

## The Absorption of Direct Dyes by Crosslinked Cellulose. I. The Equilibrium of Dyeing\*

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### Synopsis

The effect of the degree of chemical crosslinking of cellulose with two bifunctional crosslinking agents (dimethylol ethylene urea (DMEU) and bis (hydroxyethyl) sulfur (BHES)), on the equilibrium absorption of the direct dyes Chlorazol Sky Blue FF (C.I. Direct Blue 1) and Chrysophenine G (C.I. Direct Yellow 12) has been reported. The results show the increasing reduction of equilibrium dye absorption with increasing crosslink density. However, the maximum loss of absorption is about less than half of the amount absorbed by uncrosslinked cellulose. The results have been interpreted by reference to the parameters affecting the free energy of dyeing and the relevant models (pore model and gel model) available for explaining the fine structure of swollen cellulose.

### INTRODUCTION

Since the late 1920's, cellulosic textiles have been treated industrially with bifunctional reactants derived from formaldehyde to impart dimensional stability, wrinkle recovery, and shape retention. As soon as these finishing treatments were introduced into practice, it was recognized that by the application of the crosslinking agents, by high-temperature cure, the fibers became virtually undyeable by direct and vat dyes. In accordance with the generally accepted concepts of the dyeing process, the practical lack of dyeability might be caused by any of three mechanisms: lack of affinity of the dye to the fiber, slow rate of diffusion of the dye in the fiber, or inaccessibility of the fiber to the dye. However, no systematic effort is reported in the literature to find out which of these mechanisms is responsible for the behavior of crosslinked cellulosic fiber. Our experiments reported here were designed to answer this question. We also hoped that the investigation will shed some light on the molecular architecture of the crosslinked cellulosic fibers.

The experimental approach consisted in the preparation and characterization of crosslinked cellulose samples of varied degree of crosslinking, and determi-

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nation of the rate and equilibrium of dyeing as a function of the degree of crosslinking. To ascertain that the equilibrium has been reached, it is necessary to follow the rate of absorption. Therefore, rate measurements experimentally precede the equilibrium determinations. However, the interpretation of the rate data in terms of diffusion rates requires the use of equilibrium values. For sake of convenience, we report in this paper the equilibrium values reached, and in a second paper the rate measurements.

Prior to this study, we investigated the dyeing behavior of crosslinked cellulose in the form of cotton fabric.<sup>1,2</sup> The results obtained will be published elsewhere. The irregularity of the shape of cotton fiber and the overlapping of diffusional boundary layers in the yarn make it difficult to express the results of diffusion experiments on fabrics in fundamental terms. To avoid this difficulty for the present study, cellophane film was selected as a model substrate in place of cellulosic fibers. It served frequently in this role in many of the classical investigations of the physical chemistry of dyeing.

Meaningful interpretation of the equilibrium values requires that the absorbent does not change during the experiments. With crosslinked cellulose, there is the possibility that the degree of crosslinking changes during the dyeing experiments, particularly if long dyeing times at high temperatures are involved. Prior to the dyeing experiments, we studied this question and found that by establishing the optimal pH values in the dye bath, the crosslinks can be preserved.

For calculation of the free energy of dyeing, the swelling of the films in the dye bath was determined.

## EXPERIMENTAL

### Crosslinking

The regenerated cellulose film, obtained from the du Pont Company, had the tradename Cellophane PD-215. To remove the plasticizer present, the film was soaked in running water for 24 hr, seeped in 0.05*N* HCl for 24 hr, and washed with distilled water until test with AgNO<sub>3</sub> showed the absence of chloride ions.

As representatives of crosslinking agents, we selected two reactants, namely, 1,3-bis(hydroxymethyl)-2-imidazolidinone, commonly called dimethylol-ethyleneurea (DMEU) obtained under the commercial name of Rhonite 1 (Rohm and Haas Co.), and bis(hydroxyethyl) sulfone (BHES) (J. P. Stevens and Co., Inc.). The catalysts used were ZnCl<sub>2</sub> for DMEU and KHCO<sub>3</sub> for BHES.

The crosslinking was carried out (analogous to the pad-dry-cure technique) by soaking the film in aqueous solutions of the reactants and catalysts, blotting, drying, and subjecting it to air of 150–160°C in an oven for 5 min. It is important to note that the crosslinking takes place under anhydrous conditions. Crosslinking in the swollen state (wet crosslinking) is known to leave the dyeability of cellulosic fibers practically unimpaired and is not the subject of the present investigation.

Cellophane film is rather brittle in dry state in the absence of the plasticizer. The brittleness was further increased by the crosslinking, which made the han-

dling of the dry film extremely difficult. Therefore, the film was always stored by immersing in distilled water during the experiments until weighing the sample to determine its size.

### DETERMINATION OF THE DEGREE OF CROSSLINKING

The degree of crosslinking was varied by variation of the concentration of the reactant in the bath while keeping the ratio catalyst/reactant constant. The determination of the degree of crosslinking was based on determination of the nitrogen content (of the DMEU-treated film) and sulfur content (of the BHES-treated film) retained after rinsing. From this value, the density of crosslinks or the average dimension of the mesh of the molecular network can be estimated on the basis of several assumptions. First, an assumption is to be made regarding the efficiency of the crosslink. The reactant can form a monofunctional substituent and it can polymerize with itself, and in both cases less than one crosslink would be formed by a retained reactant molecule. This

TABLE I  
Absorption Equilibrium of Chrysophenine G by Cellophane BHES Crosslinks.  
Parameters of the Isotherm Equation  $C_D = KC_0^{na}$

Film	Sulfur content, %	$M_{CH}^b$	$K$	$n$
Temperature 70°C				
S <sub>0</sub>	0		2.50	.59
S <sub>3</sub>	0.16	6,700	2.25	.585
S <sub>4</sub>	0.24	4,440	2.30	.595
S <sub>5</sub>	0.37	2,900	2.20	.590
S <sub>6</sub>	0.65	1,640	1.75	.545
S <sub>7</sub>	1.14	940	1.50	.570
Temperature 80°C				
S <sub>0</sub>	0		1.65	.55
S <sub>3</sub>	0.16	6,700	1.62	.565
S <sub>4</sub>	0.34	4,440	1.61	.56
S <sub>5</sub>	0.37	2,900	1.60	.55
S <sub>6</sub>	0.65	1,640	1.45	.55
S <sub>7</sub>	1.14	940	1.30	.555
Temperature 90°C				
S <sub>0</sub>	0		1.50	.62
S <sub>3</sub>	0.16	6,700	1.49	.63
S <sub>4</sub>	0.24	4,440	1.40	.62
S <sub>5</sub>	0.37	2,900	1.36	.61
S <sub>6</sub>	0.65	1,640	1.32	.64
S <sub>7</sub>	1.14	940	1.20	.64
Temperature 100°C				
S <sub>0</sub>	0		1.35	.80
S <sub>3</sub>	0.16	6,700	1.30	.81
S <sub>4</sub>	0.24	4,440	1.26	.71
S <sub>5</sub>	0.37	2,900	1.25	.73
S <sub>6</sub>	0.65	1,640	0.93	.70
S <sub>7</sub>	1.14	940	0.88	.70

<sup>a</sup>  $C_0$ : Dye concentration in bath (g/l.);  $C_D$ : dye in film (g/100 g).

<sup>b</sup>  $M_{CH}$ : Molecular weight of cellulose chain between crosslink junctions.

effect can be expressed by an efficiency factor of less than unity. Frick and co-workers<sup>3</sup> determined the efficiency factor of DMEU in cotton by combining formaldehyde and nitrogen analyses and in the same region as our concentrations found values between 0.4 and 0.8. We adopted a constant factor of 0.5. For BHES, we assumed that neither monofunctional substitution nor polymerization occurs in any appreciable extent and adopted an efficiency factor of 1.0.

The second assumption concerns the shape of the crosslinked network. We based our calculation on a ladder model, i.e., we consider neighboring cellulose chains linked to each other by the crosslinks in the form of rungs of a ladder. This ladder model replaces for sake of simplicity the three-dimensional network, which would be closer to reality.

The third assumption is that only the so-called amorphous portion of the cellulose is accessible to the reactant and crosslinked by it. In calculating the crosslink density, we assume that only 0.66 g cellulose per gram cellophane participates in the crosslinking reaction.

Tables I and II list the two series of crosslinked cellophane samples with their nitrogen or sulfur content. The last column lists the crosslink density expressed as molecular weight of the anhydroglucose units between the crosslink junctions of the accessible cellulose chains based on the three assumptions stated. It is

TABLE II  
Absorption Equilibrium of Chrysofenine G by Cellophane DMEU Crosslinks.  
Parameters of the Isotherm Equation  $C_D = KC_0^n$ <sup>a</sup>

Film	Nitrogen content, %	$M_{CH}$ <sup>b</sup>	$K$	$n$
Temperature 70°C				
X <sub>0</sub>	0		2.20	.51
X <sub>1</sub>	0.11	16,900	1.81	.48
X <sub>2</sub>	0.17	11,000	1.75	.50
X <sub>3</sub>	0.21	9,000	1.70	.51
X <sub>5</sub>	0.35	5,300	1.57	.50
Temperature 80°C				
X <sub>0</sub>	0		1.60	.49
X <sub>1</sub>	0.11	16,900	1.45	.48
X <sub>2</sub>	0.17	11,000	1.42	.48
X <sub>3</sub>	0.21	9,000	1.40	.495
X <sub>5</sub>	0.35	5,300	1.30	.49
Temperature 90°C				
X <sub>0</sub>	0		1.38	.51
X <sub>1</sub>	0.11	16,900	1.22	.505
X <sub>2</sub>	0.17	11,000	1.17	.50
X <sub>3</sub>	0.21	9,000	1.02	.48
X <sub>5</sub>	0.35	5,300	0.92	.48
Temperature 100°C				
X <sub>0</sub>	0		1.07	.63
X <sub>1</sub>	0.11	16,900	0.95	.62
X <sub>2</sub>	0.17	11,000	0.93	.63
X <sub>3</sub>	0.21	9,000	0.90	.63
X <sub>5</sub>	0.35	5,300	0.88	.63
X <sub>7</sub>	0.78	2,400	0.83	.63
X <sub>8</sub>	1.97	950	0.73	.62

<sup>a</sup>  $C_0$ : Dye concentration in bath (g/l.);  $C_D$ : dye in film (g/100 g).

<sup>b</sup>  $M_{CH}$ : Molecular weight of cellulose chain between crosslink junctions.

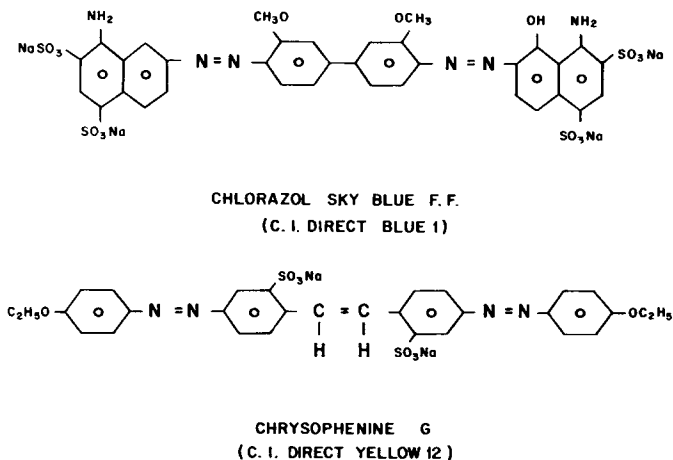


Fig. 1. Direct dyes used.

to be noted that only the highest degrees of crosslinking ( $X_8$  and  $S_7$ ) approach the reactant content usually found in commercially finished "wash-wear" cotton.

### STABILITY OF CROSSLINKS

Previous experiments have shown that unless the pH of the dyebath is adjusted to maintain maximum stability of the crosslinks, these are partially lost during the long exposure to the hot dyebath required to ensure the close approach to the absorption equilibrium of dyeing. Therefore, appropriate buffer solutions were used in the dyeing experiments. Cellophane crosslinked with BHES was found to retain at least 97% of its original sulfur content after exposure for 72 hr to a dyebath buffered at pH 5.2 containing 1 g/l. Chrysophenine G. The nitrogen content of DMEU-crosslinked cellophane after 48 hr in a dyebath of 100°C and pH 9.2 was 98% of its original value.

Indirect but convincing evidence of the stability of the crosslinks can be seen in the fact that a steady state of dye transfer was maintained at least for the first 2 hr through the crosslinked cellophane membranes, as reported in the third paper of this series.

### DYEING PROCEDURE

Two direct dyes were used in this study, namely, (1) Chrysophenine G, C.I. Direct Yellow 12, obtained from Allied Chemical Corporation, New York, under the trade name ERIO YELLOW Y conc. 250% B.C. 69075; (2) Chlorazol Sky Blue FF, C.I. Direct Blue 1, obtained in form of presscake from American Cyanamid Company, Bound Brook (Fig. 1). The two dyes were purified by the method of Robinson and Mills.<sup>4</sup> The elemental analyses showed both purified dyes to be electrolyte-free and associated with 1.5 and 9 moles of water of crystallization, respectively. Dye concentrations are expressed in terms of anhydrous dye content.

The apparatus used for dyeing is shown schematically in Figure 2. It consists of a three-necked, flat-bottomed, 500-ml flask connected to a reflux condenser,

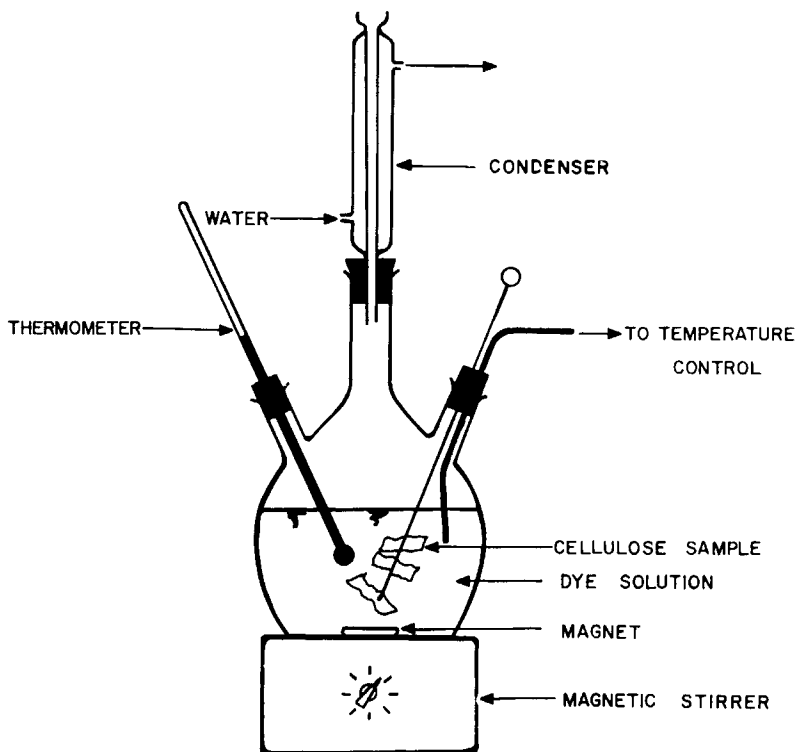


Fig. 2. The dyeing apparatus.

and resting on top of a magnetic stirrer, in an air thermostat box. In most cases, two flasks were placed side by side so that experiments could be performed at two dyebath concentrations at the same temperature simultaneously. A 33-mm Teflon-coated magnet in each flask and a magnetic stirrer at high speed provided rapid agitation. Temperature within  $\pm 0.3^\circ\text{C}$  was maintained by a Fisher temperature control. Samples of various crosslink densities and weighing about 15 mg each were strung on a stainless steel wire and inserted through the necks of the flasks. Samples crosslinked with DMEU were dyed in dyebaths buffered at pH 9.2 with 0.00125M Borax and 0.001M NaOH. For BHES-crosslinked samples, a dyebath buffered at pH 5.13 with 0.005N potassium hydrogen phthalate and 0.00226N NaOH was used. All dyebaths contained 5.0 g/l. analytical-grade NaCl. The samples to be dyed were exposed for the specified time (timed by an electrical seconds clock to the nearest 0.1 sec) in the stirred dyebath, removed, plunged into ice-cold water, blotted between filter paper, dried, and weighed. The dye content of the bath was reduced by the absorption at most by 0.3%, and therefore the dyebath could be considered from point of view of kinetics as infinite.

The dye in the samples of known weight was extracted with a 25% aqueous solution of pyridine. A complete extraction was accomplished at room temperature by leaving the samples in the pyridine solution for 24 hr, with the exception of the highly crosslinked samples which required a longer time and/or higher temperature. The concentration of the dye extract was determined using a Beckman DK-2A spectrophotometer with 25% aqueous pyridine as reference.

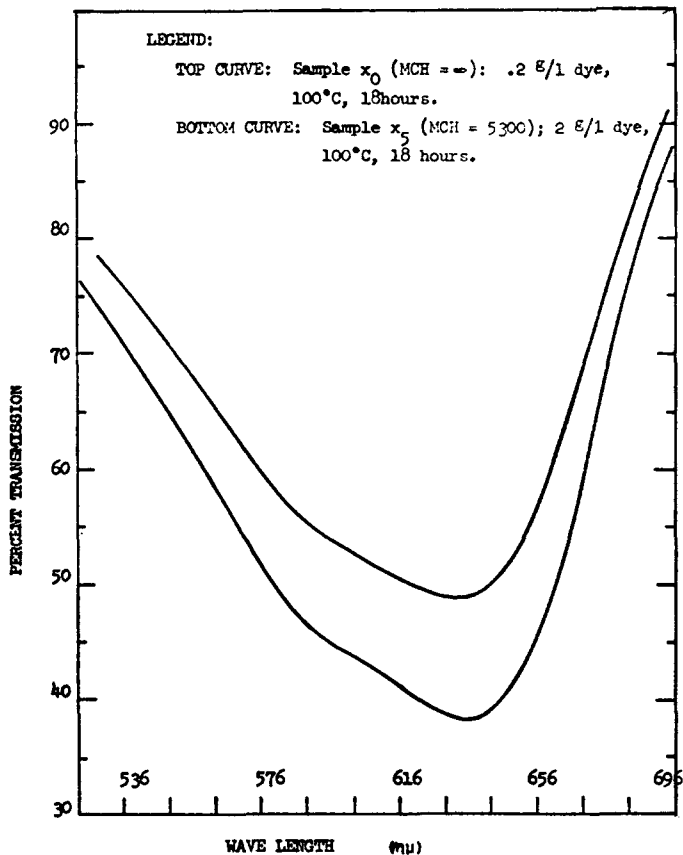


Fig. 3. Absorption spectra of Chlorazol Sky Blue FF extracts.

Chlorazol Sky Blue FF solutions were measured at a wavelength of 6300 Å, while Chrysophenine G extracts were measured at 4000 Å.

For Chrysophenine G, the procedure was complicated by the fact that the dye is phototropic. In their investigation, Willis et al.<sup>5</sup> recommended either illuminating the dye solutions just before measurements or storing the solutions in the dark for at least 18 hr before taking readings. The latter method was adopted. Measurements were made in the dark or under very weak illumination.

Rice<sup>2</sup> had found an interaction between Chlorazol Sky Blue FF and DMEU in highly crosslinked cotton which shifted the peak of the absorption equilibrium toward the red wavelength. No such interaction was noticed with cellophane, as shown in Figure 3. The standardization curves for both Chlorazol Sky Blue FF and Chrysophenine G showed compliance with Beer's law in the concentration range encountered in the study as shown for Chrysophenine G in Figure 4. The concentration of dye in the film was determined from this graph and expressed as gram dye per 100 gram cellulose.

The concentration of dye in the fiber at equilibrium with the dyebath was determined by continuing the exposure of the cellulose film to the bath until measurement of the dye content showed that no further change occurred. Even for the most highly crosslinked sample at the lowest temperature (70°C), not more than 15 hr was required to reach equilibrium.

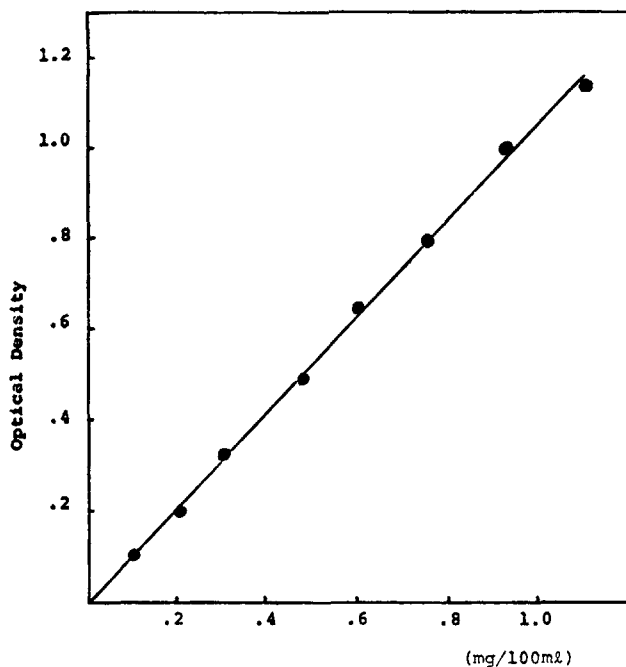


Fig. 4. Chrysophenine G concentration (mg/100 ml).

## RESULTS

The amount of dye absorbed by the cellulose film in equilibrium with the dyebath has been determined in a series of experiments in which the dyes, their concentration in the dyebath, the temperature, and the degree of crosslinking of the cellulose have been varied. Some of the results are graphically represented by Figures 5 and 6.

For all degrees of crosslinking, a Freundlich-type of isotherm is obtained, as demonstrated by the straight lines of the log-log plots (Figs. 7 and 8). Therefore, the results can be described by the two constants of the equation

$$C_D = KC_0^n \quad (1)$$

where  $C_D$  is the equilibrium amount of dye in the film (g dye/100 g film) and  $C_0$  is the concentration of the dye in the bath (g dye/l. bath). The values of  $K$  and  $n$  vary with the temperature and the degree of crosslinking, as shown in Tables III and IV which cover all the results including those represented by the graphs. In most cases, the exponent remains essentially constant at a given temperature, independent of the degree of crosslinking. The factor  $K$ , however, uniformly decreases at any given temperature with the degree of crosslinking, reflecting the reduction of the amount of dye absorbed. The maximum loss of absorption appears to be somewhat less than half of the amount absorbed by uncrosslinked cellulose.



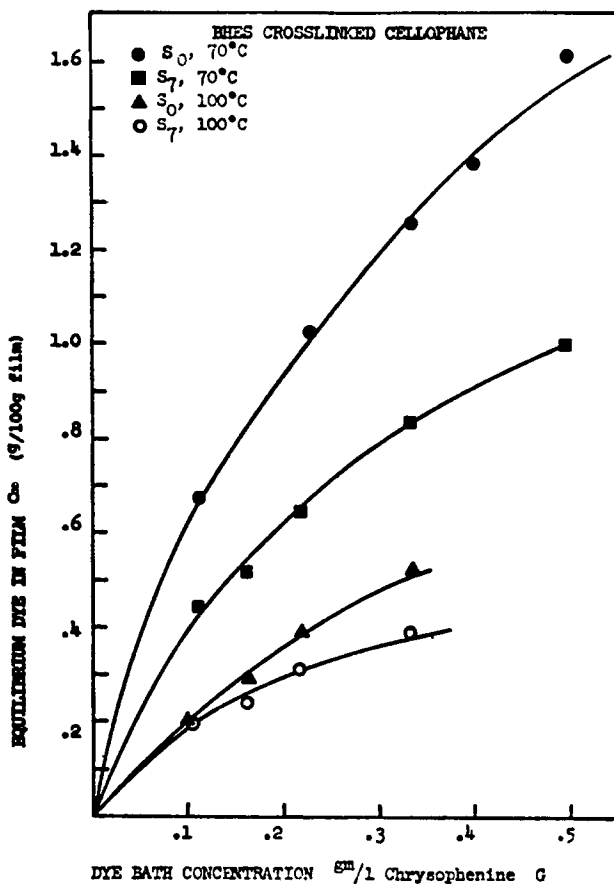


Fig. 5. Absorption isotherms.

## DISCUSSION

As expected, the results show the increasing reduction of dye absorption with increasing degree of crosslinking. However, even in the most densely crosslinked specimens, which approach the density of commercially crosslinked cotton fibers, the reduction observed is not large enough to account for the practical undyeability of the crosslinked fibers. It will be shown in the second paper of this series that the reduced rate of dyeing rather than the reduced equilibrium absorption is primarily responsible for the lack of dyeability.

The reduction of the equilibrium absorption by the crosslinking can be attributed to various changes in the interaction between the swollen cellulose and the dye molecules. First, we have to consider the chemical change, namely, the substitution of up to one hydroxyl group in every sixth anhydroxyranose unit by the crosslinker; secondly, the reduced accessibility of the tightened polymeric network; and thirdly, the reduced swelling volume. The role of these factors should be reflected in the thermodynamic functions of the dyeing process.

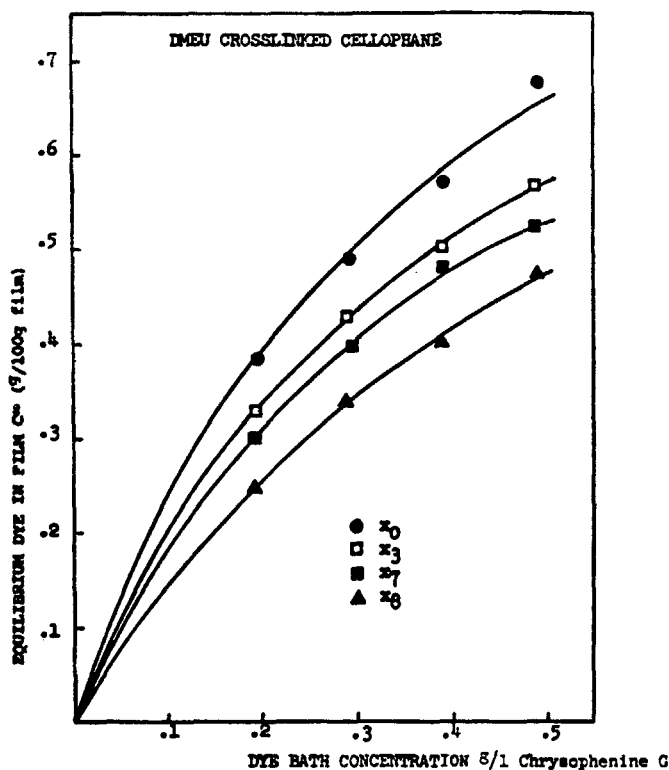


Fig. 6. Absorption isotherm, 100°C.

### ENTHALPY OF DYEING

The enthalpy of dyeing ( $\Delta H$ ) can be calculated according to Vickerstaff<sup>6</sup> on the basis of the van t'Hoff equation

$$\Delta H = R \frac{T_1 \times T_2}{T_1 - T_2} \ln \frac{c_1}{c_2} \quad (2)$$

where  $c_1$  and  $c_2$  are the dye concentrations of the bath (in place of activities) leading to identical values of the equilibrium absorption of the dye at the temperatures  $T_1$  and  $T_2$  (degrees Kelvin).

Column 3 of Table V shows that the application of the equation to our data yields values between 13 and 14 kcal/mole dye. Although they seem to decrease with increasing degree of crosslinking, within the bounds of the experimental error of  $\pm 1$  kcal/mole they should be considered constant. The only conclusion permitted is that the value of the enthalpy of dyeing is substantially unaffected by the crosslinking. The forces of attraction between the cellulose and the dye are apparently not much altered by the partial modification of the cellulose.

### SWELLING AND THE FREE ENERGY OF DYEING

The standard free energy or affinity of dyeing,  $G$ , is calculated, according to Vickerstaff,<sup>6</sup> from the equation

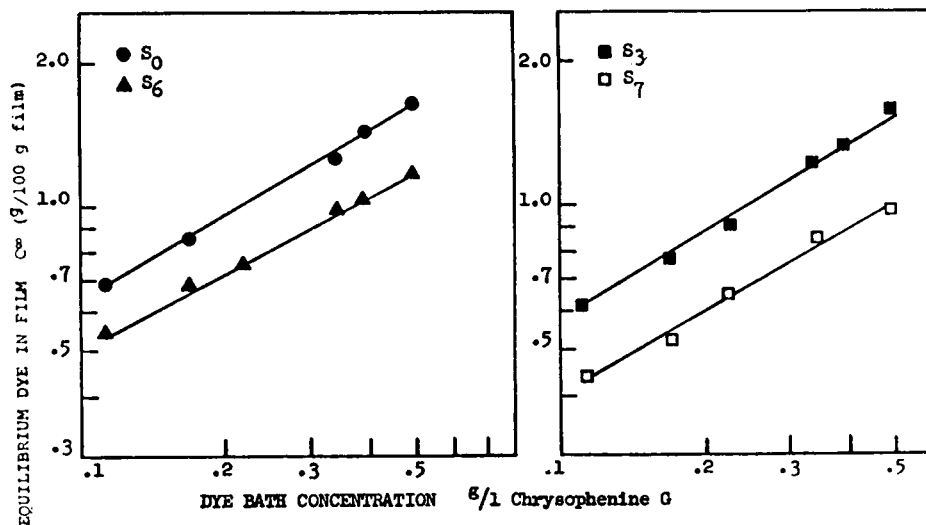


Fig. 7. Absorption isotherm, 70°C. BHES-crosslinked cellophane.

$$-G = (RT \ln D_F \times Na_F^z) - (z + 1) \ln V \quad (3)$$

where  $D_F$  and  $Na_F$  are the concentrations (in place of activities) of the dye and the sodium ion (assumed to be the only cation present) in the film (in moles per kg dry film), respectively; similarly,  $D_S$  and  $Na_S$  are their concentrations in the bath (moles per liter);  $z$  is the number of electric charges of the dye ion (2 for Chrysophenine G and 4 for Chlorazol Sky Blue FF); and  $V$  is the "internal volume" (liters per kg dry film) in which the dye ion and its compensating sodium ion are accumulated. The sodium ion concentration in the film is calculated on the basis of the Donnan equilibrium from the equation

$$Na_F = 0.5 D_F + z^2 D_F^2 + 4V^2 Na_S Cl_S^{0.5} \quad (4)$$

where  $Cl_S$  is the concentration of the chloride ions in the bath, assuming them to be the only anions present aside from the dye anion.

The meaning and calculation of  $V$  in the above equations have been the subject of much discussion in the scientific literature, but remain rather arbitrary. For our calculations, we assumed that  $V$  is equal to the volume of water absorbed by the cellophane film. This is theoretically the highest possible value, and it serves mainly for comparing the relative values of free energy of dyeing at various degrees of crosslinking. We assume further that the absorbed water has the density of 1 g/ml. The details of the swelling experiments will be published elsewhere, but it is noted that they were carried out at room temperature, whereas the absorption of the dye for which the free energy was calculated was determined at 100°C, another reason to consider the free energy values obtained only valid for the purpose of comparison. The values of  $V$  used are listed in column 5 of Table V.

The values of the free energy of dyeing so calculated are listed in the last column. They appear practically unaffected by the crosslinking or in some cases even appear to increase slightly as the amount of dye absorbed, listed in column 5, decreases. The role of the internal volume  $V$  in the free-energy equation allows

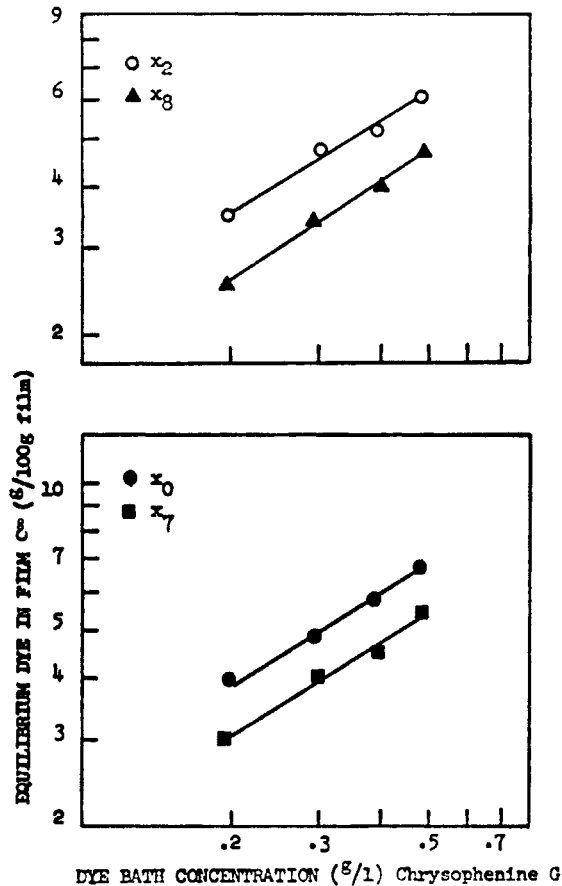


Fig. 8. Absorption isotherm, 100°C. DMEU-crosslinked cellophane.

this possibility. That the affinity remain unchanged could be explained in the simplest terms by the assumption that crosslinking makes a portion of the cellulose inaccessible to both water and dye. It could, however, also be explained by the assumption that while the accessibility of the cellulose remains unchanged, the volume of the absorbed dye ions and their gegenions becomes smaller as the network tightens. Probably the observed reduction of dye absorption by the crosslinked film results from both: partial blocking of cellulose chains and confinement of the remainder to smaller volume. Increased free-energy value, where beyond experimental error, indicates that the reduction of internal volume is less than assumed on the basis of the swelling values. We will return to these questions in the discussion of the rate of absorption in the following paper.

Reference should be made here, however, to the results of the investigation by Blouin, Martin, and Rowland<sup>7</sup> of chromatographic columns built from cotton particles. They found that crosslinking with formaldehyde by the pad-dry-cure method reduced the swelling, the internal volume, and the permeability limit of cotton. Their observations indicate that the fractional decrease of the internal volume is more pronounced than the fractional decrease of swelling. Porter and Schreiber<sup>8</sup> studied the effect of crosslinking on the porosity of cotton in the expanded state, which was preserved by solvent exchange after having been swollen

TABLE III  
Absorption Isotherms: Chrysophenine G BHES Crosslinks

Sample	McH	Temperature, °C	<i>k</i>	<i>n</i>
S <sub>0</sub>	∞	70	2.50	0.590
S <sub>3</sub>	6,700	70	2.25	0.585
S <sub>4</sub>	4,440	70	2.30	0.595
S <sub>5</sub>	2,900	70	2.20	0.588
S <sub>6</sub>	1,640	70	1.75	0.545
S <sub>7</sub>	940	70	1.50	0.574
S <sub>0</sub>	∞	80	1.65	0.550
S <sub>3</sub>	6,700	80	1.62	0.565
S <sub>4</sub>	4,440	80	1.61	0.560
S <sub>5</sub>	2,900	80	1.60	0.552
S <sub>6</sub>	1,640	80	1.45	0.550
S <sub>7</sub>	940	80	1.30	0.555
S <sub>0</sub>	∞	90	1.50	0.620
S <sub>3</sub>	6,700	90	1.50	0.630
S <sub>4</sub>	4,440	90	1.49	0.620
S <sub>5</sub>	2,900	90	1.36	0.610
S <sub>6</sub>	1,640	90	1.32	0.640
S <sub>7</sub>	940	90	1.20	0.640
S <sub>0</sub>	∞	100	1.35	0.800
S <sub>3</sub>	6,700	100	1.30	0.810
S <sub>4</sub>	4,440	100	1.26	0.710
S <sub>5</sub>	2,900	100	1.25	0.730
S <sub>6</sub>	1,640	100	0.93	0.700
S <sub>7</sub>	940	100	0.88	0.700

TABLE IV  
Absorption Isotherms: Chrysophenine G DMEU Crosslinks

Sample	McH	Temperature, °C	<i>k</i>	<i>n</i>
X <sub>0</sub>	∞	70	2.20	0.510
X <sub>1</sub>	16,900	70	1.81	0.480
X <sub>2</sub>	11,000	70	1.75	0.500
X <sub>3</sub>	9,000	70	1.70	0.510
X <sub>5</sub>	5,300	70	1.57	0.500
X <sub>0</sub>	∞	80	1.60	0.490
X <sub>1</sub>	16,900	80	1.45	0.480
X <sub>2</sub>	11,000	80	1.42	0.480
X <sub>3</sub>	9,000	80	1.40	0.495
X <sub>5</sub>	5,300	80	1.30	0.490
X <sub>0</sub>	∞	90	1.38	0.510
X <sub>1</sub>	16,900	90	1.22	0.505
X <sub>2</sub>	11,000	90	1.17	0.500
X <sub>3</sub>	9,000	90	1.02	0.480
X <sub>5</sub>	5,300	90	0.92	0.480
X <sub>0</sub>	∞	100	1.07	0.630
X <sub>1</sub>	16,900	100	0.95	0.620
X <sub>2</sub>	11,000	100	0.93	0.630
X <sub>3</sub>	9,000	100	0.90	0.627
X <sub>5</sub>	5,300	100	0.88	0.630
X <sub>7</sub>	2,400	100	0.83	0.630
X <sub>8</sub>	950	100	0.73	0.620

TABLE V  
Swelling and Free Energy of Dyeing<sup>a</sup>

Sample	McH	Wet weight/ dry weight	Water weight fractions	Absorbed water $V$ , l./kg dry film	Free energy of dyeing, kcal/mole
S <sub>0</sub>	∞	2.34	0.57	1.34	-2.63
S <sub>3</sub>	7,300	2.20	0.54	1.20	-2.61
S <sub>6</sub>	1,420	1.92	0.48	0.92	-2.62
S <sub>7</sub>	1,120	1.67	0.40	0.67	-2.78

<sup>a</sup> The free energy of dyeing was calculated at a Chrysophenine G dyebath concentration of 0.222 g/l. The specific volume of water at dyebath temperature is assumed to be 1.00 cm<sup>3</sup>/g.

by water. They found that the internal surface absorbing nitrogen after cross-linking with 1.6% formaldehyde was reduced to approximately one quarter that of uncrosslinked cotton. This would also indicate a stronger reduction of both the amount of cellulose chains accessible for interaction with the dye and the internal volume than is reflected in the reduction of the swelling. The concept of internal volume used in the equation for free energy assumes a uniform distribution of the ions in it. In reality, the gegenions, in accordance with the Debye-Huckel-Stern theory of double layer, have a strong tendency to accumulate in the proximity of the absorbed dye ions. Therefore, it is to be expected that the reduction of the swelling of the highly swollen cellophane film will have a less drastic effect on the real internal volume available for the gegenions than the reduction of the swelling of cotton has on its internal volume as indicated by its chromatographic behavior and nitrogen absorption.

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