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Thermodynamics of adsorption of laccaic acid on silk

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Abstract

The hybrid-race silk yarn was dyed till equilibrium with natural lac dye (laccaic acid) and the thermodynamics of dyeing were investigated. The adsorption isotherm obtained was identified to be a Langmuir type. When the temperature increased, the partition ratio and the standard affinity decreased drastically. The values of heat of dyeing and entropy of dyeing were−13.20 kcal/mol and-0.03 kcal/mol/K, respectively. The effect of memecylon used as a mordant on silk dyeing with lac dye was also studied. It revealed that using memecylon promoted the adsorption of laccaic acid on silk and increased the attraction between laccaic acid and silk surfaces. © 2002 Published by Elsevier Science Ltd.

Keywords: Adsorption isotherm; Lac dyeing; Silk dyeing; Thermodynamics; Memecylon

1. Introduction

Silk fiber is a protein fiber that is produced from silk worms. It is composed of different alpha amino acids orienting to form a long chain polymer by condensation and polymerization. Silk fiber consists of 97% protein and the rest are wax, carbohydrate, pigments, and inorganic compounds. The proteins in silk fiber are 75% fibroin and 25% sericin by weight, approximately [1]. The sericin makes silk fiber to be strong and lackluster, therefore, it must be degummed before dyeing.

Lac dye (C.I. Natural Red 25; C.I. 75450) [2] is obtained from the dried bodies of an insect, *Coccus laccae* (*Laccifer lacca* Kerr), found growing on the twigs of certain tree native to southeast Asia. The color matter of the lac dye is identified to be two substances: (1) laccaic acid which is soluble in water producing a red color and has two major components: laccaic acid A and B whose structures are shown in Fig. 1; (2) erythrolaccin which dissolves in alcohol producing a pale-yellow color [3–5]. Laccaic acid represents about 0.50–0.75% by weight of crude stick lac [6].

In Thailand, the government has promoted the culturing of these insects on the rain-trees to produce a resin known as stick lac, especially in the northeastern part. Stick lac is used as a raw material for making shellac. During this process, the red pigment in the lac is removed by dissolving with water and is thrown away. The red solution from the lac can be used as a natural-red dye for silk or cotton dyeing, which has been done widely in the northeast of Thailand. However, there are some persistent problems of color fastness and repetition of color shade. Most natural red-color dyes have high solubility in water, therefore, the color fastness to washing of the dyed fabric is

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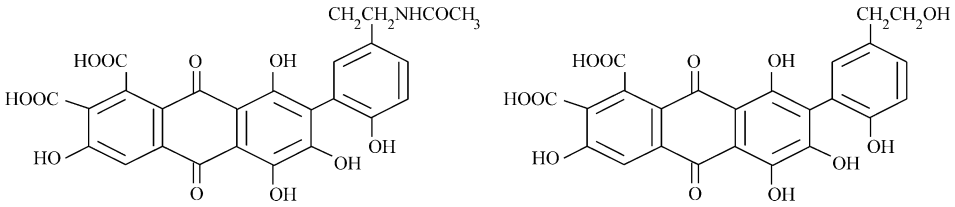

Fig. 1. Structure of laccaic acid A (left) and laccaic acid B (right).

quite low. In order to improve its color fastness, most of the dyeing processes were conducted using metal salts (e.g. potassium dichromate, stannous chloride, ferrous sulfate and copper sulfate) as mordants [7–16]. The metal ions can act as acceptors to electron donors to form co-ordinate bonds with the dye molecule, which is insoluble in water [17]. However, the wastewater containing heavy metal ions from these mordants may affect on the environment and public health. In the northeast of Thailand, the farmers have used some mordants with the silk dyeing, for example, alum, iron oxide, and memecylon (*Memecylon scutellatum* Naud.) by trial and error. There are no scientific data (i.e. thermodynamic properties) of the process of lac dyeing on silk. Thus, this research work aims to study the thermodynamic properties of adsorption of laccaic acid on silk substrate and also the effect of memecylon on this phenomenon. We hope that this information will help the farmers to improve the quality of the lac-dyed silk products and motivate natural color dyeing in Thailand.

2. Experimental

2.1. Materials

2.1.1. Silk yarn

The silk yarn used is a hybrid-race silk (Chul 5) produced by Chul Thai Silk Co., Ltd. It was degummed in a soap solution of 15% (o.w.f.) at 80–90 °C for 15 min, at a liquor ratio of 30:1 and washed thoroughly in water. Then, it was treated in 1% (v/v) acetic solution at 50 °C for 15 min and washed in water again until the rinsed water was neutral. Finally, it was dried at room temperature.

2.1.2. Stick lac

Stick lac (300 g) was finely ground by LOBO mill and was first extracted by ethanol 900 ml for 15 min to remove erythrolaccin. After filtration, the lac was extracted again with 3 l of distilled water for 24 h to obtain a red solution of lac dye.

2.1.3. Mordant

Dried leaves of memecylon (500 g) were boiled with 2 l of water for 90 min. After filtration, a yellow-green solution was obtained.

2.2. Instrumentation

Dyeing was carried out in a SP110 UGOLINI srl dyeing machine equipped with programmable control of time and temperature of dyeing and speed of circulation. The amount of laccaic acid remaining in the dye solution was detected by measuring absorbance of the solution using an UV-vis spectrophotometer (UV-160A, Shimadzu).

2.3. Methods

Ten grams of silk yarn were dyed with different dye concentrations at 28, 60 and 80 °C, keeping the material-to-liquor ratio at 1:180. The pH of the initial dye solution was measured by a pH meter (MettlerToledo model 1120). The amount of dye in the residual bath ($[D_\sigma]$) was measured by using the UV-vis spectrophotometer and the dye uptake by silk fiber ($[D_\phi]$) was calculated by subtraction. The graph of laccaic acid concentrations of standard solutions versus absorbance at wavelength 490 nm, at which the maximum absorbance was reached, was prepared and used to determine the concentration of an unknown solution. For each dyeing, the absorbance of dye solution was

monitored until it was unchanged. Then, the equilibrium concentrations of laccaic acid in the residual bath and the dye uptake were calculated using the standard graph. Subsequently, an adsorption isotherm of laccaic acid on silk, i.e. $[D_\phi]$ vs. $[D_\sigma]$, was plotted and classified.

The effect of memecylon to the adsorption of laccaic acid on silk was investigated in a similar manner except the dyeing was conducted at 60, 80 and 100 °C. The dye solution was prepared by mixing the lac dye and memecylon solutions (3:1 v/v). The absorbance of the dye solution was measured at wavelength 520 nm.

3. Results and discussion

The pH values of the dye solutions are shown in Table 1. All dye solutions are acidic. The adsorption isotherm of lac dye, i.e. laccaic acid, on silk yarn can be classified as a Langmuir type, shown in Fig. 2. It is noticed that the equilibrium dye uptake continues to increase with increae of dye concentration until it reaches the saturation point. Prior to reaching the saturation, the relations between $[D_\phi]$ and $[D_\sigma]$ can be considered as a linear function. Therefore, its slope is constant and it yields a partition ratio (K). Then, the standard affinity ($-\Delta\mu^o$) was calculated by using the equation [18,19]

$$-\Delta\mu^o = RT\ln K \tag{1}$$

where R is the gas constant. The results are presented in Table 2. It is found that when the temperature increases, the partition ratio and the standard affinity decrease drastically. Moreover, at higher temperature the lower dye uptake saturation can be reached. However, it was observed that each dyeing conducted at higher temperature reached the equilibrium point in much less time.

Furthermore, a graph of $\ln K$ vs. $1/T$ was plotted (Fig. 3) and from the equation

$$\ln\frac{K_2}{K_1} = \frac{-\Delta H^o}{R}\frac{1}{T_2} - \frac{1}{T_1} \tag{2}$$

heat of dyeing (ΔH^o) was calculated from a slope of the line. Finally, $-\Delta\mu^o$ vs. T was plotted (Fig. 4) and an entropy of dyeing (ΔS^o) was determined from this relation

$$\Delta\mu^o = \Delta H^o - T\Delta S^o \tag{3}$$

The obtained values of ΔH^o and ΔS^o are -13.2 kcal/mol and -0.03 kcal/mol·K, respectively. It means that adsorption of laccaic acid on silk yarn is an exothermic process, so raising the temperature leads to lower affinity and less dye being adsorbed at equilibrium.

The effect of memecylon as a mordant on silk dyeing with lac dye was investigated and the results are presented in a similar manner (see Figs. 5–7 and Table 3). The obtained isotherm is still a Langmuir type (the saturation part was omitted). Compared to the dyeing without memecylon at the same temperature the partition ratio and the standard affinity increase about 40 and 2 times, respectively. It reveals that using memecylon promotes the adsorption of laccaic acid on silk and increases the attraction between laccaic acid

Table 1
Initial concentrations and pH values of lac dye solutions

At 28 °C		At 60 °C		At 80 °C	
Initial conc. (mg/ml)	pH	Initial conc. (mg/ml)	pH	Initial conc. (mg/ml)	pH
0.054	5.32	0.037	5.41	0.044	5.37
0.108	5.01	0.071	5.23	0.074	5.20
0.138	4.92	0.111	5.03	0.090	5.13
0.171	4.65	0.148	4.82	0.149	4.82
0.223	4.42	0.185	4.60	0.198	4.55
0.343	3.82	0.280	4.12	0.251	4.27

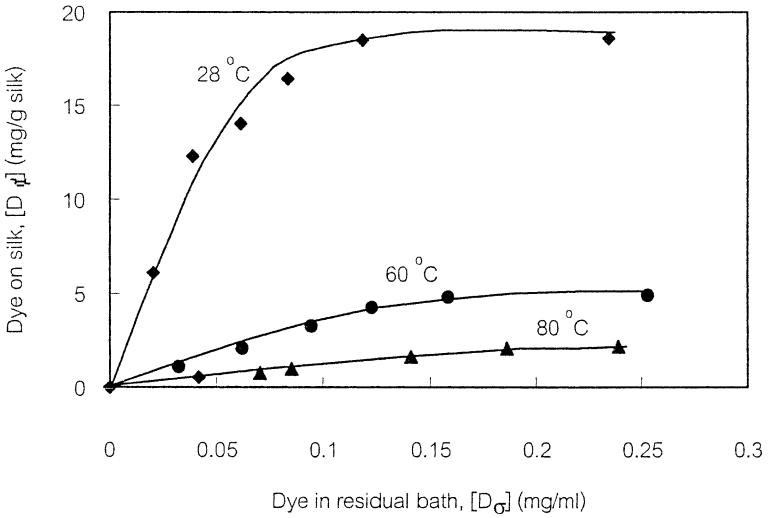

Fig. 2. Adsorption isotherm of dyeing laccaic acid on silk yarn.

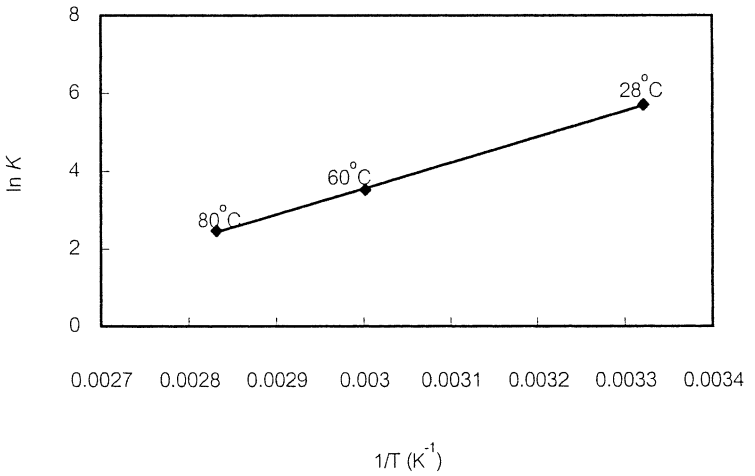

Fig. 3. Relations between $\ln K$ and $1/T$ from silk dyeing with laccaic acid.

Table 2
Partition ratio and standard affinity of silk dyeing with laccaic acid

Temperature (°C)	Partition ratio	Standard affinity (kcal/mol)
28	301.5	3.41
60	34.2	2.34
80	11.9	1.74

Table 3
Partition ratio and standard affinity of silk dyeing with laccaic acid and memecylon

Temperature (°C)	Partition ratio	Standard affinity (kcal/mol)
60	1,358.4	4.77
80	532.5	4.40
100	255.7	4.11

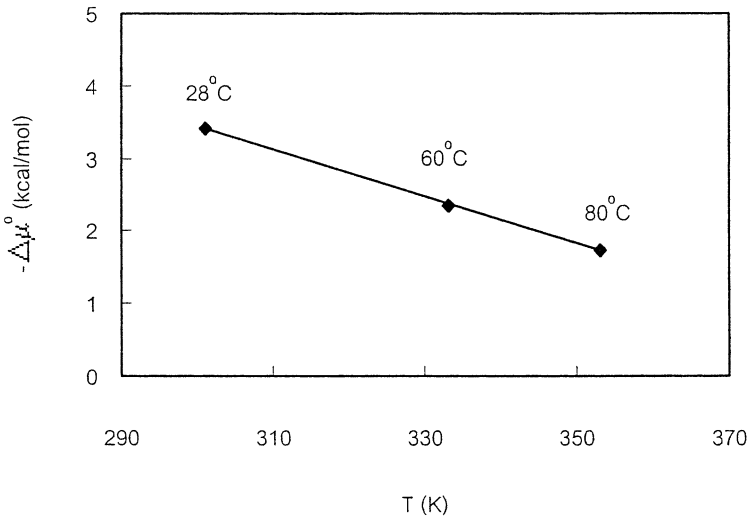

Fig. 4. Relations between $-\Delta\mu^{o}$ and T from silk dyeing with laccaic acid.

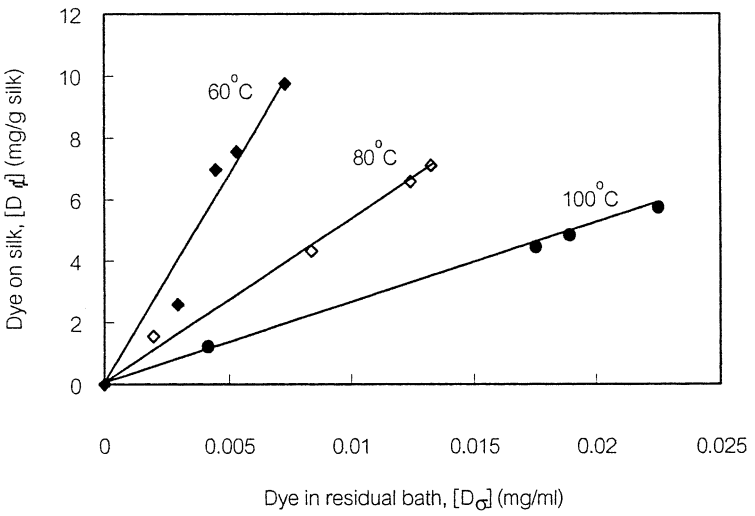

Fig. 5. Adsorption isotherm of silk dyeing with laccaic acid and memecylon.

Table 4
Initial concentrations and pH values of lac dye and memecylon solutions

At 60 °C		At 80 °C		At 100 °C	
Initial conc. (mg/ml)	pH	Initial conc. (mg/ml)	pH	Initial conc. (mg/ml)	pH
0.017	5.25	0.011	5.30	0.011	5.30
0.043	5.07	0.033	5.14	0.042	5.07
0.047	5.03	0.049	5.02	0.046	5.03
0.061	4.91	0.052	5.00	0.054	4.96

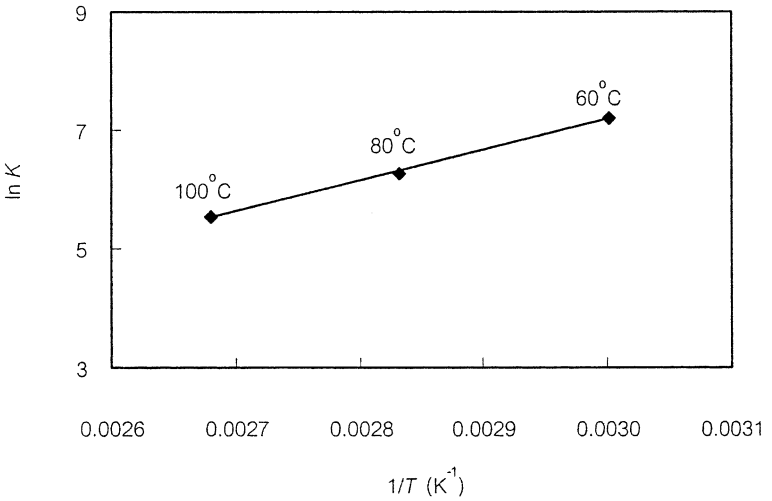

Fig. 6. Relations between $\ln K$ and $1/T$ from silk dyeing with laccaic acid and memecylon.

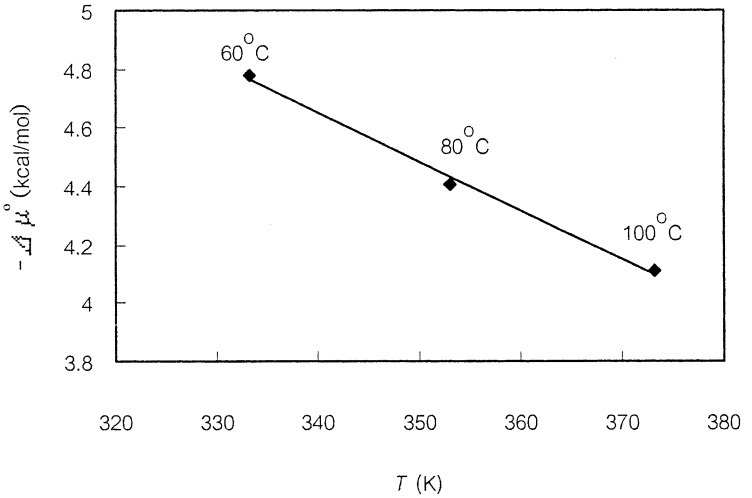

Fig. 7. Relations between $-\Delta\mu^{\circ}$ and T from silk dyeing laccaic acid and memecylon.

and silk surfaces. From chemical analysis it is found that the memecylon solution is composed mainly of tannic acid, which increases the acidity of dye solution (see Table 4) and enhances the adsorption of laccaic acid on the protein fiber. From slopes of graphs in Figs. 6 and 7, the heat of dyeing and the entropy of dyeing were calculated to be −10.3 kcal/mol and −0.02 kcal/mol·K, respectively. It seems that the dyeing with memecylon evolves less heat, compared to the dyeing without memecylon.

4. Conclusions

Thermodynamics of silk dyeing with the laccaic acid extracted from natural stick lac was investigated. It is found that the adsorption isotherm of laccaic acid on silk is a Langmuir type. The partition ratio (K), the standard affinity ($\Delta\mu^{\circ}$), the heat of dyeing (ΔH°), and the entropy of dyeing (ΔS°) were determined. It is noted that the adsorption of laccaic acid on silk yarn is an exothermic process. The effect of memecylon used as a mordant on silk

dyeing with laccaic acid was also studied. It reveals that using memecylon promotes the adsorption of laccaic acid on silk and increases the attraction between laccaic acid and silk surfaces.

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