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Thermodynamics Study of Natural Indigo Adsorption on Silk Yarn

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ABSTRACT

Leaves of *Indigofera tinctoria* were fermented in water. During fermentation, indican in leaves decomposed completely to indoxyl and was consecutively oxidized to indigo that finally precipitated from the fermented solution. The hybrid-race silk yarn was then dyed till equilibrium with obtained indigo reduced by $Na_2S_2O_4$ under alkaline condition and thermodynamics of dyeing process was investigated. The obtained adsorption isotherm was classified as a Langmuir type. The apparent diffusion coefficients at 33, 40 and 50°C are 1.23×10^{-12}, 8.26×10^{-13} and 4.26×10^{-13} m^2s^{-1}, respectively. The heat of adsorption and the change of entropy are -9.43 $kcalmol^{-1}$ and 0.023 $kcalmol^{-1}K^{-1}$, respectively. In addition, the saturated dye uptake was found to be decreased when the dyeing temperature was increased. The obtained results are useful for designing appropriate dyeing equipment and conditions for dyeing silk with natural indigo.

Keywords: adsorption isotherm, natural indigo, silk dyeing, heat of adsorption, diffusion.

1. INTRODUCTION

Indigo (CI Natural Blue 1; 75780) [1] is a blue dye obtained from the leaves and branches of indigofera plants (*Indigofera tinctoria*) belonging to Papilionaceae family. The indigofera plant cultivated throughout the tropical zone has grown to a height of about 1.2 m with red-violet flowers. In flowering stage, the yield of the dye has reached to peak at 0.4 % dry weight [2].

The precursor of indigo is indican, an intermediate substance in leaves and branches of indigofera plants. When the plant is soaked in water long enough, indican is hydrolyzed to indoxyl. Subsequently, indoxyl is oxidized to indigo that then precipitates and filtered off [3-5]. Natural indigo has an impurity containing small quantities of indirubin and indigo brown [6,7]. Indigo dye is considered as a vat dye for dyeing textile materials such as cellulose and silk fibers. Indigo is insoluble in water or other ordinary solvents, however, it can be transformed to indigo white form, which can be dissolved readily in an alkaline solution forming a colorless or slightly yellowish solution. When the fiber to be dyed is immersed in this colorless solution, it imbibes the indigo white. After being taken out and exposed to the air, the indigo white upon and within the fiber rapidly takes up oxygen from the atmosphere and is reversed to insoluble indigo forming a permanent blue color.

Silk is a protein fiber, which is produced by silk worms. It composes of different α-amino acids orienting to form long chain polymer by condensation. 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 [8]. The sericin makes silk fiber to be strong and lackluster; therefore, it must be degummed before dyeing.

In Thailand, similar to the European Union (EU) [9], the government has promoted the production of eco-textiles using natural colors for silk or cotton dyeing. One of the popular dyeing colors is blue indigo. However, due to the difficulty of dye preparation process most farmers prefer to use synthetic indigo instead of the natural one. Moreover, there are lacks of scientific data (i.e. thermodynamic properties) in the dyeing natural indigo to be applied in silk substrate. Thus, this research work aims to investigate the thermodynamic properties of adsorption of natural indigo on silk.

2. EXPERIMENTAL

2.1 Materials

Silk yarn. Silk yarn is a hybrid-race silk (Chul 5, Chul Thai Silk Co., Ltd., Thailand). It was degummed in soap solution of 15% weight of silk yarn at 80^{o}C for 15 min with a liquor ratio of 30:1 (ml solution : g silk) and washed thoroughly by de-ionized water. Then, washed-silk was treated in 1 % acetic acid (v/v) solution at 50^{o}C for 15 min and washed once in water until the rinsed water was neutral, subsequently dried at room temperature.

Indigo. Indigo plants (*I. tinctoria* Linn.) were fermented in water at room temperature. During the fermentation, the plant materials were turned up side down at the end of the first day. After two days, the fermented solution was filtered and then agitated by a motorized stirrer until the solution turned blue. The blue precipitate was filtered, dried, ground into fine powder, and kept in a desiccator. This natural indigo powder (blue precipitate) was used to dye silk yarn throughout this study.

2.2 Instrumentation

Dyeing was carried out in a dyeing machine (SP110, Ugolini srl, Italy) equipped with programmable controllers of time, temperature, speed and direction of fluid circulation. The amount of indigo remaining in the dye solution was detected by measuring absorbance of the solution using an UV-vis spectrophotometer (UV-160A, Shimadzu, Japan).

2.3 Methods

The soluble indigo, namely *white indigo,* was prepared by reducing blue indigo with NaOH (99%, Merck Schuchardt, Germany) and $Na_2S_2O_4$ (80%, Aldrich, USA) until the solution was completely clear having light yellow-green color. The optimum weight ratio of blue indigo:NaOH:$Na_2S_2O_4$ was found to be 1:135:135. However, the reduced solution is rapidly oxidized by air. In order to prevent the oxidation, the ratio of 1:250:250 with 60 min reducing time was then used in this study. The reduced solution having concentration in the range of 2-10 mg l^{-1} was prepared and its maximum absorbance was obtained at λ_{max} 405 nm. The standard curve is demonstrated in Figure 1.

Silk yarn (8 g) was dyed with varied dye concentrations (10-80 mg l^{-1}) at 33, 40, and 50^{o}C, keeping the silk-to-liquor ratio at 1:250 (w/v). The amount of dye in the residual bath, $[D_s]$, was measured using the UV-vis spectrophotometer and the dye uptake by silk

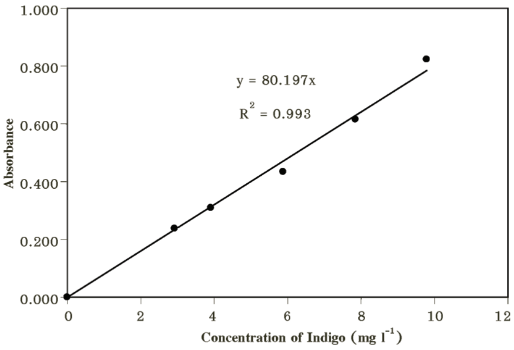

Figure 1. The relation between absorbance and concentration of reduced indigo.

yarn, $[D_f]$, was calculated by subtraction. For each dyeing, the absorbance of dye solution was monitored until it was constant. Then, the equilibrium concentrations of indigo in the residual bath and the dye uptake were determined using the standard curve. Subsequently, an adsorption isotherm of natural indigo on silk, i.e. $[D_f]$ vs. $[D_s]$, was constructed following the method reported elsewhere [10,11].

3. RESULTS AND DISCUSSION

3.1 Apparent Diffusion Coefficient

The effect of dyeing period on dye uptake is shown in Figure 2. The slope of each curve presents the rate of adsorption at corresponding temperature. When the dyeing temperature is increased, the rate of adsorption and the saturated dye uptake are decreased. Since adsorption is an exothermic process; therefore, increasing temperature causes negative effect to the saturated dye uptake. Subsequently, the apparent diffusion coefficient (D_A) was calculated using Hill's equation for infinite bath [7,10,13]:

$$\frac{[D_f]_t}{[D_f]_\infty} = 1 - 0.692\left(\exp\left(-\frac{5.785 D_A t}{r^2}\right) + 0.190\exp\left(-\frac{30.5 D_A t}{r^2}\right) + 0.0775\exp\left(-\frac{74.9 D_A t}{r^2}\right) + \ldots\right) \quad (1)$$

The result is presented in Table 1. They relate directly with the rate of adsorption; therefore, at higher rate of adsorption the higher apparent diffusion coefficient is obtained.

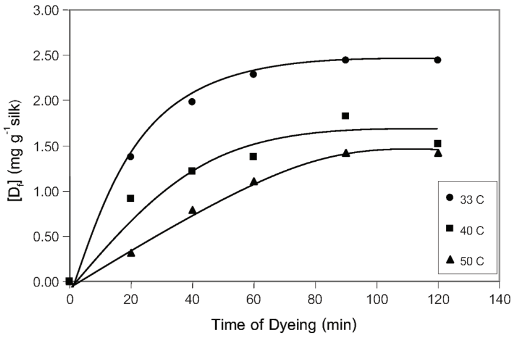

Figure 2. Effect of dyeing period on dye uptake by silk yarn at various temperatures (initial dye concentration 60 mgl^{-1})

Table 1. Effect of Temperature on Dye Adsorption.

Temperature (^{o}C)	t_{eq} (min)	$[D]_f$ at t_{eq} (mg g^{-1} silk)	D_A (m^{2}s^{-1})
33	70	2.44	1.23×10^{-12}
40	80	1.70	8.26×10^{-13}
50	90	1.42	4.26×10^{-13}

Compared with dyeing silk yarn with laccaic acid extracted from natural lac dye at 28^{o}C [10], the saturated indigo uptake is about 5 times less than saturated laccaic acid uptake, but the apparent diffusion coefficient obtained by this study is about 40 times higher. These differences may be caused by the different chemical structures of indigo and laccaic acid. The indigo has much smaller structure and lower polarity than the laccaic acid. Hence, it can diffuse faster but has less interaction with silk surface than laccaic acid.

3.2 Thermodynamic parameters

The results obtained from the dyeing experiments are plotted as adsorption isotherms in Figure 3. The isotherm is used to interpret dyeing processes and serves as a basis for the calculation of thermodynamic parameters. It can be classified as a Langmuir type. It is noticed that at low concentrations the Langmuir plot approximates to the linear solid solution model [13,14]. Prior to reaching the saturation point, the relation between $[D_f]$ and $[D_s]$ is a linear function. Thus, its slope is constant and yields a partition ratio (K) that decreases with increased temperature.

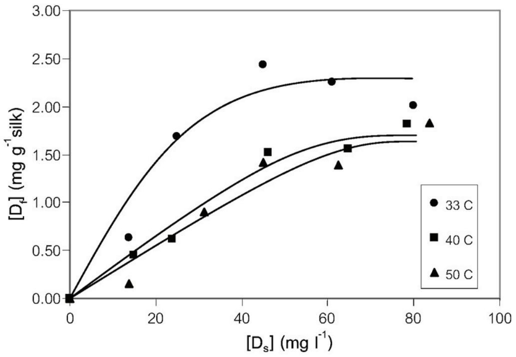

Figure 3. Adsorption isotherms for dyeing natural indigo on silk yarn.

Subsequently, the standard affinity ($\Delta\mu^o$) was calculated using the following equation [12-14]:

$$-\Delta\mu^{\circ} = RT\ln\frac{[D_f]}{[D_s]} = RT\ln K \qquad (2)$$

The results are given in Table 2. It should be noted that the standard affinity decreases with increasing temperature. This trend is also evident from the adsorption isotherms.

Table 2. Partition Ratio and Standard Affinity of Silk Dyeing with Natural Indigo.

Temperature		ln$K$	*Partition Ratio, K*	$-\Delta\mu^o$ kcal mol^{-1}
(°C)	(K)			
33	306	61.6	4.1207	2.5067
40	313	31.4	3.4468	2.1448
50	323	26.0	3.2581	2.0921

From Figure 4, heat of dyeing (ΔH^o) and entropy change of dyeing (ΔS^o) can be calculated from this relation

$$\Delta\mu^{\circ} = \Delta H^{\circ} = T\Delta S^{\circ} \qquad (3)$$

The obtained values of ΔH^o and ΔS^o are -9.43 kcalmol^{-1} and 0.023 kcalmol^{-1}K^{-1}, respectively. It confirms that the adsorption of natural indigo on silk yarn is an exothermic process, so raising the temperature leads to lower affinity and less adsorbed dye amount at equilibrium. Compared with dyeing silk with laccaic acid, in which ΔH^o and ΔS^o were -10.3 kcalmol^{-1} and 0.02 kcal mol^{-1}K^{-1}, respectively [10], it reveals that indigo was adsorbed on the silk surface with lower binding energy than that of laccaic acid.

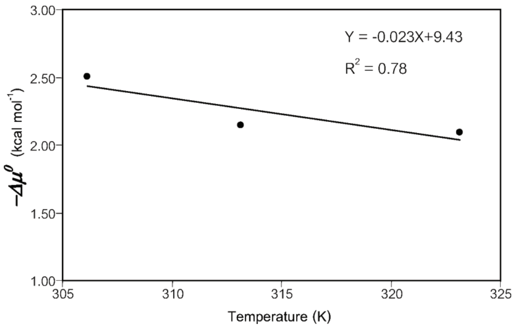

Figure 4. The relation between standard affinity and dyeing temperature.

4. CONCLUSIONS

Thermodynamics of silk dyeing with the natural indigo was investigated. It is found that its adsorption isotherm is a Langmuir type. The partition ratio (K), the standard affinity ($\Delta\mu^o$), the heat of dyeing (ΔH^o), and the entropy change of dyeing (ΔS^o) were determined. It is noted that the adsorption of natural indigo on silk yarn is an exothermic process. As the result of that the saturated dye uptake was decreased when the dyeing temperature was increased. The obtained results will be further used for designing appropriate dyeing equipment and conditions for dyeing silk with natural indigo.

Nomenclature

$[D_s]$	amount of dye in the residual bath (mg l^{-1})
$[D_f]$	amount of dye on silk yarn (mg g^{-1} silk)
$[D_f]_t$	amount of dye on silk yarn after time t (mg g^{-1} silk)
$[D_f]_\infty$	amount of dye on silk yarn at equilibrium (mg g^{-1} silk)

D_A	apparent diffusion coefficient ($m^2 s^{-1}$)
t	time of dyeing (min)
r	radius of filament (1.142×10^{-4} m)
K	partition ratio
R	gas constant, 1.9872×10^{-3} kcalmol-1 K-1
$-\Delta\mu^o$	standard affinity (kcal mol^{-1})
ΔH^o	heat of dyeing (kcal mol^{-1})
ΔS^o	entropy change of dyeing (kcal mol^{-1} K^{-1})

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