

Dyeing of Cellulose by Direct Dye in Aqueous Sodium Alginate Solution

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Synopsis

Dyeing of cellulose by direct dye in aqueous sodium alginate solutions containing sodium chloride has been studied to interpret thermodynamically the role of sodium alginate on the adsorption equilibrium of dye on cotton. The result has been compared with that of sodium chloride (low-molecular inorganic electrolyte) by an adsorption model on cellulose. We have inferred, by the membrane-equilibrium theory, that the dye has been concentrated into the internal solution of cellulose because of the presence of sodium alginate in the bulk solution.

INTRODUCTION

In aqueous inorganic electrolyte solution, the kinetics as well as thermodynamic interpretations for understanding the mechanism of dyeing cellulose with direct dye has been reported.¹⁻² In comparison, the adsorption of direct dye on cellulose in aqueous polyelectrolyte solution is rather limited.³

In a previous article,⁴ dyeing of cotton by Chrysophenine G (C.I. Direct Yellow 12) in aqueous solution of sodium alginate (polyelectrolyte) has been studied. We have inferred by the membrane-equilibrium theory that the dye has been concentrated into the internal solution of cellulose because of the presence of sodium alginate in the bulk solution.

In this report, dyeing of cotton by Chrysophenine G in aqueous sodium alginate solution containing sodium chloride has been studied to interpret the role of sodium alginate in terms of the affinity and the adsorption equilibrium of dye on cotton.

EXPERIMENTAL

Materials

The direct dye Chrysophenine G (Fig. 1) was obtained from Sumitomo Chemical Ind. Co. The dye was purified by the method of Robinson and Mills.⁵ Examination by thin-layer chromatography of cellulose powder in butanol-H₂O-pyridine (6:4:3) showed only a single spot. Inorganic electrolyte used was sodium chloride. Sodium alginate (Fig. 2) was supplied by Tokai Senko K. K. and converted into alginic acid by treatment with 1.86*N* hydrochloric acid at 40°C, 1 hr. After being washed with water, the fully swollen, alginic acid gel was neutralized with 1*N* sodium hydroxide. After standing overnight, sodium al-

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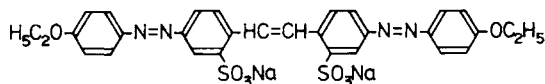


Fig. 1. Chrysophenine G (C.I. Direct Yellow 12).

ginate was isolated by methyl alcohol precipitation, followed by three successive methyl alcohol precipitations. The molecular weight of sodium alginate determined by viscosity was 100,000. The molecular weight of sodium alginate had decreased from 100,000 to 50,000 by hydrolysis during the course of dyeing. The average dimension⁴ of sodium alginate (MW 50,000) was 127 Å. The counterion activity coefficients determined by sodium ion-selective electrode^{4,6-8} was 0.5 ± 0.05 within the electrolyte concentrations used in this article.

The concentration of sodium ion shown with a pyranose unit mole and the degree of dissociation, α (see Fig. 2) in aqueous sodium alginate solutions with and without added sodium chloride was determined by the method of T. Okubo et al.⁹ at 25 and 50°C. Aqueous sodium chloride solutions were used as the standard solution to determine the concentration of sodium ions. The activity coefficient of the sodium ion of sodium chloride in both water and in aqueous sodium alginate solution is equal to 1.0. The change in single-ion-activity coefficient by hydrolysis of sodium alginate caused during the course of dyeing and with the temperature changes from 25 to 50°C was not observed.

The concentration of sodium alginate is shown with a pyranose unit mole (Fig. 2). The binding of dye to sodium alginate was negligible as determined by the dialysis equilibrium method.¹⁰ Commercial cotton was soaked in boiled deionized distilled water for 1 hr, and then treated with methyl alcohol. Its carboxyl group content as determined by the iodometry method¹¹ was 4 mequiv/kg.

Dyeing Procedure

Dyeing was carried out in 200-ml round-bottom Pyrex flasks fitted with water condensers to prevent the loss of liquor due to evaporation. The dyeing was done at temperature of $90 \pm 0.5^\circ\text{C}$ for 6 hr and the cotton weight used in every case was about 0.1 g. The concentration of dye in solution ranged from 1.004×10^{-5} to 2.164×10^{-3} mol/l. and the volume of dye bath was 100 ml in every case. The concentration of sodium chloride and sodium alginate ranged from 1×10^{-2} to 10×10^{-2} mol/l.

Dyed samples were removed from the liquor, washed in cold water until the washings did not show any coloration, blotted between filter paper to remove excess water, dried, and weighed. Accurately weighed dyed samples were ex-

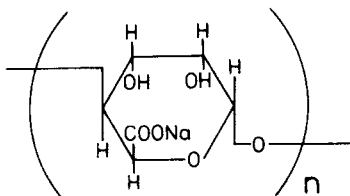


Fig. 2. Sodium Alginate (NaP). n = unit molar structure. MW 100,000^{4,6}. Counterion activity coefficient ($\alpha = 0.5$).^{4,78}

tracted with 25% aqueous pyridine. Complete extraction was accomplished at room temperature by leaving the samples in the pyridine solution for 24 hr. The concentration of dye extracted was determined using a Hitachi 124 spectrophotometer with 25% aqueous pyridine as reference. To prevent complications arising from *cis*-*trans* transformation in the case of Chrysophenine G, a stilbene derivative, the dye solution was illuminated for about 1 hr just before measurement.¹²

Solution of Equation

The third-order equation [eq. (7)] was calculated by the Nonc. 50 computer with FORTRAN programs.

RESULTS AND DISCUSSION

Figure 3 shows equilibrium adsorption isotherms at 90°C for Chrysophenine G on cotton in systems with successive additions of sodium alginate to the constant concentration of sodium chloride (1×10^{-2} mol/l.).

Figure 4 shows equilibrium isotherms at 90°C for Chrysophenine G on cotton in systems with successive additions of sodium chloride to the constant concentration of sodium alginate (2×10^{-2} unit mol/l.). The isotherms (Fig. 3) show increasing dye adsorption with the increasing additions of sodium alginate to the constant concentration of sodium chloride. The increasing dye adsorption with increasing the additions of sodium chloride at constant concentration of sodium alginate^{1,2} is illustrated in Figure 4.

The average dimension of sodium alginate (127 Å) is too large to enter into the pore of cellulose (40 Å),^{1,4} so, the role of sodium alginate in the dyeing of cellulose by direct dye differs from that of sodium chloride which is able to enter into the pores of cellulose. With a view to studying the influence of sodium alginate in the bulk solution on the dye equilibrium adsorption quantitatively, the following theoretical treatment has been adapted. That is, the results of equilibrium adsorption have been interpreted by reference to the parameters affecting

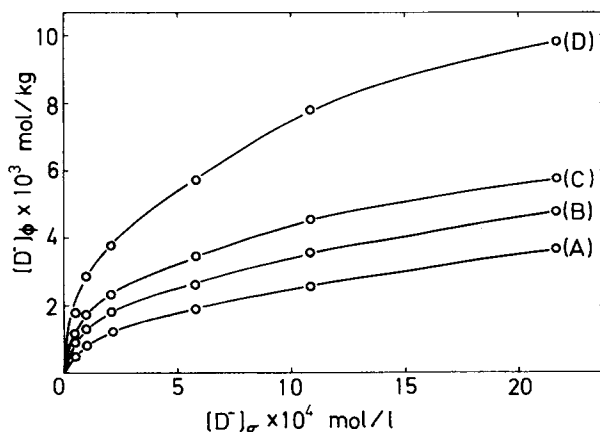


Fig. 3. Adsorption isotherms of Chrysophenine G on cotton in aqueous sodium chloride (1×10^{-2} mol/l.). The effect of addition of sodium alginate. (A) In the absence of sodium alginate; (B), (C), (D) The addition of sodium alginate (unit mol/l.) in 2×10^{-2} , 4×10^{-2} , 10×10^{-2} , respectively.

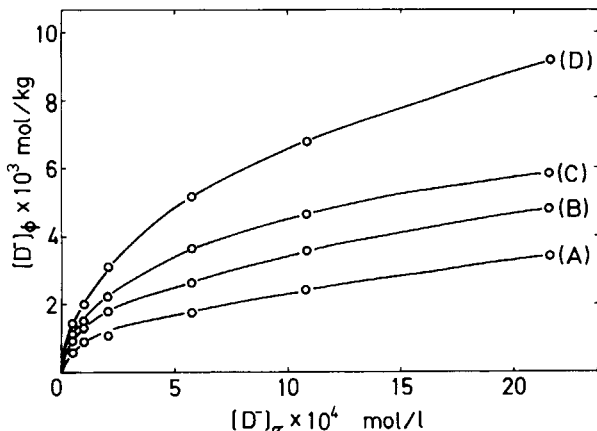


Fig. 4. Adsorption isotherms for Chrysophenine G on cotton in aqueous sodium alginate solution (2×10^{-2} unit mol/l). (A) In the absence of sodium chloride. (B), (C), (D) The addition of sodium chloride (mol/l.) at 1×10^{-2} , 2×10^{-2} , 5×10^{-2} , respectively.

the free energy of dyeing. With an adsorption model for cellulose (Fig. 5), where the dyeing system consists of an internal solution of cellulose (i phase), bulk solution I (σ phase), and bulk solution II (γ phase), we have assumed that alginate ion (P^- , polyion) is only present in bulk solution I. $[Na^+]_\sigma$, $[D^-]_\sigma$, $[Cl^-]_\sigma$, and $[P^-]_\sigma$ represent the ionic concentrations of sodium, dye, chloride, and alginate, respectively, in the bulk solution I. $[Na^+]_\gamma$, $[D^-]_\gamma$, and $[Cl^-]_\gamma$ represent those, respectively, in bulk solution II in terms of mol/l. Also, $[Na^+]_i$, $[D^-]_i$, and $[D^-]_i$ represent those, respectively, in the internal solution of cellulose.

In this dyeing system, we distinguished between dye in phase σ , $[D^-]_\sigma$, and that in phase γ , $[D^-]_\gamma$, since the state of dye in the pores of cellulose ($[D^-]_\gamma$), where sodium alginate is not present, differs from that in phase σ where sodium alginate is present.

In the σ and γ phases, according to the Donnan membrane-equilibrium theory, the ionic concentration will be related as follows:

$$[Na^+]_\sigma^z [D^-]_\sigma = [Na^+]_\gamma^z [D^-]_\gamma \quad (1)$$

$$[Na^+]_\sigma [Cl^-]_\sigma = [Na^+]_\gamma [Cl^-]_\gamma \quad (2)$$

where z is the basicity of the dye anion.

For maintaining electrical neutrality in two phases,

$$\sigma \text{ phase: } [Na^+]_\sigma = Z[D^-]_\sigma + \alpha[P^-]_\sigma + [Cl^-]_\sigma \quad (3)$$

$$\gamma \text{ phase: } [Na^+]_\gamma = Z[D^-]_\gamma + [Cl^-]_\gamma \quad (4)$$

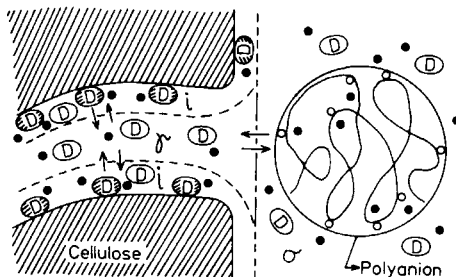


Fig. 5. Adsorption model for cellulose. D = dye anion; \bullet , sodium cation; \circ , carboxyl group on polymer chain Δ , chloride ion; polyion, P_n^- (P^- , alginate anion with pyranose unit mole).

where α represents the degree of ionization for sodium alginate (NaP) with pyranose unit mole ($\alpha = 0.5$, see Fig. 2). Thus, $\alpha[P^-]$ represents the concentration of alginate ion $[P^-]$ shown with pyranose unit mole in the bulk solution I.

Substituting the value of $[Cl^-]_\gamma$ from eq. (4) to eq. (2), one obtains

$$[Na^+]_\sigma [Cl^-]_\sigma = [Na^+]_\gamma \{ [Na^+]_\gamma - Z[D^-]_\gamma \} \quad (5)$$

Also, substituting the value of $[D^-]_\gamma$ from eq. (1) to (5), one obtains

$$[Na^+]_\sigma [D^-]_\sigma = [Na^+]_\gamma \left\{ [Na^+]_\gamma - Z \frac{[Na^+]_\sigma^z [D^-]_\sigma}{[Na^+]_\gamma^z} \right\} \quad (6)$$

Rearranging eq. (6), eq. (7) is obtained.

$$[Na^+]_\gamma^{z+1} - [Na^+]_\sigma [Cl^-]_\sigma [Na^+]_\sigma^{z-1} - Z [Na^+]_\sigma^z [D^-]_\sigma = 0 \quad (7)$$

From eq. (7), $[Na^+]_\gamma$ is obtained.

On the other hand, in the γ phase and i phase, according to Donnan's equilibrium theory, the ionic concentration will be as follows;

$$[Na^+]_\gamma^z [D^-]_\gamma = [Na^+]_i^z [D^-]_i \quad (8)$$

$$[Na^+]_\gamma [Cl^-]_\gamma = [Na^+]_i [Cl^-]_i \quad (9)$$

For maintaining electrical neutrality in two phases,

$$\gamma \text{ phase: } [Na^+]_\gamma = Z[D^-]_\gamma + [Cl^-]_\gamma \quad (10)$$

$$i \text{ phase: } [Na^+]_i = Z \frac{[D^-]_\phi}{V} + [Cl^-]_i \quad (11)$$

where V represents the volume (0.22 l/kg dry fiber¹) and $[D^-]_\phi$ is the concentration of dye ions adsorbed by cellulose in terms of mol/kg dry fiber.

Combining eqs. (2), (9) and (11), one obtains

$$[Na^+]_i = \frac{1}{V} ([D^-]_\phi) \left\{ \frac{Z}{2} + \left(\frac{Z^2}{4} + \frac{V^2 [Na^+]_\sigma [Cl^-]_\sigma}{[D^-]_\phi^z} \right)^{1/2} \right\} \quad (12)$$

From eqs. (1) and (8), one obtains

$$[D^-]_i = \frac{[Na^+]_\sigma^z [D^-]_\sigma}{[Na^+]_i^z} \quad (13)$$

where $[Na^+]_\phi = V[Na^+]_i$, $[Na^+]_\phi$ is the concentration of sodium ions adsorbed in the cellulose phase in terms of mol/kg dry fiber.

The following equation has been used to calculate direct-dye standard free energies of adsorption ($\Delta\mu^0$).

$$-\Delta\mu^0 = RT \ln [Na^+]_\phi^z [D^-]_\phi / V^{z+1} [Na^+]_\gamma^z [D^-]_\gamma \quad (14)$$

where R is the gas constant in appropriate units and T is the absolute temperature.

Table I shows the affinity values and equilibrium adsorptions of Chryso-phenine G on cotton in aqueous sodium alginate solutions containing the constant concentration of sodium chloride at 90°C, while Table II shows values for aqueous sodium chloride solutions containing the constant concentration of sodium alginate at 90°C. Affinity values of dye on cotton (Tables I and II) have almost constant values within the concentration changes of sodium alginate and sodium

TABLE I
Affinities and Equilibrium Adsorption of Chrysophenine G on Cotton in Aqueous Sodium Alginate (NaP) Solutions Containing the Constant Concentration of Sodium Chloride (1×10^{-2} mol/l.) at 90°C

Electrolyte		[D ⁻] _{0s} mol/l. ($\times 10^4$)	[Na ⁺] _{0s} mol/l. ($\times 10^2$)	[D ⁻] _{1s} mol/l. ($\times 10^5$)	[Na ⁺] _{1s} mol/l. ($\times 10^2$)	[D ⁻] _{2s} mol/l. ($\times 10^5$)	[Na ⁺] _{2s} mol/l. ($\times 10^2$)	[D ⁻] _{3s} mol/l. ($\times 10^5$)	[Na ⁺] _{3s} mol/l. ($\times 10^2$)	[D ⁻] _{4s} mol/kg ($\times 10^4$)	[Na ⁺] _{4s} mol/kg ($\times 10^3$)	$-\Delta\mu^0$, kcal/mol
NaCl mol/l. ($\times 10^2$)	NaP unit mol/l. ($\times 10^2$)											
1.00	0	1.00	1.02	1.00	1.02	1.00	1.02	4.98	1.45	8.06	3.19	3.11
1.00	2.00	1.00	2.02	19.7	1.44	9.04	2.13	9.04	2.13	12.78	4.68	3.00
1.00	4.00	1.00	3.00	29.3	1.77	12.61	2.70	12.61	2.70	17.04	5.93	2.98
1.00	10.00	1.00	6.02	57.7	2.51	21.93	4.07	21.93	4.07	28.06	8.96	2.94

TABLE II
Affinities and Equilibrium Adsorption of Chrysophenine G on Cotton in Aqueous Sodium Chloride Solutions Containing Constant Concentration of Sodium Alginate (NaP) (2×10^{-2} mol/l.) at 90°C

Electrolyte		[Na ⁺] _σ	[D ⁻] _σ	[Na ⁺] _γ	[D ⁻] _γ	[Na ⁺] _δ	[D ⁻] _δ	[Na ⁺] _ε	[D ⁻] _ε	[Na ⁺] _φ	-Δμ ⁰
NaP, unit mol/l. (×10 ²)	NaCl, mol/l. (×10 ²)	mol/l. (×10 ²)	mol/l. (×10 ⁴)	mol/l. (×10 ²)	mol/l. (×10 ⁵)	mol/l. (×10 ²)	mol/l. (×10 ⁵)	mol/l. (×10 ²)	mol/kg (×10 ⁴)	mol/kg (×10 ³)	kcal/mol
2.00	1.00	2.02	1.00	1.44	19.7	2.13	9.04	2.13	12.8	4.68	3.11
2.00	2.00	3.02	1.00	2.47	15.0	3.24	8.74	3.24	14.9	7.12	3.15
2.00	5.00	6.02	1.00	5.50	12.0	6.48	8.67	6.48	20.0	14.25	3.36

chloride used, respectively. A good agreement of affinity values observed (Table I) in the presence of and absence of sodium alginate shows the adaptability of our proposed theory with the model in this dyeing system (Fig. 5). The constant value of affinity observed in spite of concentration changes supports the adaptability of the proposed theory on the dyeing system for cellulose.^{1,2}

On the other hand, the dye concentration in the γ phase, $[D^-]_\gamma$, (Table I) apparently increases with successive additions of sodium alginate, whereas $[D^-]_\gamma$ in Table II does not increase with successive additions of sodium chloride, although the increase of adsorbed dye, $[D^-]_\phi$ on cotton with successive additions of electrolytes (Table I and II) is observed. The role of sodium alginate which can not enter into the pores of cellulose differs from that of the smaller sodium chloride which can enter into the pores.

The increase of $[D^-]_\gamma$ with successive additions of sodium alginate (Table I) infers that the dye has been concentrated into the pores of cellulose due to the presence of sodium alginate in bulk solution I, according to the Donnan membrane equilibrium. Thus, the dyeing behavior of cellulose by direct dye in aqueous sodium alginate solution functions similarly to a concentrated solution of dye in the absence of inorganic salt. These results (Table I and II) are consistent with the dye concentrations used in this article.

It might be difficult to consider the role of sodium alginate in hydrolysis during the course of dyeing. However, the results obtained from the dyeing of cotton by Chrysophenine G in aqueous solutions of sodium polystyrene sulfonate,¹³ which is not hydrolyzed during the course of dyeing, give the reproducibility with the experimental data described in this article.

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Received May 18, 1979

Accepted May 16, 1980