Indian Journal of Fibre & Textile Research
Vol. 33, June 2008, pp. 185-188

Thermodynamic and kinetic studies of adsorption of berberine on silk

Gui-zhen Ke[a] & Wei-lin Xu
Wuhan University of Science and Engineering, Wuhan 430073, P R China
and
Wei-dong Yu
Textile Materials and Technology Laboratory, Donghua University, Shanghai 200051, P R China

Received 24 October 2007; accepted 28 December 2007

Dyeing properties of silk fabric with berberine have been studied in terms of the thermodynamic and kinetic factors, including standard affinity, enthalpy change, entropy change, dyeing rate, diffusion coefficient and activation energy of the diffusion. The results show that the adsorption isotherm of berberine on silk fabric belongs to Langmuir type. The analysis of dyeing thermodynamics shows that the adsorption of berberine on silk fabric is an exothermic process. When the fabric is dyed at higher temperature, the lower affinity and less dye uptake are obtained; however, the higher temperature increases the initial dyeing rate and diffusion coefficient.

Keywords: Berberine, Dyeing, Kinetic study, Silk

IPC Code: Int. Cl.[8] D01C

Natural dyes are obtained from plants, minerals and animals; most of them are extracted from plants which are herbs themselves. According to the chemical structure, the natural plant dye can be divided into indigo type, anthraquinone type, flavone type, alkaloids type, multi-hydroxybenzene type, diketone type, benzopyran type, and carotenoid type.[1,2] Berberine is a widely distributed berberidaceaen alkaloids that has been employed in traditional medicine as an antiprotozoal and antidiarrheal agent.[3] It is found mostly in roots of *rhzioma coptidis* and stems of *phellodendron*. As the only cationic natural plant dye, berberine is yellow crystal and soluble in water and organic solvents such as ethanol. It can be used for dyeing natural fibre such as silk and wool.[4]

Silk, a protein fibre, has been the most treasured natural fibre since it was discovered in 2,700 BC. Because of its natural sheen, pleasant feel and extraordinary high tensile strength, it is often called the queen of fibres. Silk is made of fibroin and sericin and its macromolecules contain multiple alpha amino acids.[5] In this study, silk fabric has been dyed with berberine aqueous solution and the dyeability is studied in terms of the thermodynamic and kinetic properties, i.e. standard affinity, enthalpy change, entropy change, diffusion coefficient and activation energy of the diffusion.

Scoured and bleached silk plain fabrics [power woven habotai (75g/m^2)] were purchased from the Refining Branch Factory of Hangzhou Xingchen Silk Company. Berberine was supplied by Jingmei BioTech Co. Ltd with ≥95% purity. Shimadzu 2550 UV-vis spectrophotometer was used to measure the UV-vis absorbance of the dye solutions before and after exhaustion.

To prepare control solution of berberine, accurately weighed 0.2g berberine was taken in 200mL measuring flask, distilled water was added to dissolve berberine and the solution was diluted to volume. Exactly measured 1, 4, 5, 6, 8, 10mL control solutions were taken out separately into 100mL flask, diluted to scale using distilled water, and then absorbance was measured at 345nm (λ_{max} of the dye). Finally, the following linear regression calibration equation was obtained:

$$A=61.432C,\ R^2=0.9969,\ SD=0.105 \quad \ldots (1)$$

where A is the absorbency; C, the concentration of dyeing solution; R, the linear relative coefficient of the equation; and SD, the standard deviation of the equation.

In above solutions of different dye concentrations, silk fabric was dyed at 60°, 80°and 95°C for 5h, keeping liquor-to-material ratio at 200:1. The initial *p*H of the dyeing solution was adjusted at 6.5. The absorbency of residual dyeing solution was measured with UV-vis spectrophotometer and the dye concentrations of final bath ($[D]_s$, g L^{-1}) was calculated using calibration curve of the berberine dye[Eq.(1)] according to Lambert-Beer law. The dye concentration in the fibre at equilibrium ($[D]_f$, g/kg) was

[a] To whom all the correspondence should be addressed.
E-mail: kgz66@126.com

obtained with subtraction. Then absorption isotherm of berberine on silk was drawn. For the study of dyeing rate, silk fabrics (0.5 g) were dyed with 0.04g/L dye concentration at the temperatures of 60°, 80°and 95°C, keeping the liquor-to-material ratio at 200:1. Dyeing diffusion coefficient and activated energy were calculated accordingly.

The adsorption isotherm of berberine on silk fabric is shown in Fig. 1, which can be assigned as a Langmuir type.[6] It is observed that the dye uptake in fibre($[D]_f$) continues to increase with the increase in dye concentration before it reaches the saturation point. Prior to reaching the saturation, the relationship between dye in solution($[D]_s$) and dye uptake in fibre($[D]_f$) can be considered as a linear function.[7] Therefore, its slope is constant and a partition coefficient (K) of the dye between the fibre ($[D]_f$) and the dyeing solution ($[D]_s$) was obtained from the adsorption isotherm. Then, the standard affinity ($-\Delta\mu°$) of the dye was estimated using the following equation[8]:

$$-\Delta\mu° = \mathrm{R}T \ln \frac{[D]_\mathrm{f}}{[D]_\mathrm{s}} = \mathrm{R}T \ln K \qquad \ldots (2)$$

where R is the gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$); and T, the absolute temperature (K). The results are shown in Table 1.

It is found that when the temperature increases, the partition ratio and the standard affinity decrease obviously. Moreover, at lower temperature the higher dye uptake saturation can be reached. Furthermore, a graph of ln$K$ versus $1/T$ was plotted (Fig. 2), as per the following equation:

$$\ln K_2 - \ln K_1 = \frac{-\Delta H°}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ldots (3)$$

The heat of dyeing ($-\Delta H°$) was calculated from a slope of the line. [8] Finally, $-\Delta\mu°$ versus T was plotted (Fig. 3) and the entropy of dyeing ($\Delta S°$) was calculated using the following Gibbs equation:[6]

$$\Delta\mu° = \Delta H° - T\Delta S° \qquad \ldots (4)$$

The $\Delta H°$ value is found to be -18.34kJ/mol. The enthalpy change ($\Delta H°$) means the amount of the released thermal energy when dye molecules are adsorbed into fibre chains. Negatively larger value indicates more strongly embedded dye molecules within the fibre.[8] The obtained value of $\Delta S°$ is -0.0086kJ/mol·K. In most dyeing process, the entropy change($\Delta S°$) shows negative values because adsorbed dyes become more restrained within fibre molecules than in dyeing solution. Therefore, the value of the entropy change could be regarded as the measure of immobility of dyes within the fibres.[9] Results of enthalpy and entropy changes indicate that the adsorption of berberine on silk is an exothermic process, and hence raising the temperature leads to

Table 1–Partition coefficient (K) and the standard affinity ($-\Delta\mu°$) of berberine on silk

Temperature, °C	K	$-\Delta\mu°$, kJ/mol
60	265.4	15.45
80	188.4	15.37
95	140.7	15.13

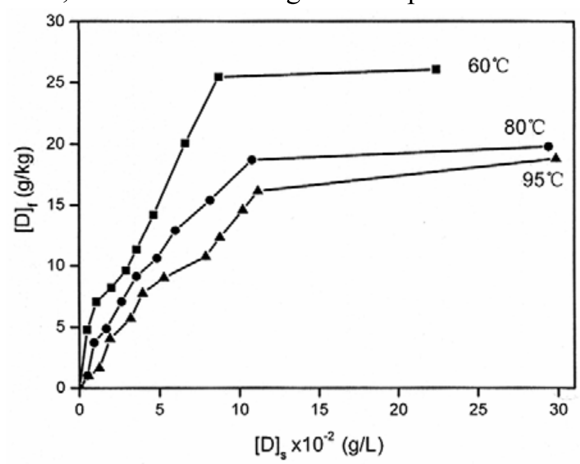

Fig. 1–Adsorption isotherm of berberine on silk

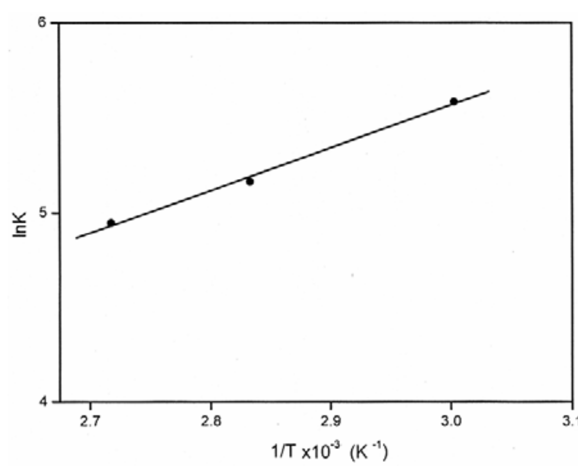

Fig. 2–Relationship between ln$K$ and $1/T$ for silk dyeing with berberine

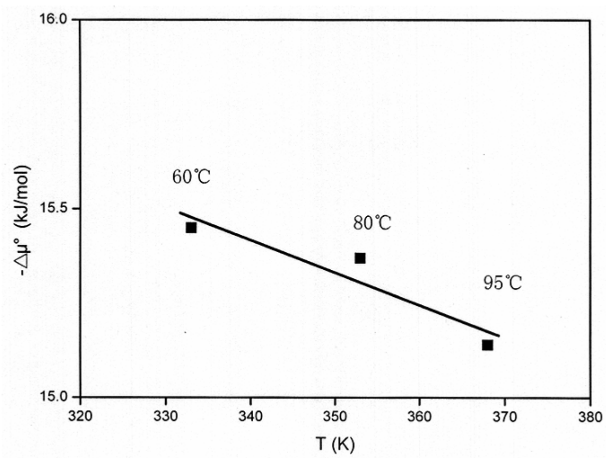

Fig. 3–Relationship between -Δμ° and T for silk dyeing with berberine

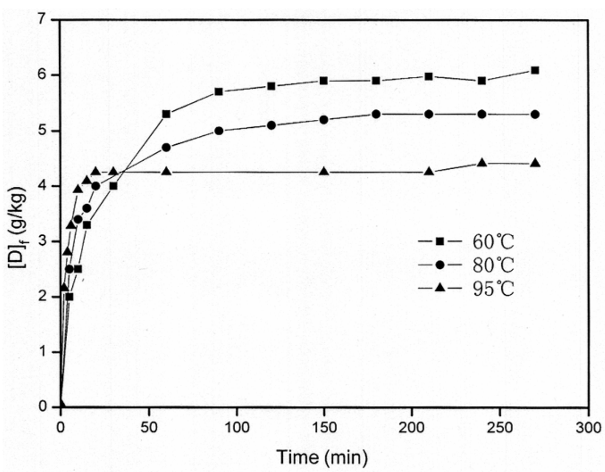

Fig. 4–Dyeing rate of berberine on silk at different temperatures

lower affinity and less dye being adsorbed at equilibrium.

However, when the dyeing is conducted at higher temperature, the equilibrium point can be reached in much less time, which is observed in dyeing rate of beberine at different temperatures (Fig. 4). At higher temperature, the fabric contains more dye in the early stages but less dye in the latter stages of the dyeing. Thus, higher temperature increases the dyeing rate but decreases the ultimate exhaustion if the dyeing time is long enough, which corresponds to the results of thermodynamic analysis.

The graph showing the relationship between C_t/C_∞ and $t^{1/2}$ in the initial stage of dyeing was plotted (Fig. 5) and the diffusion coefficient was calculated from the following equation[9]:

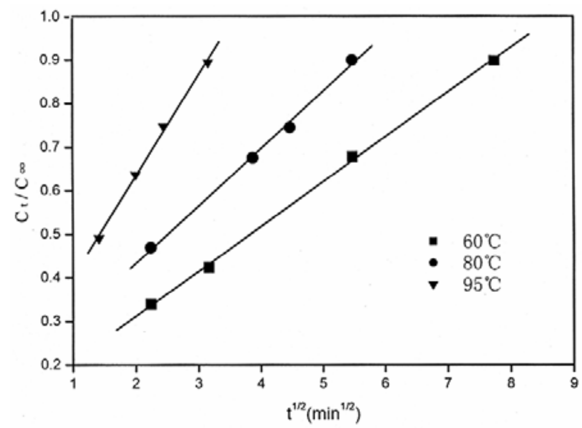

Fig.5–Relationship between C_t/C_∞ and $t^{1/2}$ for diffusion coefficient

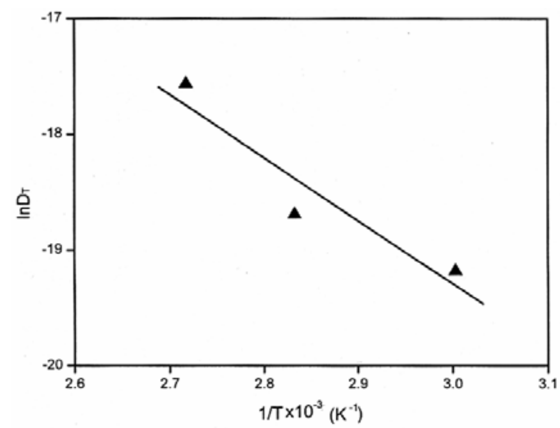

Fig.6–Relationship between lnD_T and $1/T$ for activation energy

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{D_T t}{\pi r^2}} \quad \ldots (5)$$

where C_t is the dye exhaustion at a time t (g/kg); C_∞, the dye exhaustion in the equilibrium (g/kg); D_T, the diffusion coefficient ($cm^2 \cdot min^{-1}$); t, the dyeing time; and r, the radius of fibre (cm). Here, the radius of silk is 0.0015cm. The calculated diffusion coefficients (D_T) of silk are found to be 4.669×10^{-9}, 7.616×10^{-9} and 2.353×10^{-8} at 60°, 80°and 95°C temperatures respectively.

It is observed that as the temperature increases, the diffusion coefficients also increases, which means that the mobility of the fibroin chains greatly increases with increasing temperature. In general, the better diffusion character and higher diffusion rate can shorten dyeing time and also reach better dyeing uniformity.

A graph of lnD_T *vs*. 1/*T* is shown in Fig. 6 and according to the following Eq. (6), the activation energy of the diffusion is calculated from the slope of the line.[6] This parameter describes the relationship between the diffusion coefficient and the dyeing temperature and also represents the energy barrier that a dye molecule should overcome to diffuse into the fibre molecules.[6]

$$\ln D_T = \ln D_0 - E / \mathrm{R}T \quad \ldots (6)$$

where D_T is the diffusion coefficient at a temperature *T* ($cm^2 \cdot min^{-1}$); D_0, the constant; *E*, the activation energy ($J \cdot mol^{-1}$); R, the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$); and *T*, the absolute temperature (K). The activation energy is found to be 45344$J \cdot mol^{-1}$.

The adsorption isotherm of berberine on silk has been classified as a Langmuir type. The standard affinity is determined approximately using partition coefficient. The enthalpy of dyeing and the entropy of dyeing show negative values, which indicates that the adsorption of berberine on silk fabric is an exothermic process. The higher temperature increases the initial dyeing rate but decreases the ultimate exhaustion. The diffusion coefficients increase with the increase in temperature and the activation energy is also determined.

Industrial Importance: The study helps in improving the quality of the berberine-dyed silk products and motivates natural dyes in dyeing application.

References

1 Teli M D, Roshan P & Pardeshi P D, *Colorage*, 12(2000) 43.
2 G Kerry G & C David T, *Plant Growth Regulation*, 34(2001) 57.
3 Zhang H J, *Manual for Identifying of Chinese Native Medicinal Materials* (Guangdong Tour Publishing Company, Guangdong), 2000.
4 Sun Y S, *Silk*, 1(2003)31.
5 Yao M, Zhou J F, Huang S Z, Shao L H, An R F & Fan D Q, *Textile Materials*, 2nd edn (China Textile Press, Beijing), 1990.
6 Cai S Y & Tian T, *Principle and Technology of Textile Dyeing and Finishing*, 2nd edn (China Textile Press, Beijing), 2004.
7 Paisan K, Aroonsiri S & Nontalee C, *Dyes Pigm*, 53(2002) 179.
8 Kurogi N, *Theory of Dyeing Chemistry* (Textile Industry Publishing Company, Beijing), 1981.
9 Kima T K, Sonb Y A & Limc Y J, *Dyes Pigm*, 67(2005) 229.