

Studies on the Sorption and Permeation of Acid dyes through Silk fibroin Membrane(Ⅱ)

—Dual Sorption of Acid dyes in Silk fibroin—

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견 피브로인 막을 통한 산성염료의 흡착과 투과에 관한 연구(Ⅱ)

—견 피브로인에 대한 산성염료의 dual 흡착—

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적 요

본 연구에서는 견에 대한 산성염료의 염착기구를 규명하기 위하여 전하수가 다른 산성염료에 의한 흡착실험을 수행하여, 견섬유와 피브로인막의 구조와 염료의 구조를 관련시켜서 산성염료의 흡착거동에 관한 해석을 하였다. 산성염료에 sulfonic acid group이 도입됨에 따라서 partition coefficient(K_p)는 감소하였지만 Langmuir type sorption constant(K_L)는 증가하였고, 염색의 pH와 온도의 증가에 따라 K_p , K_L 값은 증가하였다. 전하수가 1, 2인 Dye I 과 Dye II 는 견섬유와 피브로인 막에 대하여 stoichiometric adsorption이 잘 적용될 수 있었으나 전하수가 3인 Dye III 는 잘 적용되지 않았다. sulfonic acid group이 산성염료에 도입됨에 따라 각각의 sulfonic acid group의 표준치화력은 감소하였고, 모든 엔탈피 값은 음(-)으로 나타난 반면에 엔트로피 값은 양(+)으로 나타났다. 견섬유와 피브로인 막의 흡착 constant를 비교한 결과, 견 피브로인에 대한 산성염료의 흡착거동은 견 피브로인의 구조에 영향을 받는다는 것을 알 수 있었다.

I. Introduction

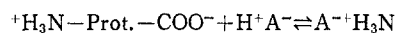
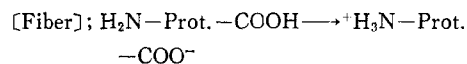
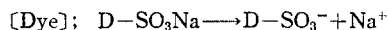
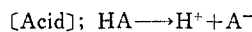
The sorption of dye is externally simple, but the sorption mechanism is complicated with various dyeing conditions. The whole dyeing process can be described three distinct stages:

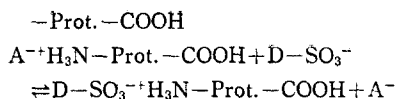
- First step) Diffusion of dye through the aqueous dyebath to the surface of the fiber.
- Second step) Adsorption of dye on the outer surface of the fiber.
- Third step) Diffusion of dye from the surface into the center of the fiber.

Generally, in the process of dye diffusion, the first step is very fast in comparison with the third step and the dye is sorbed in a moment in the second step.

The dyeing mechanism of acid dye on the protein fiber is described as an ion-exchange mechanism (Komiya and Iijima, 1974).

As follows:





It follows preferentially that acid anions are attached to the positively charged amino groups first, and then these are substituted with dye anions. This ion exchange mechanism can be explained by the fact that the affinity of dye anion is higher than that of acid anion.

In general, the equilibrium uptake of acid dyes for the protein fiber can be described as Langmuir adsorption isotherm (Vickerstaff, 1954). It follows that the maximum amounts of dye sorbed are the same as the equivalent amino group contents in fiber. The pH of the dyebath is important in acid dyeing system. No adsorption of dye takes place higher than at pH 9, but it increases with decrease of pH. It means that the dye anions taken up by fiber are attached to the positively charged amino-groups. With further decrease of pH, this mode of adsorption is often accompanied by an excess dye sorption, i.e., the amount of dye sorbed exceeds the equivalent amino group content in fiber, which is referred to as over dyeing (Peters, 1975). Some explanations for the over dyeing were suggested by several workers (Deters, 1975; McGregor et al., 1962; Back and Zollinger). Back and Zollinger (1959) have pointed out that some chromium complex dyes are sorbed on nylon by two mechanism, i.e., a Nerst type partition and a Langmuir type adsorption.

On the other hand, McGregor et al. (1962) have suggested the bimodel diffusion of dye in nylon, namely the dye adsorption on the charged amino groups and the amide groups in nylon. Hopper et al. have assumed that the diffusion of acid dyes in nylon is described in terms of the electrochemical potentials of the dyes rather than adsorption model.

Unfortunately, the over dyeing in silk fibroin is little reported. Moreover, the interpretation related to the silk fibroin structure for the dyeing mechanism scarcely discussed. So the work described in this paper deals with the sorption of mono-, di- and trisulfonic acid dyes in silk fibroin, and interpreta-

tion can be made relating to silk fibroin structure. In addition, the studies on the affinities and thermodynamics of those dyes for the silk fibroin will be described.

II. Experimental

1. Materials

The silk fibroin fiber and the membrane used in

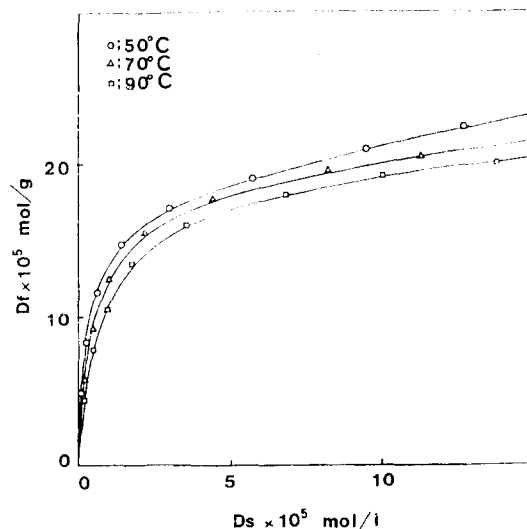


Fig. 1. Adsorption isotherms of Dye I in silk fibroin fiber at pH 2.

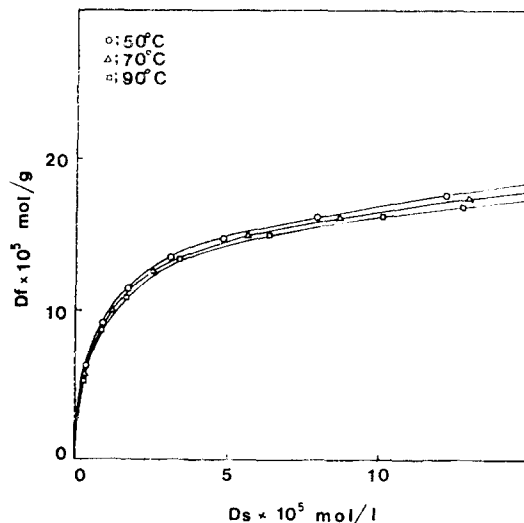


Fig. 2. Adsorption isotherms of Dye I in silk fibroin fiber at pH 3.

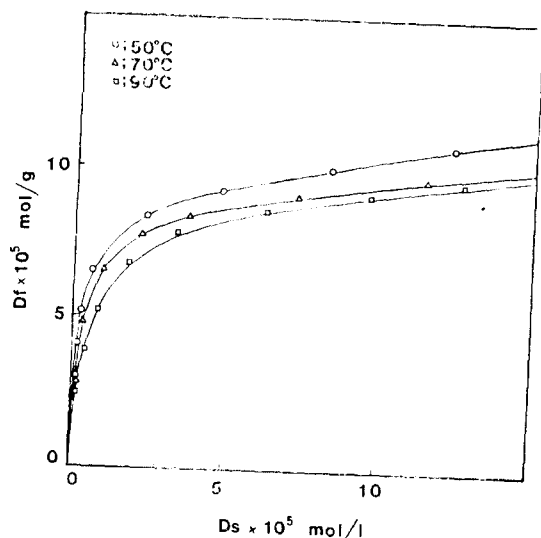


Fig. 3. Adsorption isotherms of Dye II in silk fibroin fiber at pH 2.

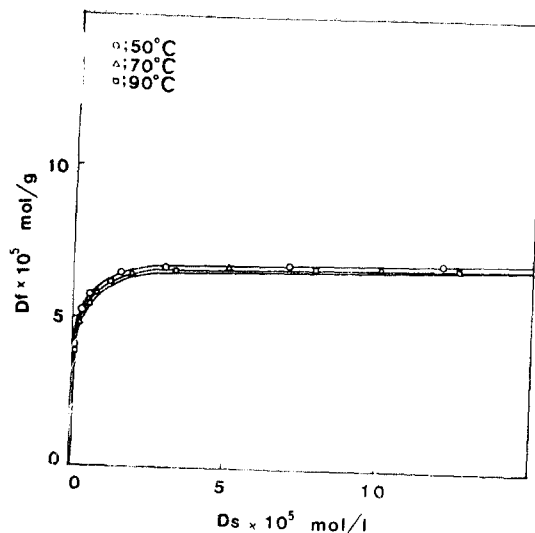


Fig. 5. Adsorption isotherms of Dye III in silk fibroin fiber at pH 2.

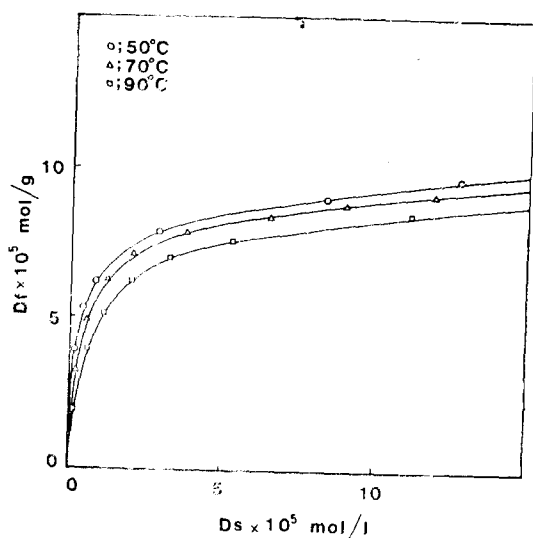


Fig. 4. Adsorption isotherms of Dye II in silk fibroin fiber at pH 3.

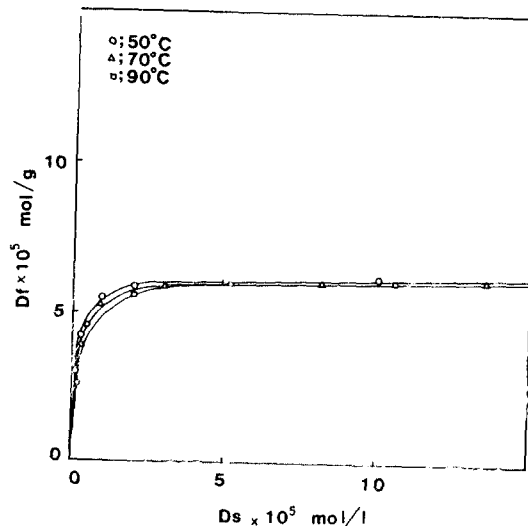


Fig. 6. Adsorption isotherms of Dye III in silk fibroin fiber at pH 3.

this experiment were the same as those obtained in previous work (Bae, 1989).

The acid dyes used were Orange II (C.I. Acid Orange 7) (Dye I), Sunset Yellow (C.I. Food Yellow 3) (Dye II), and sulfanilic acid- \rightarrow 2-naphthol-3,6-disulfonic acid (Dye III). The Dye I and Dye II were purified with the commercial reagent (Merck Co. and Tokyo kasei Co.) by repeating recrystallization from pure water-ethanol and were found to be

homogeneous by paper chromatography.

The developers were as follows;

Dye I ; Dimethylformamide : n-butanol : water
= 11 : 11 : 3 vol.

Dye II ; Dimethylformamide : Acetic acid :
water = 4 : 1 : 4 vol.

Dye III was synthesized by diazotization and coupling of sodium sulfanilate (Japan Wako Co., reagent grade) with R acid (Tokyo kasei Co.). The red

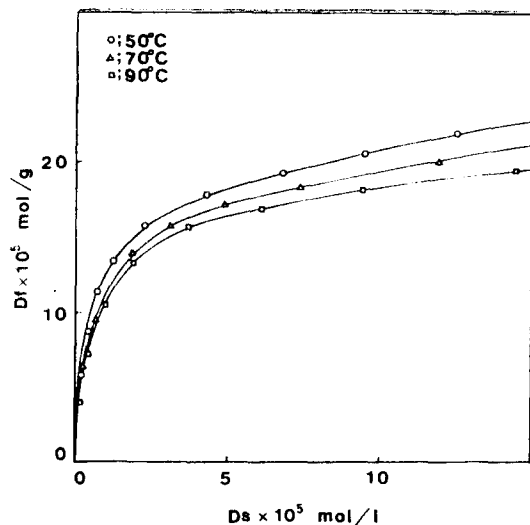


Fig. 7. Adsorption isotherms of Dye I in silk fibroin membrane at pH 2.

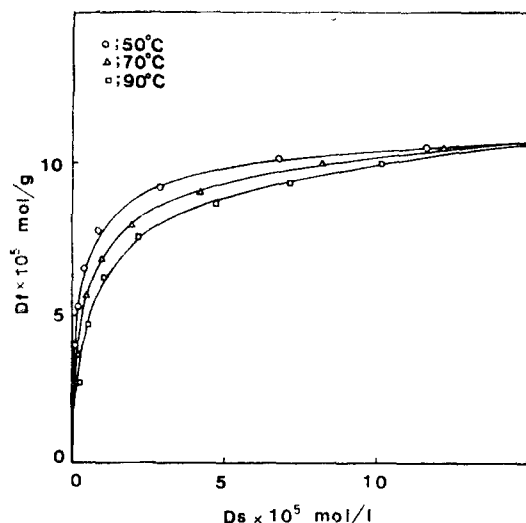


Fig. 9. Adsorption isotherms of Dye II in silk fibroin membrane at pH 2.

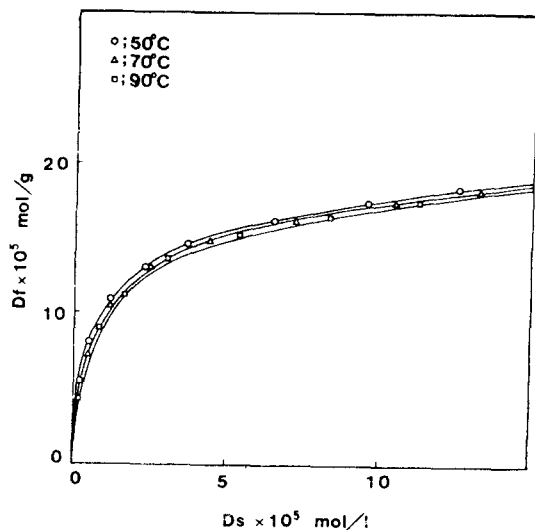


Fig. 8. Adsorption isotherms of Dye I in silk fibroin membrane at pH 3.

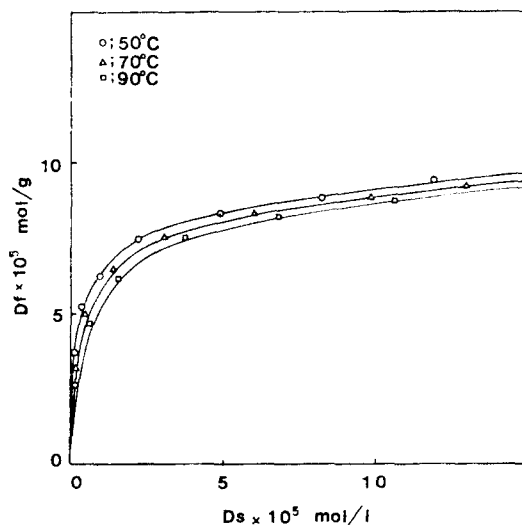


Fig. 10. Adsorption isotherms of Dye II in silk fibroin membrane at pH 3.

crystal obtained was proved to be pure by elemental analysis(CHN S/O Carlo Erba) (Obsd. C : S : N = 7.2 : 3.0 : 1.0; Calcd. C : S : N = 6.9 : 3.4 : 1.0) and proved homogeneous by paper chromatography. The developer is dimethylformamide, acetic acid and water(1 : 4 : 4 vol.).

2. Sorption Isotherms

Equilibrium sorption isotherms were determined by soaking the silk fibroin fibers and the membranes

(ca. 50mg) which were previously treated with blankbath at 50, 70 and 90°C, respectively. pH was adjusted by the appropriate amount of hydrochloric acid. The time allowed to reach the equilibrium was confirmed by a preliminary experiment.

At the end of the predetermined period the silk fibroin fiber and the membrane were removed from the dyebath. The residual dyestuff concentration(D_s) was determined spectrophotometrically(Pye Unicam

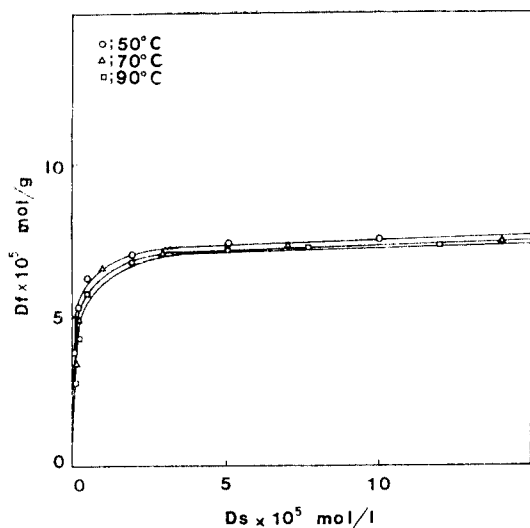


Fig. 11. Adsorption isotherms of Dye III in silk fibroin membrane at pH 2.

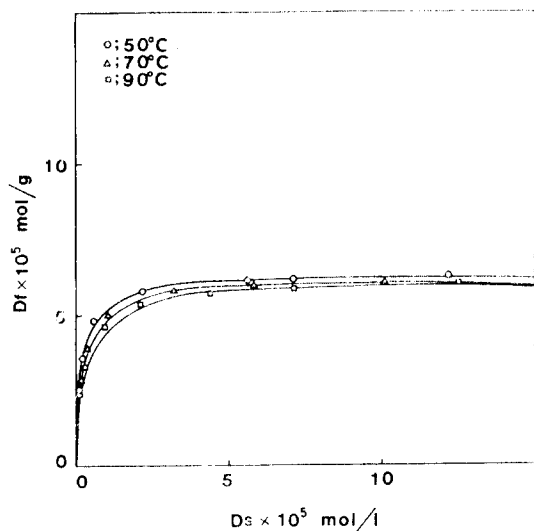


Fig. 12. Adsorption isotherms of Dye III in silk fibroin membrane at pH 3.

PU 8800 UV/visible spectrophotometer) using a prepared calibration curve. The amount of dyestuff taken up (Df) was calculated from the difference between the dyestuff contents in the bath before and after dyeing. Adsorption isotherms of each dye in silk fibroin fiber and membrane were shown in Fig. 1~12.

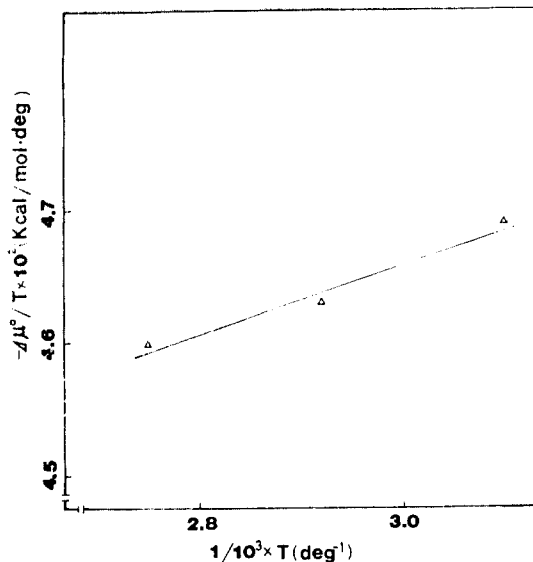


Fig. 13. A plot of $-\Delta\mu^\circ/T$ vs. $1/T$ for Dye II, pH 2, in membrane.

III. Results and discussion

In the case of dyeing of silk fibroin with acid dyes, the binding of the dye anions with amino groups of silk fibroin can be explained by an ion-exchange mechanism. It has been well known that the polybasic dyes are also sorbed stoichiometrically. The mechanism may be represented schematically as

Table 1. The structure of dyes used

Dyes	Structure	Abire.
A. Orange 7 C.I. 15510		Dye I
A. Food Yellow 3 C.I. 15985		Dye II
Sulfanilic acid-R acid		Dye III

$z(\text{Prot.}-\text{NH}_3^+\text{A}^-)+\text{D}^{z-}\rightleftharpoons(\text{Prot.}-\text{NH}_3^+)_z\text{D}^z+z\text{A}^-$
 where z is the basicity of dye anion, Prot. represents silk chain and carboxyl group, NH_3^+ is the amino end-group of the silk fibroin, and A^- is an outgoing anion pre-sorbed from the acid solution used to adjust the pH of the dyebath. According to this scheme, it means that the dye anions taken up by silk fibroin are attached to the positively charged amino groups. As described in the introduction, dyeing with acid dyes is often accompanied by over-dyeing, specially in low pH.

The dye molecules in the silk phase can be divided into two distinct populations in equilibrium, i.e., the adsorbed (L) and dissolved (P) dye molecules, Langmuirean and Nernstean species, respectively. Thus, the total uptake of dye in the acid dyeing of silk fibroin is described by the following bimodel sorption equation,

$$C=C_p+C_L$$

$$=K_p C_0 + \frac{K_L S C_0}{z(1+K_L C_0)} \quad (1)$$

Table 2. Equilibrium constants K and Saturation values S for the dyeing of silk fibroin fiber with acid dyes

pH	Temp(°C)	$K_L(l/mol)$	$K_P(l/g)$	$S \times 10^5$ (eq/g)
Dye I	50	230,000	0.365	17.68
	2 70	178,000	0.272	17.53
	90	136,500	0.211	18.51
	50	145,000	0.241	15.55
	3 70	125,000	0.173	16.11
	90	116,000	0.141	16.66
Dye II	50	430,500	0.179	17.54
	2 70	304,500	0.122	17.18
	90	195,500	0.110	17.00
	50	417,000	0.137	16.06
	3 70	294,500	0.105	16.20
	90	171,000	0.092	15.80
Dye III	50	985,000	0.013	20.34
	2 70	880,000	0.011	20.22
	90	650,000	0.009	20.46
	50	715,000	0.008	18.46
	3 70	590,000	0.008	18.38
	90	340,000	0.007	18.41

where C_0 is the dye concentration in the dyebath, S the saturation value assumed to be the amino group content, K_p partition coefficient in l/g and K_L langmuir type sorption constant in l/mol .

It is, however, convenient to rewrite eq.(1) in terms of the fractional site saturation θ to give

$$C = \frac{\theta}{K(1-\theta)} + \frac{S\theta}{z} \quad (2)$$

where $\theta=(zC_L/S)$ and $(K=K_L/K_p)$. And in order to determine K_L , K_p and S , eq.(1) can be rewritten as following equation.

$$C(K_L+1/C_0)=K_L K_p C_0 + K_p + K_L S/z \quad (3)$$

By changing the K_L value in eq.(3), the relationship of C_0 and $C [K_L+1/C_0]$ is determined by the least square method with computer, thus the K_L , K_p and S value can be obtained from these two relationship. The results are summarized in table 2 and 3.

As can be seen clearly in table 2 and 3, K_p decreases, while K_L increases, with the introduction of sulfonic acid group into these dyes. Supposed that the introduction of sulfonic acid group increase

Table 3. Equilibrium constants K and Saturation values S for the dyeing of silk fibroin membrane with acid dyes

pH	Temp(°C)	$K_L(l/mol)$	$K_P(l/g)$	$S \times 10^5$ (eq/g)
Dye I	50	273,000	0.380	17.93
	2 70	240,000	0.270	17.85
	90	145,000	0.251	17.78
	50	168,000	0.252	15.71
	3 70	129,000	0.190	16.36
	90	118,000	0.144	16.88
Dye II	50	566,000	0.182	18.52
	2 70	317,000	0.165	18.73
	90	210,000	0.143	18.89
	50	420,000	0.141	15.98
	3 70	308,000	0.104	16.25
	90	192,000	0.089	16.44
Dye III	50	1,080,000	0.015	22.36
	2 70	949,000	0.011	21.76
	90	723,000	0.012	21.78
	50	800,000	0.007	18.60
	3 70	680,000	0.008	18.51
	90	495,000	0.008	18.40

the solubility of dye, then dye anion tends to make a monolayer on the silk fibroin. The more dye anion have the tendency to make a monolayer on the silk fibroin, in the results the value of K_p decreases and that of K_L increases. Actually, the value of K_p was very small on Dye III and that of K_L was very large compared with Dye I.

On the other hand, the values of K_p and K_L decrease with increasing the temperature. It means that increasing of the temperature make both the silk fibroin and dye anion active, but relatively more desorption of dye is occurred with the temperature. And the value of K_L at low pH was higher than at high pH. It can be explained that since the amino group of silk fibroin is more easily charged at low pH, it can attach easily to dye anion.

The obtained saturation values (S) of Dye I and II both in the fiber and the membrane were less than amino group contents of the silk fibroin, whose value was 19.1×10^{-5} eq/g determined by analysis of amino acid (Kato, 1975). However, the values of Dye III are larger than amino group contents of silk fibroin at pH 2. Overall values are larger in the silk fibron membrane than in the fiber. From stoichiometric point of view, these results disagree with the data which are obtained by amino acid analysis in previous work that is, the contents of the basic amino acid for the total amino acid in the fiber is larger than that membrane. This stoichiometric disagreement can suggest that the structure of silk fibroin influence the dye uptake.

The basic amino acid group contents located in crystalline region are about 20% and those in amorphous region are about 80% (Katayama et al., 1973). Hence, the basic amino group contents located in amorphous region are 15.28×10^{-5} eq/g. The obtained saturation values of Dye I and II in table 2 and 3 are smaller than the whole amino group contents in silk fibroin, while are larger than those located in amorphous region. Of course, it is very difficult to find actual places where the dyes are sorbed. Nevertheless, considering of these results, it can be suggested that the Dye I and II molecules can partially attach to the basic amino groups located in crystalline regions.

In many instances (Katayama et al., 1984; Katayama et al., 1973), the saturation values in equivalent unit nearly correspond to charged amino group content even in the case of tetra and pentabasic acid dyes. One of the explanation on this phenomena was presented assuming the $H_3O_4^+$ bridge hypothesis (Katayama et al., 1973), that is, since the instances between amino groups is longer than those between sulfonic acid groups of the dyes, when sulfonic acid groups of polybasic dyes can not be attached to the charged amino group, the trihydrate of the hydronium ion, which can migrate through solution to have not a rigid structure, may form a bridge by its outer water molecules to bind the sulfonic acid anion with the positively charged amino group. For polybasic dyes, however, it is difficult to visualize how a polybasic dye can physically saturate the fixed sites. In the case of tribasic dye, Dye III, the obtained saturation value was larger than the whole basic amino group content of silk fibroin at pH 2. It is pointed out that the actual binding with all the basic groups does not occur even if a neutralization of the electrical charge on the silk fibroin is established. It suggests in silk fibroin that as the structure of the silk fibroin fiber and the membrane may influence the sorption behaviour in the case of tribasic dye, Dye III, the stoichiometric sorption is hardly possible. In detail, all the basic groups of dyes can not bind at the electrical charged amino groups on the silk fibroin owing to stereochemical hindrance. In other words, the tribasic dye molecule is attached to only two sites using two sulfonic acid groups, that is, one remaining sulfonic acid group of the dye molecule is located far apart from the amino group and it can not be attached to the site. On the other hand, the silk fibroin membrane has higher saturation value than the fiber in spite of having lower basic amino acid content. This result means that although the whole amino group contents in silk fiber are larger than those in membrane, the actual amino group contents to which dye anion can attach in the silk membrane are larger than those in the fiber.

Thermodynamic parameters such as standard affinity, enthalpy and entropy of adsorption were calculated

Table 4. Thermodynamic magnitudes for the dyeing of silk fibroin by Dye I

	pH	Tcmp. (°C)	$-\Delta\mu_L^0$ (kcal/mol)	$-\Delta\mu_P^0$ (kcal/mol)	$-\Delta H_L^0$ (kcal/mol)	$-\Delta H_P^0$ (kcal/mol)	ΔS_L^0 (c.u)	ΔS_P^0 (e.u)
Fiber	2	50	10.82	3.62			14.67±0.06	1.17±0.19
		70	11.14	3.64	6.08±0.02	3.24±0.02	14.75±0.06	1.17±0.15
		90	11.41	3.67			14.68±0.06	1.18±0.14
	3	50	13.18	3.35			33.07±0.09	0.53±0.22
		70	13.80	3.33	2.50±0.03	3.18±0.07	32.94±0.09	0.44±0.23
		90	14.50	3.38			33.06±0.08	0.55±0.19
Memberane	2	50	10.16	3.64			2.01±0.30	2.29±1.55
		70	10.59	3.75	9.51±0.1	2.9 ±0.5	3.15±0.29	2.48±1.46
		90	10.48	3.79			2.67±0.28	2.45±1.38
	3	50	13.37	3.38			24.06±0.30	0.25±2.16
		70	14.01	3.40	5.6 ±0.1	3.3 ±0.7	24.52±0.09	0.29±2.04
		90	14.52	3.39			24.57±0.28	0.25±1.93

Table 5. Thermodynamic magnitudes for the dyeing of silk fibroin by Dye II

	pH	Tcmp. (°C)	$-\Delta\mu_L^0$ (kcal/mol)	$-\Delta\mu_P^0$ (kcal/mol)	$-\Delta H_L^0$ (kcal/mol)	$-\Delta H_P^0$ (kcal/mol)	ΔS_L^0 (c.u)	ΔS_P^0 (c.u)
Fiber	2	50	17.88	3.16			16.35±0.31	1.11±0.34
		70	18.27	3.09	12.60±0.10	2.80±0.11	16.53±0.29	0.85±0.32
		90	18.58	3.19			16.47±0.28	1.07±0.30
	3	50	22.25	2.99			18.54±0.77	2.38±0.43
		70	22.92	2.99	16.26±0.25	2.22±0.14	19.42±0.73	2.24±0.41
		90	23.08	3.07			18.79±0.69	2.34±0.39
Membrane	2	50	15.15	3.17			31.89±0.22	3.93±0.06
		70	15.87	3.30	4.85±0.07	1.9 ±0.02	32.13±0.20	4.08±0.06
		70	16.61	3.39			32.13±0.20	4.08±0.06
	3	50	22.26	3.01			45.91±0.30	0.96±1.20
		70	23.29	2.99	7.43±0.10	2.7 ±0.4	46.24±0.29	0.85±1.17
		90	24.33	0.05			46.56±0.28	0.96±1.10

by Gilbert-Rideal theory in tables 4,5 and 6 The standard affinity of acid dye calculated using the following Gilbert-Rideal equations.

$$\frac{-\Delta\mu_L^0 + RT \ln z}{2.303(z+1)RT} = \log \frac{\theta_D}{1-\theta_D} + \text{pH} \quad (4)$$

$$-(z\Delta\mu_H^0 + \Delta\mu_D^0) = -\Delta\mu_{H,D} = -\Delta\mu_L^0 \quad (5)$$

$$-\mu_P^0 = RT \ln K_p \quad (6)$$

Where z is the dye basicity, R the constant, T absolute temperature, $\theta_D = C_L/S$, K_p partition coefficient in eq(1), $-\Delta\mu_H^0$ the standard affinity of hydrochloric acid.

The standard affinity of hydrochloric acid for silk fiber at the temperature of 50°C, 70°C and 90°C are about 7.7, 8.1 and 8.5kcal/mol at pH 2, respectively.⁶⁴⁾

As can be seen clearly in tables 4 and 5, $-\Delta\mu_P^0$ decreases with the introduction of sulfonic acid group into these dyes, while it increases $-\Delta\mu_L^0$. And $-\Delta\mu_L^0$ also increases with increasing the temperature. The standard affinity means that how ease dye molecules attach to the charged amino group. The results obtained indicate that the dye molecule can

Table 6. Thermodynamic magnitudes for the dyeing of silk fibroin by Dye III

	pH	Temp. (°C)	$-\Delta\mu_L^0$ (kcal/mol)	$-\Delta\mu_P^0$ (kcal/mol)	$-\Delta\mu^0$ (kcal/mol)	$-\Delta H_P^0$ (kcal/mol)	ΔS_L^0 (c.u)	ΔS_P^0 (c.u)
Fiber	2	50	26.08	1.48			50.09±0.62	-2.20±0.03
		70	27.39	1.45	9.90±0.2	2.19±0.01	50.99±0.55	-2.16±0.03
		90	28.11	1.39			50.17±0.55	-2.20±0.03
	3	50	31.17	1.17			43.16±5.63	0.43±0.37
		70	32.39	1.24	17.23±1.85	1.03±0.12	44.75±5.39	0.61±0.35
		90	32.88	1.21			43.11±5.10	0.50±0.33
Membrane	2	50	21.99	1.57			20.40±9.3	0.22±0.60
		70	22.12	1.59	15.4 ±3.0	1.5 ±0.2	19.59±8.7	0.26±0.58
		90	23.38	1.60			21.98±8.3	0.28±0.56
	3	50	31.46	1.18			74.18±4.6	1.21±0.30
		70	32.96	1.24	7.5± 1.5	0.79±0.1	74.23±4.4	1.31±0.28
		90	34.50	1.31			74.38±4.1	1.43±0.28

easily bind the charged amino group by introduction of sulfonic acid group. But, $-\Delta\mu_P$ of Dye II and III are less than that of Dye I. Namely, the introduction of sulfonic acid group decrease the $-\Delta\mu_D^0$. In other word, $-\mu_D^0$ of each sulfonic acid group is decreased with the introduction of sulfonic acid group. $-\Delta\mu_D^0$ of Dye I, II and III in the silk fibroin fiber were about 3.02, 1.02 and 0.96 kcal/mol, respectively. It is known that the introduction of hydrophilic group decreases $-\Delta\mu_D^0$ and that of hydrophobic group increases $-\Delta\mu_D^0$.

The enthalpy and entropy were obtained using the eq(7) and (8). One example of plots is shown in Fig. 17 for the calculation of ΔH^0

$$\Delta H^0 = \frac{(\Delta\mu^0/T)}{(1/T)} \quad (7)$$

$$\Delta\mu^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

As can be seen in tables 4,5 and 6, all enthalpies were negative, resulting that the sorption of these dyes is an exothermic reaction. And, on the whole, the entropies were positive. These phenomena can be explained by the change of state of water molecule according to the sorption by Iijim(1961). Namely, water molecules ordered in the site for dye anion or ordered around the dye anion are disordered according as the sorption is carried out.

IV. Conclusion

In this study, in order to elucidate the sorption mechanism of acid dyes for the silk fibroin, the sorption behaviour of various acid dyes was discussed in relation to the structure of silk fibroin and acid dyes.

1. It was found that the total uptake of dye in the acid dyeing of silk fibroin can be described by Nernst partition and Langmuir sorption.

2. Partition coefficient (K_p) decreased, while Langmuir type sorption constant (K_L) increased with the introduction of sulfonic acid group into acid dyes.

3. The value of K_p and K_L decreased with the increasing the temperature and pH.

4. In the case of Dye I and Dye II, the stoichiometric adsorption can almost be adapted in both silk fiber and membrane, but in the case of Dye III, it can hardly be adapted directly.

5. The standard affinity of respective sulfonic acid group were decreased with the introduction of the sulfonic acid group.

6. All enthalpy values were negative, on the other hand, on the whole the entropy values were positive.

7. The difference of constant values between silk

fiber and membrane have suggested that the sorption behaviour can be influenced by the structure of silk fiber and membrane.

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