Colouration of wool and silk with *Rheum emodi*

Debasish Das[a]

Institute of Jute Technology, 35 Ballygunge Circular Road, Kolkata 700 019, India

Sankar Ray Maulik

Visva Bharati University, Silpa Sadana, Sriniketan 731 236, India

and

Subhash Chandra Bhattacharya

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

Silk and wool fabrics have been dyed with colourant extracted from *Rheum emodi* in the absence and presence of magnesium sulphate, aluminium sulphate and ferrous sulphate mordants for producing shades of different colours, ranging from yellow to olive green. Colouring component of *Rheum emodi* has close resemblance with a typical anthraquinonoid type disperse dye; the uptake of such colouring component by the protein fibres remains unaffected within a wide *p*H range of 4 – 8. Colour uptake, rate of dyeing and affinity of colour are found to be more for silk than that for wool under all the conditions studied. The dyeing mechanism corresponds to the partition mechanism, confirming that this anthraquinonoid-based colourant is adsorbed by silk and wool fibres as a disperse dye and the dyeing process is endothermic. The use of ferrous sulphate and aluminium sulphate produces significant improvement in depth of shade, when both the substrates are treated with such salts prior to application of the colourant. Coloured protein fibres, in general, show a common light fastness and wash fastness ratings of 4 and 3 respectively. Ferrous sulphate, however, improves the colour fastness properties and colour retention on washing of both wool and silk fabrics further.

Keywords: Adsorption isotherm, Dyeing, Kinetic study, Mordanting, *Rheum emodi*, Silk, Wool

IPC Code: Int.Cl.[8] D06P

1 Introduction

Rheum emodi, commonly known as *dolu*, is a stout herb of 1.5-3 m in height, distributed in the Himalayas from Kashmir to Sikkim at an altitude of 3300 – 5200 m. The stout roots are the chief source of Himalayan rhubarb and finds application chiefly in medicine as a purgative and astringent tonic and can also be used for colouration of textile materials.[1-7] The root contains a number of anthraquinone derivatives based on rhein, emodin, aloe-emodin and chrysophanol. These are found free and as quinone, anthrone or dianthrone glycosides.[3–4] However, the chief colouring component of *Rheum emodi* is chrysophanic acid[1], the structure of which is given in Fig.1. The present study is aimed at applying colouring component of *Rheum emodi* on wool and silk followed by evaluating some fundamental parameters of dyeing, such as rate of dyeing, adsorption isotherm, standard affinity, heat of dyeing and entropy of dyeing, and assessing different colour fastness properties.
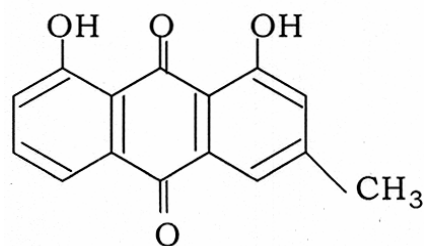

Fig. 1—Chrysophanic acid

2 Materials and Methods

2.1 Materials

Plain weave scoured wool and loom state silk fabrics, having 236 ends/dm & 430 ends/dm, 204 picks/dm & 212 picks/dm, and 150 g/m^2 & 50 g/m^2 weight respectively were used for the study. The colourant was obtained from M/s ALPS Industries Ltd., India for dyeing of wool and silk fibres. The colourant was also purified by dissolving in ethanol, followed by filtration and recrystallisation for kinetic and thermodynamic studies. All the chemicals used were of laboratory reagent grade. Kinetic study was

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[a]To whom all the correspondence should be addressed.
E-mail: ijt@cal2.vsnl.net.in/s_r_moulik@yahoo.co.in

carried out on silk and wool fibres having an average radius of 6.2×10^{-4} cm and 3.6×10^{-4} cm respectively.

2.2 Methods

2.2.1 Degumming and Bleaching of Silk

The loom state silk fabric was degummed at 90^0C for 1.5 h in an aqueous solution containing soap (6.0 g/L) and sodium carbonate (2.0 g/L). The degummed silk fabric was then bleached at 85^0C for 1 h in a solution containing hydrogen peroxide (0.9%), non-silicate stabilizer (0.15%) and sodium carbonate (0.1%). Material-to-liquor ratio for both degumming and bleaching operations was maintained at 1:20. Bleached fabric was washed at 70°C for 10 min, cold washed and finally dried.

2.2.2 Dyeing of Wool and Silk

2.2.2.1 In Absence of Mordant

Silk and wool fabrics were dyed with *Rheum emodi* (10% owf) at a material-to-liquor ratio of 1:50 in a laboratory model open bath beaker dyeing machine. The dye bath temperature was maintained at 90^0C for 1 h. The *p*H of the dye bath was set at different specified levels ranging from 2 to 10 at the beginning of the dyeing process. Hydrochloric acid, acetic acid and sodium carbonate were used for the adjustment of *p*H at such specified levels.

2.2.2.2 In Presence of Mordant

Dyeing of silk and wool fabrics with *Rheum emodi* (10% owf) was carried out separately in presence of different specified mordants following three different methods, namely pre-mordanting, post-mordanting and simultaneous mordanting; 5g/L mordant concentration was employed in all the cases. In the pre-mordanting method, the fabrics were first immersed in an aqueous solution of mordants for 45 min at 70^0C and rinsed thoroughly with water. The mordanted fabrics were then dyed at 90^0C for 1 h with a material-to-liquor ratio of 1:50. For simultaneous mordanting, the fabrics were immersed in a bath containing both mordant and dye solution. The dyeing temperature was kept at 90^0C and dyeing was carried out for 1 h with a material-to-liquor ratio of 1:50. In case of post- mordanting, the dyeing was carried out in the absence of mordants at 90^0C for 1 h and a cold wash was given thereafter. Dyed fabrics were then mordanted in a separate bath at 70^0C for 45 min. The soaping of all the treated fabrics was done, employing 2g/L non-ionic detergent at 60^0C for 10 min. Finally, the fabric samples were cold washed and dried.

2.2.3 Measurement of Wavelength of Maximum Absorption

The wavelength of maximum absorption (λ_{max}) of *Rheum emodi* solution at different specified *p*H was measured using U-2000, UV-visible absorbance spectrophotometer of HITACHI, Japan, after diluting the solution to an appropriate level.

2.2.4 Estimation of Percentage Exhaustion

The exhaustion of *Rheum emodi* from aqueous dye bath into different specified substrates at different specified *p*H was determined from the concentration of dye in fibre at the end of dyeing colorimetrically. The weight of the dye in fibre was determined from absorbance value (measured at 512nm) of 5% (w/w) potassium hydroxide solution containing dyed fibre against a blank. Such solution was prepared in each case by dissolving 100 mg of dyed fibre in 100 mL of 5% (w/w) aqueous potassium hydroxide solution in view of the fact that *Rheum emodi* and both the protein fibres are soluble in potassium hydroxide solution. The blank solution for such purpose was prepared by dissolving 100 mg of fibre in 100 mL of such 5% (w/w) potassium hydroxide solution. Concentrations of dye in potassium hydroxide solutions containing such dyed fibre were obtained from the absorbance value of the later with the help of a calibration curve previously constructed in the same spectrophotometer using standard dye solutions. Such standard dye solutions were prepared by dissolving separately 10, 20, 40, 80, 100 mg of dye in 5% (w/w) potassium hydroxide solution. Each of 100 mL of such potassium hydroxide solutions used for preparing calibration curve also has 100 mg of protein substrate in it.

2.2.5 Kinetic Study

For measurement of rate of dyeing (dyeing kinetics), an infinite bath (1:1000) was prepared and buffered with 0.2M sodium acetate and 0.2M acetic acid to give a constant *p*H of 4.2 ± 0.2. The dye uptake in terms of weight of dye in fibre was measured at different specified time intervals ranging from 15 min to 24 h at 90^0C for both silk and wool fibres following the same procedure as described for the estimation of percentage exhaustion.

2.2.6 Calculation of Diffusion Coefficient

The apparent diffusion coefficient of *Rheum emodi* applied on silk and wool fibres was calculated by Hill's equation[8] for an infinite bath and the approximations given by Etters[9], Rais and Militky[10], Urbanik[11] and Shibusawa[12].

2.2.7 Thermodynamic Studies

For thermodynamic studies, dyeing was carried out using a range of concentrations of dye solution over a period of 24 h at 60^0C and 90^0C, keeping the material-to-liquor ratio at 1:200. The dye liquor was buffered as mentioned for kinetic study. The amount of dye in the fibre and in the dye bath was estimated colorimetrically using the spectrophotometer as per the standard procedure reported elsewhere.[8,13] For estimation of dye uptake in fibre, the dyed wool and silk fibres were dissolved in 5% (w/w) aqueous potassium hydroxide solution. The concentration of dye in such potassium hydroxide solution was obtained from the absorbance value with the help of a suitable calibration curve previously constructed in the same spectrophotometer. The concentration of dye in the residual bath was estimated from the difference between weight of the dye in fibre and initial weight of the dye taken in the aqueous dye bath following the procedure as mentioned above.

2.2.8 Assessment of Dye Receptivity in terms of K/S

In order to determine the dye receptivity, the *K/S* value of fabric samples dyed using aqueous solution of *Rheum emodi* under the specified conditions was determined in a Mcbeth 2020+ reflectance spectrophotometer interfaced with a computer. The reflectance values (*R*) of the dyed fabric at the wavelength of maximum absorption (λ_{max} = 420nm) were converted to the corresponding *K/S* value using the following Kubelka-Munk equation:

$$K/S = [(1-R)^2 / 2R]$$

where *K* is the absorption coefficient; and *S*, the scattering coefficient.[14] A higher *K/S* value indicates better dye receptivity of the substrates. The result shown here is the average of seven scans over a wavelength range of 400-700 nm for each sample.

2.2.9 Assessment of Colour Fastness Properties

Light fastness was assessed in accordance with IS: 2454-1984 on an MBTF (Mercury Bulb Tungsten Filament) light fastness tester. The wash fastness was assessed in accordance with IS: 3361-1984 (ISO- II) on a Launder-O-meter.

3 Results and Discussion

3.1 Wavelength of Maximum Absorption

Table 1 shows wavelength of maximum absorption (λ_{max}) and observed colour of aqueous solution of *Rheum emodi* in absence and presence of acid, alkali and mordanting agents. In the absence of any of the above agents, aqueous solution of this dye gives a *p*H value of ~ 6.0 with a yellow-brown colour, showing its λ_{max} at 406 nm. In the *p*H range of 2 - 6 there is no shifting of λ_{max} value. But with the increase in *p*H of the aqueous solution, a bathochromic shift in wavelength of maximum absorption (λ_{max}) towards higher wavelength is observed, giving a λ_{max} value of 457 at *p*H of 10. The colour of the aqueous solution also changes steadily from yellow-brown to brown-red in consequent to such shifting of λ_{max} with the increase in *p*H value of aqueous solution. Under alkaline condition there is also an increase in absorbance value; this may be due to the ionization of hydroxyl group of the dye in alkaline medium, which increases aqueous solubility of such dye. Among the mordanting agents used, magnesium sulphate causes insignificant shifting of λ_{max} value without any precipitation of colouring component. The aqueous coloured solution of this dye becomes almost colourless upon addition of aluminium sulphate in consequent to immediate formation and precipitation of complex [15] or "lake" by the colouring component present in *Rheum emodi*. Formation of such chelate with the colouring component present in this dye upon addition of ferrous sulphate is also observed and

Table 1—Wavelength of maximum absorption of aqueous solution of *Rheum emodi*

Aqueous solution of R. emodi treated with	pH	Wavelength of maximum absorption nm	Colour observed
None	6	406	Yellow brown
Acetic acid	4	403	Yellow brown
Hydrochloric acid	2	397	Yellow
Sodium carbonate	8	439	Brown red
Sodium carbonate	10	457	Dark brown red
Magnesium sulphate	6	406	Yellow brown
Aluminium sulphate	3.15	Immediate complex formation and precipitation observed	Brown yellow ppt
Ferrous sulphate	5.35	Precipitation observed slowly	Black ppt

the complex in such case is observed to remain in aqueous phase for some time before the precipitation takes place. The fact that such rate of precipitation of trivalent aluminium is much more than that of bivalent iron, as reported earlier, is also observed in this case.[16] Aqueous solution of this dye in presence of aluminium and ferrous sulphate produces brown-yellow and black coloured lake respectively.

3.2 Effect of Variation in *p*H

In view of the anthraquinonoid structure of the dye and its poor solubility in aqueous medium (~ 28%), it is apparent that the dye is non-polar in nature in acidic and neutral *p*H; in alkaline *p*H, however, the ionization of phenolic hydroxyl group promotes the solubility of dye in aqueous medium (~ 55%) and the dye dissolves completely in 5% (w/w) potassium hydroxide solution. Application of such dye is, therefore, expected to be hardly influenced by the dye bath *p*H within the range of 2–8 (refs 17, 18) and only non-polar force of attraction should be considered in developing affinity of the dye for different fibres. Effect of variation in *p*H on the exhaustion of dye bath in the absence of any mordanting agents on wool
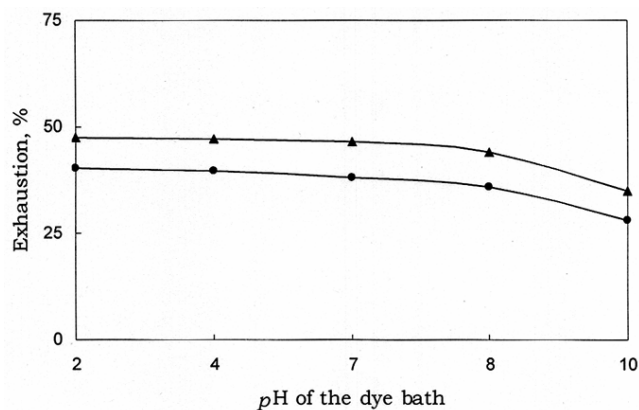

Fig. 2—Exhaustion of *Rheum emodi* on (●) wool and (▲) silk against dye bath *p*H

and silk is shown in Fig.2. The exhaustion of this dye is found to be higher on silk than on wool in the whole range of *p*H considered. The affinity of such non-polar dye for a substrate predominantly depends on non-polar character of fibre.[18–20] The higher exhaustion of this dye in silk is due to the presence of higher percentage of non-polar hydrocarbon in silk than that in wool fibre.[20] The affinity of such dye, however, appears to reduce significantly on wool and silk substrates only when the phenolic hydroxyl group is dissociated under fairly alkaline condition due to the formation of phenolate ion.[8] In view of reported significant hydrolytic degradation of protein fibres at *p*H of around or less than 2.5 and above 7 at elevated temperature of dyeing for a prolong time [18], an appreciable dye uptake at *p*H ~ 4 in absence of any salt for both the fibres is considered to be of practical significance.

3.3 Effect of Variation in Mordanting Methods

The aqueous solution of *Rheum emodi* has been applied on wool and silk fabrics employing magnesium sulphate, aluminium sulphate and ferrous sulphate as mordanting agents following pre-, post- and simultaneous mordanting methods. Results of such study assessed in terms of *K/S* are listed in Table 2. It is apparent from the structure that this colourant is capable of forming stable complexes with the metal ions as is also evident from the study when different mordants produce shades of different colour ranging from yellow to olive green (Table 2). For pre- and post-mordanting methods, the ability of the mordanting agents to incorporate the colouring component in the structure of wool and silk fibres follows the following order:

Ferrous sulphate > Aluminium sulphate > Magnesium sulphate ~ No mordant

The difference in *K/S* value of the dyed substrates for pre- and post- mordanting methods with the above

Table 2—Effect of variation in mordanting methods
[*K/S* value without mordant: Silk – 5.14, and Wool – 2.56]

Substrate	Mordanting agent	*K/S* (λ = 420 nm)			Colour appeared on substrate
		Pre- mordanting	Post- mordanting	Simultaneous mordanting	
Silk	Magnesium sulphate	5.24	5.17	5.13	Yellow
	Aluminium sulphate	6.62	6.43	3.62	Yellow
	Ferrous sulphate	8.55	7.96	4.74	Olive green
Wool	Magnesium sulphate	2.54	2.33	2.47	Yellow
	Aluminium sulphate	3.44	3.23	2.06	Yellow
	Ferrous sulphate	4.18	3.79	3.08	Olive green

three mordanting agents may be observed as the consequence of relative ability of metal ions to form complex [15, 21] with the colouring component present in *Rheum emodi*. Iron and aluminium (with their superior complex forming ability) form complex more readily in aqueous phase prior to transportation of colouring matter on to the substrate than does magnesium, thus giving poor *K/S* value of the dyed substrates for simultaneous mordanting method. For pre- or post-mordanting method, however, superior complex forming ability of aluminium and ferrous [15] could be realised in the fibre as evident from the *K/S* value of the respective samples (Table 2). Effect of variation in mordanting methods of three different mordanting agents as described above on the silk substrates is found to be similar to that observed on wool substrates (Table 2).

3.4 Effect of Variation in Dose of Mordanting Agents

Effect of variation in dose level of mordanting agents on *K/S* values of wool and silk fabrics, when dyed with *Rheum emodi*, is shown in Table 3. It is

Table 3—Effect of variation in dose of mordanting agents

Substrate	Mordanting agent	Dose level g/L	*K/S* (λ = 420 nm)
Silk	Nil	Nil	3.18
	Magnesium sulphate	1	3.23
		5	3.48
		10	3.43
	Aluminium sulphate	1	4.03
		5	5.98
		10	5.91
	Ferrous sulphate	1	5.62
		5	6.61
		10	6.55
Wool	Nil	Nil	2.41
	Magnesium sulphate	1	2.40
		5	2.52
		10	2.46
	Aluminium sulphate	1	3.08
		5	3.74
		10	3.73
	Ferrous sulphate	1	3.43
		5	4.46
		10	4.38

Table 4—Kinetic parameters and diffusion coefficient of *R. emodi* for silk and wool fibres

Fibre	C_t / C_∞ [a]	Diffusion coefficient $\times 10^{-11}$, cm^2/s				
		Hill	Urbanic	Etters	Rais and Militky	Shibusawa
Silk	0.57	1.75	1.74	1.76	1.73	1.78
Wool	0.41	0.20	0.28	0.28	0.27	0.25

[a]C_t and C_∞ are the concentrations of dye in fibre expressed in g/ after 30 min (*t* = 30 min) of dyeing and when equilibrium is reache (∞ ~ 1440 min i.e. 24 h).

observed that the depth of shade follows a common increasing trend with the increase in dose levels of respective mordants up to a concentration of 5 g/L, afterwards there is a leveling off trend/decreasing trend in the depth of shade with further increase in dose level of mordant (Table 3).

3.5 Rate of Dyeing and Diffusion Coefficient

Results of dye uptake by silk and wool fibres dyed at 90^{0}C for various time periods are shown in Fig.3. For incorporation of such non-polar dye in the structure of wool and silk, the non-polar hydrocarbons of the protein fibres are considered to be chiefly responsible and the uptake of such dye by protein fibres is reported to be analogous to extraction of non-polar substance from aqueous solution by an organic solvent.[19] In this respect, silk fibre contains much more non-polar hydrocarbon than that of wool fibre [20]; this indicates faster rate of dyeing of silk fibre than that of wool fibre as also reported in the study.

The apparent diffusion coefficient was calculated by Hill's equation and other approximations given by Urbanic, Rais and Militky, Etters and Shibusawa. Table 4 shows that the diffusion coefficient of this dye is higher for silk than that for wool. The presence of higher percentage of non-polar hydrocarbons in silk fibre than that in wool fibre facilitates diffusion of such dye into the interior of silk fibre.

3.6 Adsorption Isotherm

Quantitative estimation of dye in fibre and that in dye bath till equilibrium is attained for dyeing of wool and silk fibres at 60^{0}C and 90^{0}C with *Rheum emodi* was done and the results are plotted as adsorption isotherm (Fig.4). To predict the nature of isotherm, the best fit line for three models of dye sorption, viz.
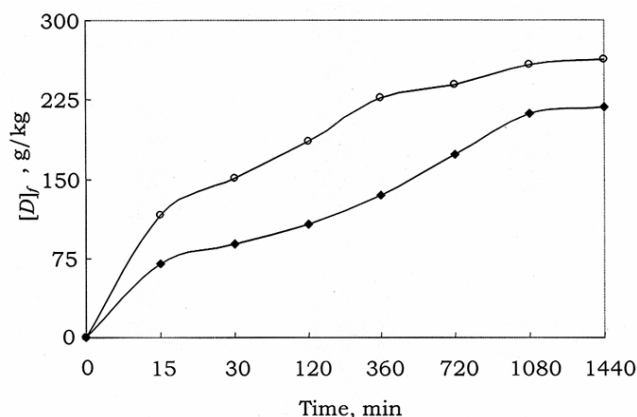

Fig. 3—Plots of dye uptake with respect to time for ($\blacklozenge$) wool and for ($\circ$) silk fibres
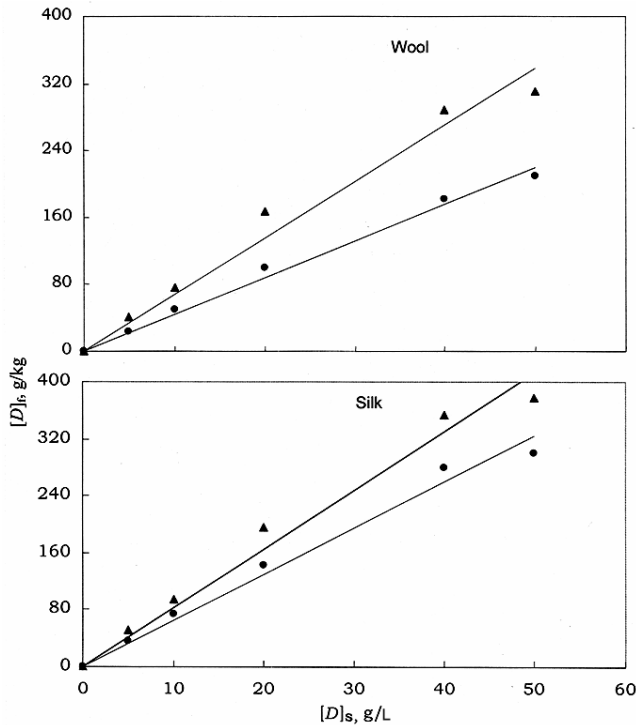
Fig. 4—Adsorption isotherm for dyeing of wool and silk with *Rheum emodi* at (●) 60°C and (▲) 90°C temperature

Nernst, Langmuir and Freundlich, was drawn. The best fit isotherms for both wool and silk are linear, which indicate the partition mechanism of dyeing. The experimental data fitted well to the Nernst isotherms with a high correlation coefficient (R^2 - 0.97-0.99). The slope of the isotherms, representing partition ratio, increases with the increase in dyeing temperature for both the fibres. The results obtained for the assessment of adsorption isotherms are in agreement with that obtained for dyeing of wool fibre with non-ionic dyes, as reported earlier.[17, 22]

3.7 Standard Affinity

Dyeing of wool and silk with *Rheum emodi* corresponds to the partition mechanism, the standard affinity of the dye for these fibres was calculated using the following equation[8]:

$$- \Delta \mu = RT \ln [D_f / V \times D_s] = RT \ln K_v \qquad \ldots (1)$$

where R is the universal gas constant; D_f, the concentration of dye in the fibre in g/kg; D_s, the concentration of dye in solution in g/L; and V, the volume term representing the effective volume of water in the substrates in L/kg. The values of V for wool and silk are 0.31 and 0.34 L/kg respectively.[23]

The standard affinity values obtained from Eq. (1) for both wool and silk fibres at 60°C and 90°C are

Table 5—Calculated values of thermodynamic parameters for wool and silk dyed with *R. emodi*

Fibre	$- \Delta \mu$ kJ/mol		ΔH kJ/mol	ΔS J/mol / K
	60 °C	90 °C		
Silk	8.49	10.05	8.82	51.90
Wool	7.69	9.65	14.06	65.38

given in Table 5. It is found that the value of standard affinity for both the fibres increases with the increase in dyeing temperature; the values are, however, higher for silk fibre than that for wool fibre. The high affinity of this dye on silk fibre is mainly due to the presence of more non-polar hydrocarbon chains present in silk than those present in wool fibre.[20]

3.8 Heat of Dyeing

Heat of dyeing (ΔH) was calculated using the following equation[8]:

$$\Delta H = [T_2 \times \Delta \mu_1 - T_1 \times \Delta \mu_2] / (T_2 - T_1) \qquad \ldots (2)$$

where T_1 and T_2 are the temperatures of dyeing at 60°C and 90°C; and $\Delta \mu_1$ and $\Delta \mu_2$, the standard affinity at temperature 60°C and 90°C. The values of ΔH calculated using Eq. (2) is given in Table 5. It is found that for dyeing of wool and silk with this dye, the heat of dyeing is positive, i.e. the dyeing process is endothermic and therefore more dye will be absorbed at equilibrium, attained at higher temperature.

3.9 Entropy of Dyeing

The third thermodynamic parameter, entropy of dyeing (ΔS), was calculated by the following equation[8]:

$$\Delta \mu = \Delta H - T \Delta S \qquad \ldots (3)$$

The calculated values of entropy are given in Table 5. The entropy of dyeing for both wool and silk fibres is positive; however it is higher for wool.

3.10 Colour Fastness to Light and Washing

Table 6 shows data for colour fastness to light and washing for wool and silk when dyed with *Rheum emodi* in absence and presence of mordanting agents. The colour fastness rating for light and washing of wool and silk fibres when dyed with this dye commonly appears to be 4 and 3 respectively. Aluminium sulphate and ferrous sulphate used for pre- and post- mordanting methods improve light and wash fastness ratings of both wool and silk fibres commonly by one point. For simultaneous mordanting

Table 6—Colour fastness to light and washing for silk and wool dyed with *R. emodi*

| Substrate	Type of mordants	Mordanting method	Light fastness	Wash fastness		
				Change in colour	Staining on cotton	Staining on silk
Silk	Nil	—	4	3	4	3-4
	Aluminium sulphate	Post mordanting	5	4	4	3
	Magnesium sulphate	Post mordanting	4	3	4	3
	Ferrous sulphate	Post mordanting	5	4	4	4
	Aluminium sulphate	Pre-mordanting	5	4	4	3
	Magnesium sulphate	Pre-mordanting	4	3	4	3
	Ferrous sulphate	Pre-mordanting	5-6	4	4	4
	Aluminium sulphate	Simultaneous mordanting	4	3	4	3-4
	Magnesium sulphate	Simultaneous mordanting	4	3	4	3-4
	Ferrous sulphate	Simultaneous mordanting	4	3	4	3-4
Wool	Nil	—	4	3	4	3-4
	Aluminium sulphate	Post mordanting	5	3-4	4	3
	Magnesium sulphate	Post mordanting	4	3	4	2-3
	Ferrous sulphate	Post mordanting	5-6	4	4	3-4
	Aluminium sulphate	Pre-mordanting	5	3-4	4	3
	Magnesium sulphate	Pre-mordanting	3-4	3	4	3
	Ferrous sulphate	Pre-mordanting	5-6	4	4	4
	Aluminium sulphate	Simultaneous mordanting	4	3	4	3
	Magnesium sulphate	Simultaneous mordanting	4	3	4	2-3
	Ferrous sulphate	Simultaneous mordanting	4	3	4	3-4
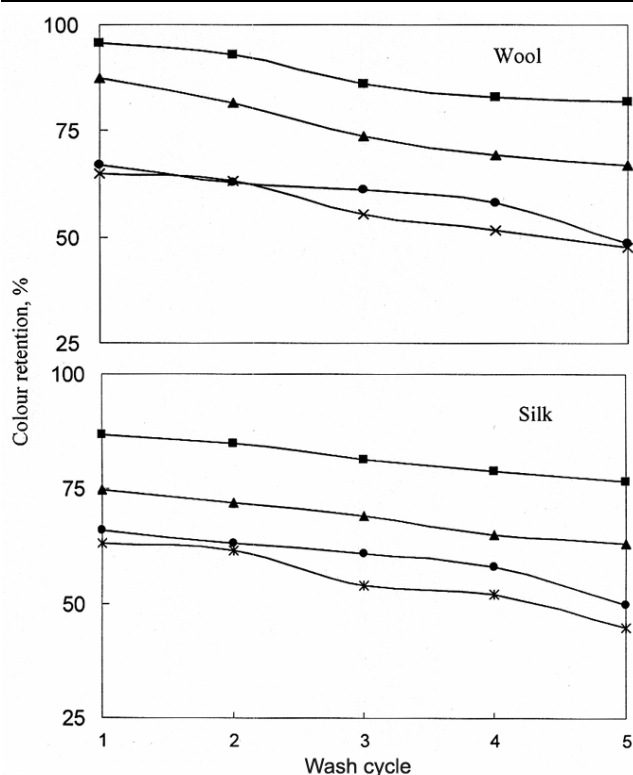
Fig. 5—Colour retention against wash cycle for wool and silk dyed with *Rheum emodi* in presence of (●) MgSO$_4$, (▲) Al$_2$(SO4)$_3$, (■) FeSO$_4$ and (∗) no salt

method, no significant change in light and wash fastness ratings is observed when such fibres are dyed with this dye in presence of sulphates of aluminium, magnesium and ferrous separately. Improvement in colour fastness to light on using aluminium sulphate and ferrous sulphate as mordanting agents is the consequence of enhancement of size of colouring component. Aluminium and iron with their good complex forming ability hold two or more of such colouring components together in the fibre structure by forming co-ordinate bonds, in addition to the formation of intermolecular hydrogen bonds between two dye molecules and between dye and fibre. Such enhancement in the rating for colour fastness to light observed to be absent in case of simultaneous mordanting method, as the aggregation of dye molecules in presence of such ferrous and aluminium ions predominantly takes place in the solution phase, prior to their transference into fibre phase. Such aggregation of dye molecules is absent in case of magnesium sulphate mordanting agent, due to relatively poor complex forming ability of it. The use of magnesium sulphate as the mordanting agent for application of this dye on protein fibres, therefore, shows no improvement in colour fastness to light.

3.11 Effect of Progressive Wash on Colour Retention

Colour retention of dyed wool and silk fabrics, expressed in terms of percentage loss of K/S value, for different wash cycles (up to 5, ISO-II) are shown in Fig. 5. The retention of colour in the dyed substrates for the use of three salts is as per the following order:

Ferrous sulphate > Aluminium sulphate > Magnesium sulphate ~No salt.

Above trend for retention of colour by the dyed substrates matches well with the relative complex forming ability of the metal ions of the inorganic salts employed in the present study.

4 Conclusions

Colouration of silk and wool with *Rheum emodi* was found to be effectively accomplished within a wide pH range of 4–8. Dye uptake, rate of dyeing and affinity of this colour are found to be higher for silk fibre than that for wool fibre. The dyeing mechanism corresponds well to the partition mechanism, confirming that this anthraquinonoid- based dye is adsorbed by silk and wool as a disperse dye and the dyeing process appears to be endothermic. Colour fastness to light and washing of silk and wool dyed with this dye in absence of any salt appears to be 4 and 3 respectively. Application of salts, such as aluminium sulphate and ferrous sulphate before and after dyeing commonly improves depth of shade, and colour fastness to light and washing of the dyed substrates. Pre- application of ferrous sulphate on wool and silk followed by dyeing with *Rheum emodi* produces most balanced improvement in colour uptake, light and wash fastness and colour retention on repeated washing of such protein fibres.

Industrial Importance: In view of good overall colour fastness properties of silk and wool fibres dyed with *Rheum emodi*, the application method of *Rheum emodi* described in the article can suitably be used for producing value-added environment friendly apparel and other textile products made from the above two protein fibres.

References
1 Gulrajani M L, Gupta D B, Agarwal V & Jain M, *Indian Text J*, 102(3) (1992) 76-83.
2 Gulrajani M L & Gupta D B, *Natural Dyes and their Application to Textiles* (Indian Institute of Technology, New Delhi), 1992, 36.
3 Gupta D B & Gulrajani M L, *J Soc Dyers Colour*, 112(8) (1996) 270.
4 *The Wealth of India, Raw Materials*, Vol IX (CSIR, New Delhi), 1972, 3 - 4.
5 Raisanen R, Nousiainen P & Hynninen P H, *Text Res J*, 71(10) (2001) 922–927.
6 Raisanen R, Nousiainen P & Hynninen P H, *Text Res J*, 71(11) (2001) 1016–1022.
7 Khan M, Khan M A, Srivastava P K & Mohammad F, *Colourage*, 51(5) (2004) 33–38.
8 Jones F, *The Theory of Colouration of Textiles*, edited by A Johnson (Society of Dyers Colorists, W Yorkshire), 1989, 133, 135, 260, & 383.
9 Etters J N, *Text Chem Color*, 12 (1980) 140.
10 Rais J & Militky J, *J Soc Dyers Colour*, 91(10) (1975) 344.
11 Urbanic A, *J Soc Dyers Colour*, 90(12) (1974) 444.
12 Shibusawa T, *J Soc Dyers Colour*, 101 (1985) 231.
13 Gupta D, Kumari S, Gulrajani M L, *Color Technol*, 117 (2001) 330.
14 Billmeyer F W & Saltzman M, *Principles of Color Technology*, 2nd edn (A Willey Interscience Publication), 1981, 140.
15 Lee J D, *Concise Inorganic Chemistry*, 5th edn (Blackwell Science Ltd.), 1996, 389 & 653.
16 Glasstone S, *Text Book of Physical Chemistry*, 2nd edn (The Macmillan Press Ltd, London), 1996, 1243-1244.
17 Bird C L & Firth J M, *J Text Inst*, 51(5) (1960) T1342-1350.
18 Bird C L, *Theory and Practice of Wool Dyeing*, 4th edn (Society of Dyers and Colorists), 1982, 36 -37 & 12.
19 Chipalkatti H R, Chipalkatti V B & Giles C H, *J Soc Dyers Colour*, 71(11) (1955) 652.
20 Sadov F, Korchagin M & Matetsky A, *Chemical Technology of Fibrous Materials* (Mir Publishers, Moscow), 1973, 68.
21 Vogel A I, *Textbook of Macro and Semi Micro Qualitative Inorganic Analysis* (Oriental Longman, New Delhi), 1985, 250-253.
22 Gulrajani M L, Bhowmik S, Oppermann W & Hardtmann G, *Indian J Fibre Text Res*, 27 (1) (2002) 91-94.
23 Morton W E & Hearle J W S, *Physical Properties of Textile Fibre* (The Textile Institute, Manchester), 1997.