joshi, S. B., *Text. Dyers & Printer*, **18**(22) (1985) 16B.
8. Panda, G., Pati, N. C., Nayak, P., *J. Macromol. Sci. Chem.*, **A17**(3) (1982) 387.
9. Wang, T. H. & Wang, C. C., *Fang Chih K'O Hsueh*, **51** (1986) 65; *Chem. Abstr.*, **106** (1987) 103677 n.
10. Ibrahim, N. A., Haggag, K. & Hebeish, A., *Angew. Makromol. Chem.*, **132** (1985) 53.
11. Wang, H. H., Lin, C. H. & Teay, C. W., *Fang. Chih Kung Ch'eng Hsuch K'an*, **10** (1983) 132; *Chem. Abstr.*, **101** (1984) 92670y.
12. Kunchev, E., Gancheva, A. & Cholakov, G., *Melliand Textilber.*, **68** (1987) 273.
13. Ibrahim, N. A. & Haggag, K., *Dyes and Pigments*, **8** (1987) 327.
14. Kamamato, T. (Toyobo Co. Ltd), Japanese Patent 7629 574 (1976); *Chem. Abstr.*, **85** (1976) 34593r.
15. Shenai, V. & Saraf, N., *Int. Dyers & Textile Printer*, **13**(9) (1980) 33.
16. Judd, D. & Wyszecki, G., *Colour in Business, Science and Industry*, John Wiley, New York, 1975.
17. Johnson, K., *Dyeing of Synthetic Fibres, Recent Developments*, Noyes Data Corp., New Jersey, 1974.
18. McGregor, R., *J. Soc. Dyers Col.*, **83** (1967) 52.
19. Seguchi, K. & Kashino, T., *Sen-i Gakkaishi*, **33** (1979) 318; *Chem. Abstr.*, **87** (1977) 103292x.
20. Seguchi, K., Ito, M. & Kashimo, T., *Sen-i Gakkaishi*, **35** (1979) 429; *Chem. Abstr.*, **92** (1980) 7747.
21. Bendak, A. & Ibrahim, I., *Tinctoria*, **83** (1986) 47.
22. Aggour, Sh. & Bendak, A., *J. Soc. Fibre Sci. Technol.*, **42** (1986) T 25.
23. Tamai, H., Hayashi, K. & Watanabe, A., *Colloid Polym. Sci.*, **255** (1977) 773.
24. Qian, J. & Song, Z., *Proc. Int. Wool Text. Res. Conf., Tokyo*, Vol. V (1985) 249.
25. Bendak, A., *Ange. Makromol. Chem.*, **81** (1979) 63.
26. Vickerstaff, T., *The Physical Chemistry of Dyeing*, Vol. 2, Oliver & Boyd, London, 1954.
27. Peters, R., *Textile Chemistry: The Physical Chemistry of Dyeing*, Elsevier Scientific, Amsterdam, 1975.