Binding of Chrysophenine G by Methyl Cellulose and Poly(vinyl Alcohol)

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Synopsis

Equilibrium constants (nK) for the binding of Chrysophenine G by methyl cellulose (MC) and poly(vinyl alcohol) (PVA) were determined spectrophotometrically in the temperature range 15–40°C. The polymer chains of PVA extended by the dye binding but those of MC shrank slightly. The enthalpy change and the entropy change for the binding by MC were negative and positive, respectively, whereas those for the binding by PVA were both negative. When the dye was bound to the extended polymer chains, the contribution of the entropy term to the binding increased. The rate of the dye bindings was studied by means of the temperature jump method. For the dye binding to PVA, the whole relaxation process finished in a very rapid step. On the other hand, for dye binding to MC, the initial rapid step was followed by two successive slower steps; the relaxation times for the slower steps were independent of the polymer concentration The results were interpreted in terms of the stiffness of polymer chain of MC; the conformational change of the stiff chains to accommodate the dye in stable states seems to be the rate determining step in each slow relaxation.

INTRODUCTION

Dyeing process can be divided into four successive steps,[1] namely:

i. Transport of dye from a bulk solution up to the outer surface of a fiber.
ii. Diffusion of dye across a stagnant solution layer adjacent to the outer surface of the fiber.
iii. Sorption of dye on the outer surface.
iv. Diffusion and sorption of dye within the fiber.

Rate of dyeing of individual dyes is an important indication for practical dyers to perform dyeing processes successfully. In the dyeing of textile fabrics, it has been recognized that the steps ii and iv control the rate of dyeing,[2,3] where the rates of sorption and desorption at the surface and within the fiber are assumed to be very rapid by comparison with these of diffusion of dye in the solution layer and fiber itself. However, McGregor and Peters[4] found that an anomalous diffusion behavior of Benzopurprine 4B in a water-swollen cellulose can be explained on the assumption that the adsorption processes within the substrate occur rather slowly compared with the diffusion processes inside the substrate.

The rate of adsorption of direct dyes inside cellulose substrates has not been measured directly due to the difficulty in the measurement. However, to estimate the character of the binding of dyes with polymer chains themselves,

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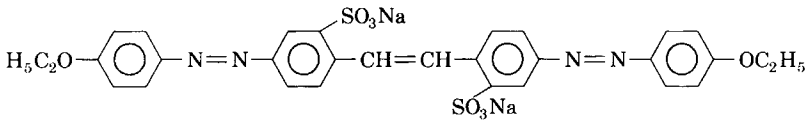
the binding of direct dyes by polysaccharides (model compounds of cellulose) in water have often been studied by an optical method from the spectral change of the dyes due to the binding.[5-8] In those studies, the dyes having the highest class of affinity on cotton, e.g., Congo Red[9] and Benzopurprine 4B[7] were used. These dyes aggregate highly in water, particularly in the presence of electrolytes at low temperature.[10] Therefore, the binding may be accompanied by the simultaneous dissociation of the aggregates; the spectral change by the binding observed many include both the change by the binding and that by the dissociation of dye. The aggregates dissociate on heating[10]; Yasunaga et al.[11] have measured the rate of dissociation of Congo Red in water in the presence of 0.1*M* of sodium chloride by means of the temperature jump technique.

Chrysophenine G [I] (C.I. Direct Yellow 12) is only a slightly aggregated[10] since the electrostatic repulsion between sulfonic acid groups of each molecule makes the aggregation difficult[12]:



[I]

In the present study, equilibria and kinetics of the binding of Chrysophenine G by methyl cellulose and poly(vinyl alcohol), the model compounds for cellulose and poly(vinyl alcohol) fiber (PVA fiber), are studied from the spectral change of the dye on the binding by polymers and the temperature jump technique, through which the effect of chain conformation of the polymers on the dye binding is clarified and the rate of the dye adsorption inside cellulose substrate will be deduced.

EXPERIMENTAL

Materials

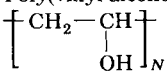
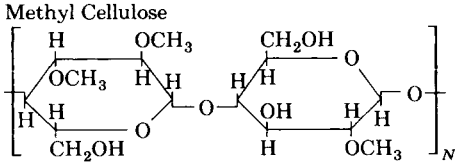
Dye. Chyrsophenine G [I] was purified from a commercial dye by the method used by Robinson and Mills[13] (λ_{max} = 402 nm, ϵ = 72,400).

Polymer. The polymers given in Table I were used.

The poly(vinyl alcohol)s were obtained from Wako Pure Chemical Industries, and purified by the repeated precipitation from aqueous solution by the addition of acetone as a precipitant. After that, the precipitations were dried *in vacuo* over phosphorous pentaoxide.

The methyl celluloses were obtained from Wako Chemical Industries. Each methyl cellulose was refluxed in acetone for 5 h, dried, dissolved in water, and then filtered. To remove salts, the filtrate was dialyzed against distilled water using a cellulose tube (Visking Corp.) until the electrical conductivity of the filtrate became a constant value. The methyl cellulose was precipitated from the solution by the addition of acetone. Then the precipitates were centrifuged and dried *in vacuo* over phosphorous pentaoxide.

TABLE I
Polymers Used

Name and structure	Abbreviation	Degree of polymerization
Poly(vinyl alcohol)  (MW = 44.05[a])	PVA 500	540[c]
	PVA 2000	1770[c]
Methyl Cellulose  (MW = 352[b])	MC 25 cps	440[d]
	MC 400 cps	1350[d]

[a] Monomeric unit basis.
[b] Based on cellobiose unit, degree of methoxylation = 1.5.
[c] Calculated from $[\eta] = K'M^{\alpha}$, $K' = 20 \times 10^{-5}$ dL/g, $\alpha = 0.76$.
[d] Calculated from $[\eta] = K'M^{\alpha}$, $K' = 316 \times 10^{-5}$ dL/g, $\alpha = 0.55$.

Amylose (degree of polymerization = ca. 18) obtained from Tokyo Kasei Industries was used without further purification.

Measurements

Absorption spectra of the equilibrium mixture of the dye and the polymers were recorded on a Simadzu MPS-50L spectrophotometer equipped with a thermostated housing; the temperature of the specimen in a cell (1 cm path length) was kept at constant temperatures ± 0.1°C. The measurements were made after placing the specimens in the dark for more than 3 days because of the photochromic property of Chrysophenine G in water; on exposure to light, the absorption maximum (λ_{max}) in the visible band (402 nm) shifts to shorter wavelength and the intensity of the band lowers. Concentration of the dye, $1.23 \times 10^{-5}M$, was used through the binding measurements.

Temperature jump (T-jump) measurements were made on a stopped-flow spectrophotometer (Union Giken RA-401) equipped with T-jump apparatus (Union Giken RA-410), on which the temperature of the equilibrium mixtures (dye, polymer, and $0.1M$ of sodium chloride) were raised from 20 to 25°C in $5–6 \times 10^{-6}$ s.

RESULTS AND DISCUSSION

Figure 1 shows the spectral change of Chrysophenine G by the addition of MC 25 cps at 25°C. The absorption peak at 402 nm sifted to longer wavelength as the concentration of the polymer was increased. Similar spectral changes were also observed by the addition of poly(vinyl alcohol)s as shown in Figure 2. It was observed that when Chrysophenine G is absorbed by cellulose film from aqueous solution, the λ_{max} in the visible region shifts from 402 to 422 nm. The spectral changes shown in Figures 1 and 2 are in accord with this

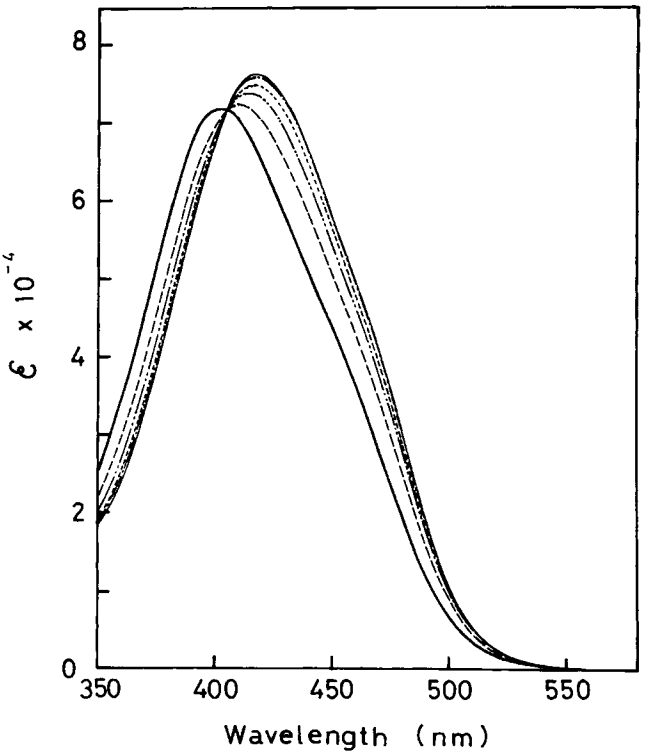


Fig. 1. Spectral change of Chrysophenine G by the addition of methyl cellulose (MC 25 cps) at 25°C. Concentration of MC 25 cps: (——) 0, (– – – –) 4.0, (— · —) 8.0, (– – – –) 12.0, (– · · –) 16.0, and (——) 24.0 × 10^{-3} base M (cellobiose unit basis).

observation. On addition to this fact, each curve in Figures 1 and 2 passed through the isosbestic point within the concentration range of the polymers used. Therefore the spectral changes shown in Figures 1 and 2 are ascribed to the binding of the dye by the polymers expressed by

$$\underset{(a-x)}{\text{free dye}} + \underset{(nP-X)}{\text{free site in polymer}} \overset{K}{\rightleftharpoons} \underset{(x)}{\text{combined dye}} \qquad (1)$$

where a and P refer to the initial concentration of the dye and the polymer, respectively, n refers to the number of binding site in an unit mole of the polymer, and K refers to equilibrium constant.

If the molar absorptivity of dye in the equilibrium mixture (ϵ_{app}) at a wavelength of λ is measured under the conditions of $nP \gg x$, the relation between ϵ_{app} and nK is expressed by[14]

$$\epsilon_{app} \approx -\frac{\epsilon_{app} - \epsilon_f}{P} \cdot \frac{1}{nK} + \epsilon_b \qquad (2)$$

where ϵ_f and ϵ_b are the molar absorptivity of the free dye and that of the bound dye in water at the wavelength of λ, respectively. Equation (2) indicates that the plot of ϵ_{app} against $(\epsilon_{app} - \epsilon_f)/P$ gives a straight line with slope of $-1/nK$ and the intercept of ϵ_b under the conditions of $nP \gg x$.

Figure 3 shows examples of the plots of eq. (2) for the equilibrium mixtures of the dye and PVA 2000, where a and P were 1.23 × $10^{-5}M$ and 5–70 × 10^{-3}

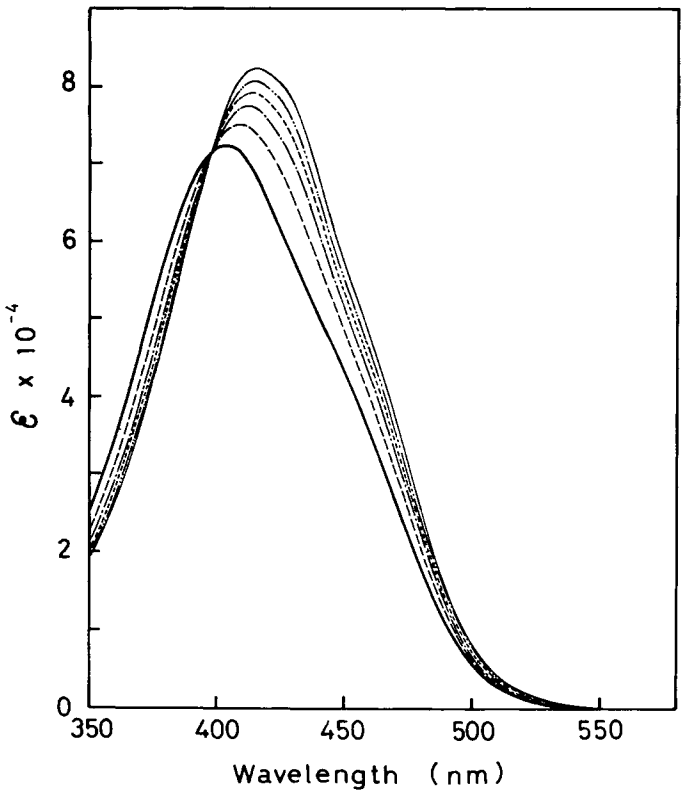


Fig. 2. Spectral change of Chrysophenine G by the addition of poly(vinyl alcohol) (PVA 500) at 25°C. Concentration of PVA 500: (——) 0, (- - - -) 4.0, (— · · —) 8.0, (·····) 12.0, (— · —) 16.0, and (——) 25.0 × 10^{-3} base M (monomeric unit basis).

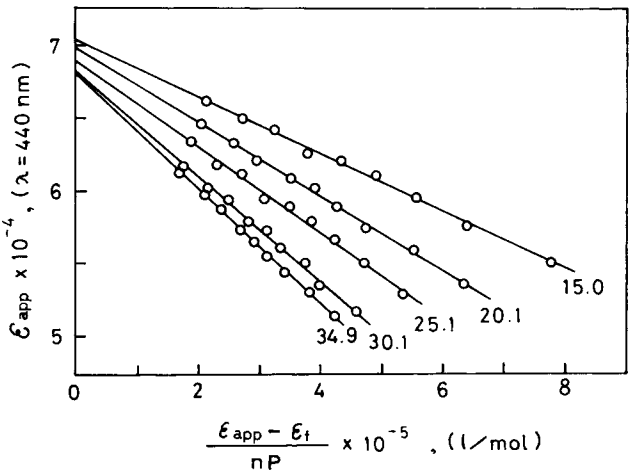


Fig. 3. Plots of eq. (3) for the binding of Chrysophenine G by PVA 2000 at 440 nm.

TABLE II
Binding of Chrysophenine G by Poly(vinyl Alcohol)s

Polymer	Concentration of sodium chloride (g ion/L)	Temp (°C)	$nK \times 10^{-3}$[a]	ΔH^0(kcal/mol)	ΔS^0 (e.u.)	$[\eta]$ (25°C) In water (dL/g)	$[\eta]$ (25°C) In dye[b] solution (dL/g)
PVA 500		20.0	10.9				
		25.0	9.42				
	0	30.1	7.80	−6.25	−2.80	0.425	0.577
		35.0	6.78				
		40.0	5.46				
		20.0	14.7				
		25.0	12.0				
	0.01	30.2	8.70	−7.72	−7.29	0.402	0.430
		35.2	7.50				
		40.1	6.42				
PVA 2000		15.0	2.84				
		20.1	2.17				
	0	25.1	1.88	−6.23	−5.96	1.044	1.149
		30.0	1.53				
		34.9	1.41				
		15.1	3.40				
	0.001	19.8	2.98	−6.91	−7.89	0.996	1.074
		25.1	2.18				
		29.9	1.94				
		19.9	2.69				
	0.1	24.8	2.16	−7.90	−11.24	0.998	1.061
		29.7	1.77				
		34.9	1.38				

[a] Calculated on mole fraction basis, where the concentration of poly(vinyl alcohol) was based on monomeric unit.
[b] Aqueous solution of Chrysophenine G ($1.23 \times 10^{-5} M$).

base M, respectively. Each plot in Figure 3 fell on a straight line, indicating that the condition $nP \gg x$ is valid for the equilibrium mixtures. Therefore, the values of nK at each temperature was calculated from the slope of the plot by means of the least square method. The thermodynamic functions for the binding, the enthalpy change ΔH^0 and the entropy change ΔS^0, were calculated from the values of nK thus determined using the standard thermodynamic relations.

Table II shows the thermodynamic functions for the binding by the poly(vinyl alcohol)s. Both the values of ΔH^0 and ΔS^0 were negative, indicating the binding occurs by the contribution of ΔH^0 term only. The binding constant decreased with an increase in the degree of polymerization (N). The addition of sodium chloride decreased both ΔH^0 and ΔS^0, i.e., the contribution of ΔH^0 term to the binding increases with the concentration of sodium chloride added.

It has been reported that for the bindings of direct dyes by polysaccharides, both ΔH^0 and ΔS^0 are positive[5-7]; the binding occurs by only the contribu-

TABLE III
Binding of Chrysophenine G by Methyl Celluloses

Polymer	Concentration of sodium chloride (g ion/L)	Temp (°C)	$nK \times 10^{-3}$[a]	ΔH^0 (kcak/mol)	ΔS^0 (e.u.)	[η] (25°C) In water (dL/g)	[η] (25°C) In dye[b] solution (dL/g)
MC, 25 cps	0	15.0	4.97	−1.75	10.8	2.298	2.004
		20.1	4.57				
		25.1	4.35				
		30.0	4.24				
		35.0	4.04				
	0.01	15.2	6.14	−3.48	5.28	2.107	1.943
		19.9	5.66				
		25.0	5.16				
		30.0	4.72				
		35.2	4.10				
MC, 400 cps	0	15.0	4.71	−3.53	4.53	4.279	4.263
		20.1	4.05				
		25.1	3.87				
		29.9	3.44				
		35.1	3.10				

[a] Calculated by mole fraction basis, where the concentration of methyl cellulose was based on cellobiose unit.
[b] Aqueous solution of Chrysophenine G ($1.23 \times 10^{-5} M$).

tion of ΔS^0 term. Table III shows the thermodynamic functions for the binding of Chrysophenine G by the methyl celluloses. The values of ΔH^0 and ΔS^0 were negative and positive, respectively; the binding occurs by the contributions of both ΔH^0 and ΔS^0 terms. The binding constant decreased with an increase in the degree of polymerization. The addition of sodium chloride ($0.01 M$) increased the contribution of ΔH^0 term to the binding and decreased that of ΔS^0 term.

For the binding of Chrysophenine G by amylose (N = ca. 18), we have obtained $nK = 7.65 \times 10^5$ (mole fraction basis) at 25.2°C. The values of nK obtained in this study are much less than those reported for the direct dye binding by polysaccharides, as shown below:

Dye	Polymer	Temp (°C)	$nK \times 10^{-5}$ (mole fraction basis)
Congo Red	Amylose (N = 17)	23	7.31[5]
	Amylose (N = 860)	23	7.20[5]
Benzopurprine 4B	Amylose (N = 4100)	25	1.71[6]
	Ficol (N = 1240)	23	353[7]

However, this is in accord with the fact that Chrysophenine G has a lower affinity on cellulose ($\Delta\mu^0$ = 3.31 kcal/mol at 90°C[15]) and PVA fiber ($\Delta\mu^0$ = 3.0 kcal/mol at 70°C[16]) than those of Congo Red on PVA fiber ($\Delta\mu^0$ =

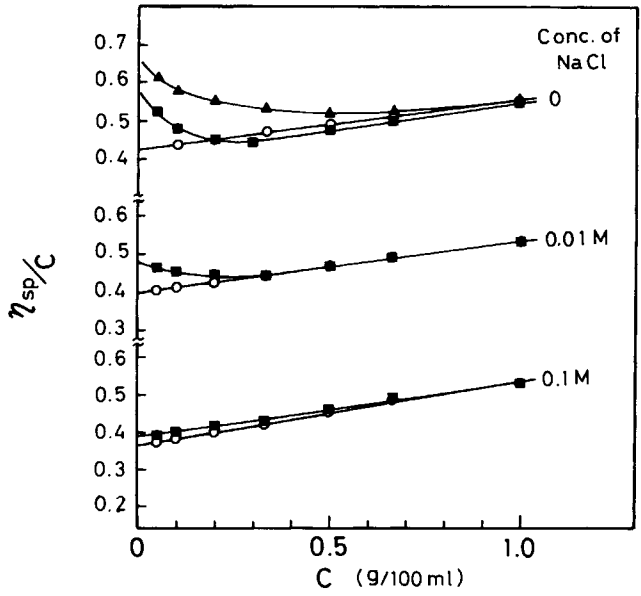


Fig. 4. Effect of the addition of Chrysophenine G on the reduced viscosity of PVA 500 in water at 25°C. Concentration of Chrysophenine G: (—○—) 0; (—■—) 1.23×10^{-5} M; (—▲—): $1.00 \times 10^{-3}M$.

5.23 kcal/mol at 70°C[16]) and Benzopurprine 4B on cotton ($\Delta\mu^0$ = 6.06 kcal/mol at 90°C[17]).

It has been reported that dye bindings by polymers in water induce conformational changes of the polymers.[8,18,19] When ionic dyes bind to non-ionic polymer chains, in general, the polymer chains expand by the Coulombic repulsions between the electrical charges of the dye ions fixed on the polymer chains.[8,18-20] However, in some cases, the polymer coils shrink by the dye binding since the dye binding act as an extensive crosslinking.[18,19]

Figure 4 shows the difference in the reduced viscosity of PVA 500 in water and in the aqueous solutions of Chrysophenine G at 25°C. When the polymer was dissolved in water, the reduced viscosity, η_{sp}/C, decreased linearly with decreasing polymer concentration, C (g/dL), regardless of the concentration of sodium chloride added (—○—). On the other hand, in the dye solution of $1 \times 10^{-3}M$, in the absence of added salt (—▲—), the reduced viscosity increased rapidly with decreasing polymer concentration. In the dilute dye solution ($1.23 \times 10^{-5}M$, which is the dye concentration used in the measurements of nK's given in Tables I and II), the reduced viscosity increased rapidly as the polymer concentration was decreased below 0.2 g/dL (—■—). However, the addition of sodium chloride suppressed the rapid increase in the reduced viscosity. These findings indicate that the polymer chain behaves as a polyelectrolyte as the result of the dye binding; the polymer chain is expanded by the Coulombic repulsions between the dye anions fixed on the polymer. The expansion is reduced by the addition of salts due to their shielding effect for the repulsive powers. The viscometric behavior of PVA 2000 in water and the dye solution were similar to those of PVA 500.

Figure 5 shows the reduced viscosities of MC 25 cps in water (—○—) and in the dye solutions of $1 \times 10^{-5}M$ (—■—) at 25°C. The reduced viscosity

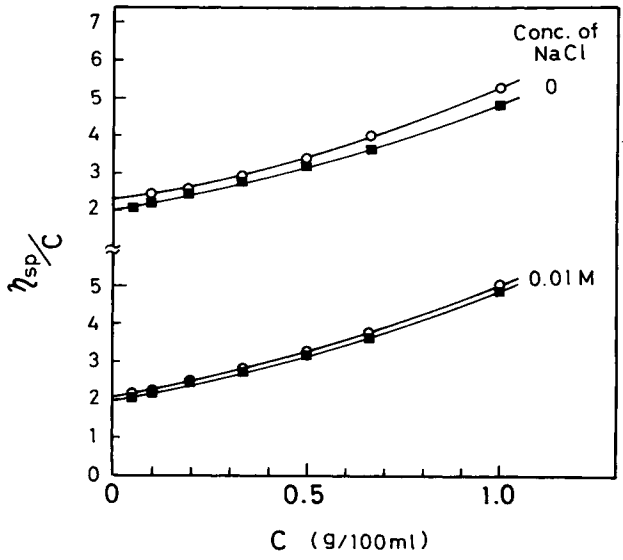


Fig. 5. Effect of the addition of Chrysophenine G on the reduced viscosity of MC 25 cps in water at 25°C. Concentration of Chrysophenine G: (— ○ —): 0; (— ■ —) $1.23 \times 10^{-5}M$.

decreased gradually with decreasing polymer concentration regardless of the additions of the dye and sodium chloride. The reduced viscosity in the dye solution was slightly lower than that in water over the whole range of the polymer concentration measured. These indicate that the dye binding gives only a slight effect on the conformation of the stiff chains of methyl cellulose which shrink slightly on the dye binding. Nishida et al.[7] has reported that the polymer chain of Ficol in water shrink by the binding of Benzopurprine 4B.

The intrinsic viscosity, $[\eta]$, of poly(vinyl alcohol)s in water and in the dye solution ($1.23 \times 10^{-5}M$) are given in the last two columns of Table II, respectively. The comparison of ΔS^0 with $[\eta]$ in the dye solution indicates that the value of ΔS^0 decreases with $[\eta]$; the negative contribution of the ΔS^0 term to the binding increased as the polymer conformation was changed to compact form. This finding is in accord with the fact that ΔS^0 for the dyeing of PVA fiber with Chrysophenine G decreases as the degree of acetalization is increased.[16]

It has been pointed out that cellulose dyeing could be considered a manifestation of hydrophobic bonding.[21] When dye molecules are oriented face-to-face with a cellulose chain, van der Waals dispersion forces between the aromatic rings of the dyes and $>$CH groups in the cellulose ring can operate effectively to hold the dye molecules parallel and in contact with the cellulose. The values of $[\eta]$ for MC 25 cps are given in Table III, the contribution of ΔS^0 to the binding increased with $[\eta]$. The expanded conformation of methyl cellulose is favorable to the face-to-face orientation. Therefore, the increase in ΔS^0 with an increase in $[\eta]$ for the dye binding by MC 25 cps seems to indicate the contribution of the hydrophobic bonding to the dye binding.

The dyeing equilibrium and kinetics of direct dyes on cellulose substrates depend greatly on the fine structure of the substrates.[22] The results obtained

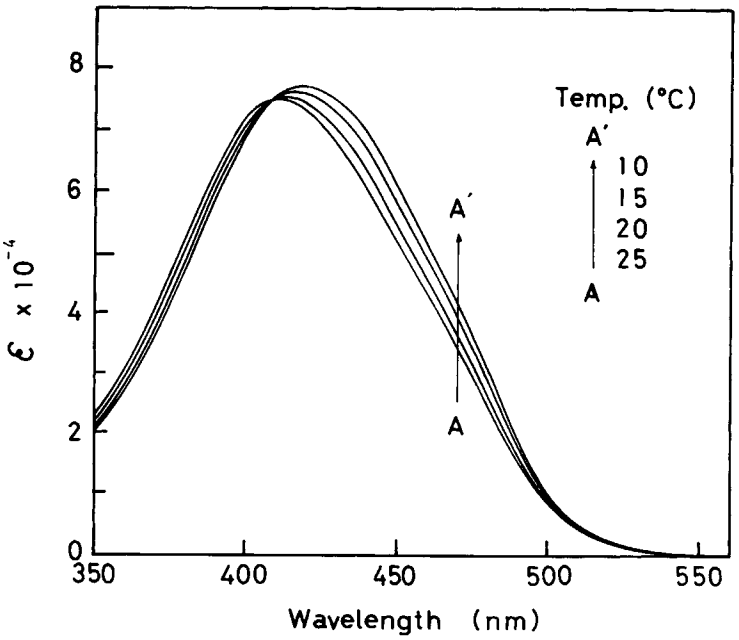


Fig. 6. Spectral change of the equilibrium mixture of Chrysophenine G and MC 25 cps on heating. Composition of the equilibrium mixture: dye, $1.23 \times 10^{-5}M$, MC 25 cps, 5.0×10^{-3} base M; sodium chloride, $0.1M$.

here suggest that the dyeing equilibrium depends on the conformation of polymer chains in amorphous regions of the polymer substrates.

Figure 6 shows the spectral change of the equilibrium mixture of Chrysophenine G and PVA 2000 on heating, indicating a part of the bound dye release from the polymer on heating. Hence the temperature perturbation of the binding equilibrium can be measured by means of T-jump method.

Figure 7(A) shows the relaxation curves thus measured. In the dye bindings by PVA 500 and 2000, the whole relaxation process finished in one step as exemplified in Figure 7(A), where the relaxation time, τ_1 = ca. 1×10^{-5} s, is too fast to determine it exactly on the apparatus used.

On the other hand, as exemplified in Figure 7(A), in the dye bindings by MC 25 and 400 cps, the initial rapid relaxation was followed by the substantially slower process. Figure 7(B) shows the Guggenheim plot for the relaxation curve of the dye binding by MC 25 cps shown in Figure 7(A), indicating that the slow relaxation consists of two processes, the slow process (relaxation time $\tau_2 = 0.036$ s) and the subsequent slower process (relaxation time $\tau_3 = 0.11$ s); the relaxation times were calculated from the slopes of the Guggenheim plot. Similar relaxation process has often been observed for albumins–ligand bindings,[23-26] in which a very rapid second-order association step is followed by subsequent first-order slow relaxation steps. The fast step and the subsequent slow steps have been attributed to the diffusion-controlled bimolecular reaction and the conformational change of the albumins to stabilize the complex, respectively.

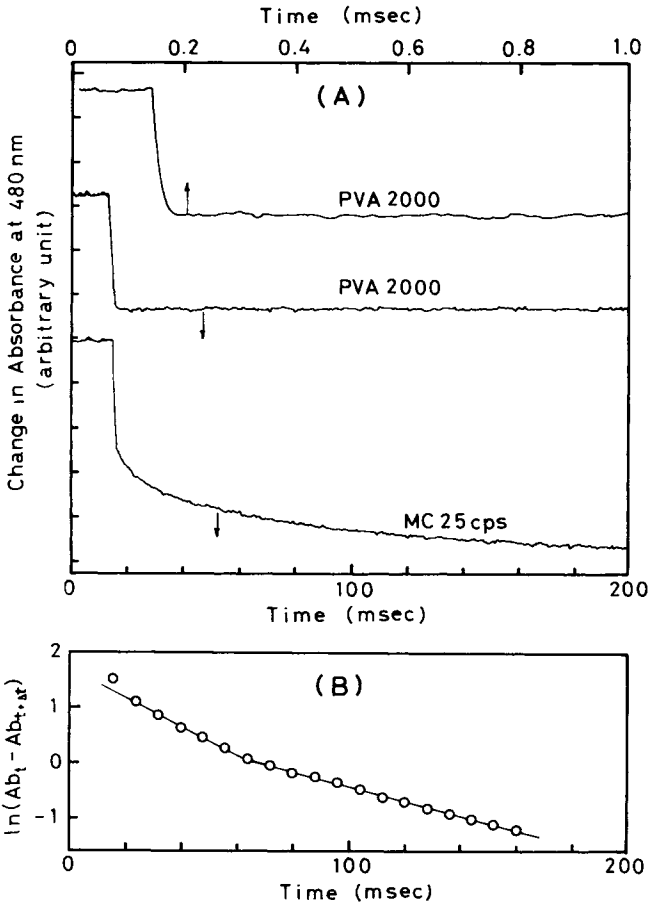


Fig. 7. Relaxations for the bindings of Chrysophenine G by PVA 2000 and MC 25 cps determined on the T-jump apparatus. Composition of the equilibrium mixtures measured; dye, $5.0 \times 10^{-5}M$, PVA 2000, 5.0×10^{-3} base M (or MC 25 cps, $10 \times 10^{-3}M$); sodium chloride, $0.1M$.

The kinetic data for the slow relaxation processes are given in Table IV, indicating that the rate of the dye binding is independent of the polymer concentration. We have found similar relaxations for the binding of azo dyes by β-naphthalenesulfonic acid–formaldehyde condensates.[27] It has been known that relaxation time for the dye binding by stiff chain polyions, e.g., Acrydine Orange–poly(adenyl acid),[28] is independent of the reactants concentration; the rate determining steps have been assigned to be the conformational change to facilitate the stable accommodation of the dye molecules.

Therefore, the slow processes in the methyl cellulose binding shown in Figure 7(A) may be attributable to the conformational change of the stiff polymer chain. The results obtained above seems to indicate that for the dye binding by flexible chain molecules, e.g., poly(vinyl alcohol), the binding reaction finishes in a very rapid process, whereas, for the binding by stiff chain molecule, e.g., methyl cellulose, the initial rapid binding process is followed by subsequent slower processes. However, the diffusion process of Chrysophenine

TABLE IV
Relaxation Times for the Binding of Chrysophnine G by Methyl Celluloses

Polymer	Concentration of polymer (base $M \times 10^3$)	Reciprocal relaxation time	
		$1/\tau_2$ (s^{-1})	$1/\tau_3$ (s^{-1})
MC,	1.0	26	10.2
25 cps	2.0	28	8.5
	4.0	28	9.4
	8.0	27	8.7
	12.0	27	8.7
	16.0	26	8.5
MC,	1.0	25	13.2
400 cps	2.5	30	9.4
	5.0	32	9.4
	10.0	28	11.0
	15.0	27	9.9

G in water-swollen cellulose[29] is much slower than these slower processes; therefore, it seems that the rate of sorption and desorption of the dye within the cellulose substrates give no effect on the dyeing kinetics.

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References

1. C. H. Giles, *Chem. Ind.*, **1966**, 92 (1966).
2. R. McGregor and R. H. Peters, *J. Soc. Dyers Colour.*, **81**, 393 (1965); R. McGregor, R. H. Peters, and K. Varol, *J. Soc. Dyers Colour.*, **86**, 442 (1970); R. McGregor, A. E. Nounou and R. H. Peters, *J. Soc. Dyers Colour.*, **90**, 246 (1974).
3. T. Shibusawa, T. Endo, Y. Kameta, and P. Rys, *Sen-i Gakkaishi*, **42**, T-671 (1986).
4. R. McGregor and R. H. Peters, *Trans. Faraday Soc.*, **60**, 2062 (1964).
5. B. Carroll and H. C. Cheung, *J. Chem. Phys.*, **66**, 2584 (1962).
6. K. Nishida, T. Akimoto, and H. Uedaira, *Kolloid Z. Z. Polym.*, **233**, 896 (1969).
7. K. Nishida, S. Yoshida, I. Ishige, and H. Uedaira, *Kolloid-Z. Z. Polym.*, **238**, 423 (1970).
8. R. C. Schulz and J. A. Trisnadi, *Makromol. Chem.*, **177**, 1771 (1976).
9. T. Urahata, *Kogyo Kagaku Zasshi*, **59**, 1171 (1956); **60** 1468 (1957).
10. S. R. Sivaraja Iyer and G. S. Singh, *Kolloid-Z. Z. Polym.*, **242**, 1196 (1970).
11. T. Yasunaga, N. Tatumoto, H. Inoue, and S. Harada, *Nippon Kagaku Zasshi*, **90**, 1 (1969).
12. R. H. Peters, *Textile Chemistry*, Elsevier, Amsterdam, Oxford, New York, 1975, Vol. III, p. 851.
13. C. Robinson and H. A. Mills, *Proc. Roy. Soc.*, **A131**, 576 (1931).
14. T. Shibusawa and F. Igarashi, *Nippon Kagaku Kaishi*, **1974**, 1544 (1974).
15. M. Nango, M. Maekawa, A. Katayama, and N. Kuroki, *Sen-i Gakkaishi*, **35**, T-252 (1979).
16. H. Yoshitake and I. Hashimoto, *Annu. Rep. 120 Committee (Dye. Finish.), Jpn. Soc. Promotion Sci.*, **8**, 34 (1956).
17. M. Maekawa, M. Nango, A. Katayama, and N. Kuroki, *Sen-i Gakkaishi*, **36**, T-44 (1980).
18. H. P. Frank, S. Barkin, and F. R. Eirich, *J. Phys. Chem.*, **61**, 1375 (1957).
19. P. Molyneux and H. P. Frank, *J. Am. Chem. Soc.*, **83**, 3169, 3175 (1961).
20. T. Motoyama and S. Okamura, *Kobunshi Kagaku*, **11**(105), 23 (1954).
21. V. G. Agnihotri and C. H. Giles, *J. Chem. Soc., Perkin II*, 2241 (1972).
22. R. McGregor and R. H. Peters, *J. Soc. Dyers Colour.*, **96**, 267 (1968).
23. T. Faerch and J. Jacobsen, *Arch. Biochem. Biophys.*, **134**, 284 (1977).

24. R. D. Gray and S. D. Stroupe, *J. Biol. Chem.*, **253**, 4370 (1978).
25. K. Murakami, T. Sano and T. Ysunaga, *Bull. Chem. Soc. Jpn.*, **54**, 862 (1981).
26. K. Murakami, *Bull. Chem. Soc. Jpn.*, **61**, 1323 (1988).
27. T. Shibusawa, *Sen-i Gakkaishi*, **43**, 614 (1987).
28. G. G. Hammes and C. D. Hubbad, *J. Phys., Chem.*, **70**, 2889 (1966).
29. J. O. Warwicker, *J. Polym. Sci. Part A*, **1**, 3105 (1963).

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