

## Studies in Chemically Modified Celluloses. X. Affinities of Direct Dyes for Chemically Modified Celluloses

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### Synopsis

A series of chemically modified celluloses with different functional groups present in various extents were prepared by separately oxidizing cotton cellulose by potassium metaperiodate, potassium dichromate-sulfuric acid, potassium dichromate-oxalic acid and further modifying them by treatment with chlorous acid and sodium borohydride. These were dyed with two purified direct dyes to equilibrium at 95°C, and their thermodynamic affinities for these substrates were determined, assuming various extents of ionization of carboxyl groups present in them. It has been shown that the affinity decreases with increase in carboxyl value of the oxycelluloses if the carboxyl groups are assumed to be un-ionized and increases with increasing carboxyl value if they are considered to be fully ionized.

### INTRODUCTION

Adsorption of direct dyes by cellulosic fibers has been studied extensively for developing kinetic as well as thermodynamic interpretations for understanding the mechanism of dyeing of cellulose with these dyes.<sup>1,2</sup> Equilibrium uptake of Chrysophenine G and Chlorazol Sky Blue FF by chemically modified celluloses containing different amounts of aldehyde, keto, and carboxyl groups was studied by Daruwalla et al.<sup>3</sup> who found that the presence of carboxyl groups in cellulose (and oxycellulose) decreased the equilibrium uptake values for both these dyes.

Shenai and Veeramani<sup>4</sup> determined the affinity of vat dyes for chemically modified celluloses prepared by separately oxidizing cellulose with (1) potassium metaperiodate, (2) potassium dichromate-sulfuric acid and potassium dichromate-oxalic acid, and by treating the resulting oxycelluloses with chlorous acid or sodium borohydride to produce aldehyde and acidic groups to various extents. While calculating the affinity, the adsorptions of sodium hydroxide by the cellulosic material and of sodium ions by the carboxylate groups of the chemically modified celluloses were taken into account. They showed that the presence of aldehyde and carboxyl groups decreased the rate of dyeing as well as the affinity of the dyes. The affinity was found to increase after the treatment of the oxycellulose with sodium borohydride. They have also reported higher affinity values (for unmodified cellulose) which are higher than those reported in the

literature, where the adsorptions of sodium ions by the carboxylate group and of hydroxyl group by cellulose were not taken into account.

While studying the sorption of mixtures of direct dyes by cellulose, Johnson, et al.<sup>5</sup> selected cellulose sheet and hypobromite oxycellulose of varying carboxyl content (determined by the methylene blue absorption method<sup>6</sup>) and showed that the diffuse adsorption model accounted adequately for the adsorption of mixtures of direct dyes if no interaction occurred between the dyes in either phase and if allowance is made for ionized carboxyl groups in the cellulose. They calculated the affinities of these dyes individually as well as in binary mixtures, assuming 0% and 100% ionization of carboxyl groups, considerably higher affinity values being obtained in the latter case. The affinity decreased with increasing carboxyl content of the oxycellulose if the carboxyl groups were supposed to be un-ionized. On the other hand, when 100% ionization of carboxyl groups was assumed, the calculated affinity values increased with increasing carboxyl content. They also used an alternative approach to allow for the effect of ionized carboxyl groups for single dyes, used by Daruwalla et al.,<sup>3</sup> for calculating the concentration of ionized carboxyl groups necessary to give the same affinity value for each oxycellulose. In effect, they assumed the validity of the diffusion adsorption model and used the isotherms as a method of measuring the degree of ionization. From these data, Johnson et al.<sup>5</sup> calculated the interpolated concentration of ionized carboxyl groups corresponding to hypobromite oxycelluloses and then determined the affinity values.

## EXPERIMENTAL

### Standard Cellulose

Carefully purified<sup>7</sup> 20 s single yarn made from Indian cotton was used as standard cellulose. It had the following properties: copper number,<sup>8,9</sup> 0.04; iodometric carboxyl value,<sup>10</sup> 0.74 mEq COOH/100 g bone-dry cellulose.

### Preparation of Oxycelluloses

**Periodate Oxycelluloses.** These were prepared by steeping standard cellulose in a solution of 0.01*M* potassium periodate at 30°C for 4 and 24 hr, keeping a liquor ratio of 50:1.

**Potassium Dichromate-Sulfuric Acid Oxycelluloses.** Standard cellulose was oxidized with 0.1*N* potassium dichromate in the presence of 0.2*N* sulfuric acid at 30°C for 2 and 24 hr.

**Potassium Dichromate-Oxalic Acid Oxycelluloses.** Standard cellulose (30 g) was treated with 750 ml 2*N* oxalic acid at 30°C, followed by adding 10 ml or 50 ml of 2*N* potassium dichromate, finally diluting to 1500 ml with distilled water and keeping at 30°C for 4 hr.

**Treatment of Oxycelluloses with Sodium Borohydride.**<sup>11</sup> The different oxycelluloses were treated with unbuffered sodium borohydride solutions (0.1*M*) at 30°C for 24 hr, keeping a liquor ratio of 50:1.

**Treatment of Oxycelluloses with Chlorous Acid.**<sup>12</sup> The oxycelluloses samples were treated with 0.2*N* sodium chlorite and 1*M* acetic acid at 30°C for 72 hr, keeping a liquor ratio of 50:1.

After all the treatments described above were completed, the samples were washed with distilled water in each case till free from the impurities and dried at 30°C before analyzing.

### **Analysis of Chemically Modified Celluloses**

The copper number<sup>8,9</sup> and iodometric carboxyl value<sup>10</sup> of the chemically modified celluloses were determined by standard methods.

### **Direct Dyes**

Two direct dyes—Chrysophenine G and Chlorazol Sky Blue FF—were selected for the study and were purified by the method of Robinson and Mills.<sup>13</sup> This involved the preparation of a fairly concentrated solution of the dye in distilled water, addition of pure crystals of sodium acetate to salt out the dye, and filtration. The filtered dye was again dissolved in distilled water and salted out by sodium acetate. The sequence was repeated five times in all. The final, filtered dye, containing sodium acetate, was extracted with absolute alcohol in a Soxhlet extractor to remove sodium acetate. The dye was filtered and then crystallized from a 50/50 ethanol/water mixture. The purified dyes were stored in a desiccator over phosphorous pentoxide.

### **Affinity of Direct Dyes for Cellulose and Chemically Modified Celluloses**

The affinity values of the two direct dyes for cellulose and chemically modified cellulose were calculated from equilibrium dyeing data. The initial concentration of the dye in the dyebath was varied in the range of 100–250 mg/l., and the dyeing was carried out in the presence of sodium chloride (5 g/l.) at  $95^{\circ} \pm 1^{\circ}\text{C}$ , keeping a liquor ratio of 50:1.

Preliminary experiments on the dyeing of cotton fibers with the two dyes at  $95^{\circ} \pm 1^{\circ}\text{C}$  for 0–8 hr had shown that equilibrium dyeing was reached in 6 hr. Further dyeing experiments were carried out for 6 hr. At the end of the dyeing, a portion of the dye solution was suitably diluted and estimated colorimetrically using an Amil Hilger Biochem absorptiometer. The exhaustion of the dyebath and hence the dye uptake (by the fiber) was calculated.

## **RESULTS AND DISCUSSION**

### **Oxidation of Cellulose**

The reducing action of sodium borohydride on aldehyde, keto, and lactone groups present in cellulose and the oxidizing action of chlorous acid on aldehyde and hemiacetal groups can be used to further modify various oxycelluloses to prepare different functional groups in certain positions of anhydroglucose units of cellulose macromolecules.

In the present investigation, standard cellulose was oxidized with three oxidizing agents at two oxidation levels (high and low). The properties of these

TABLE I  
Properties of Chemically Modified Celluloses

Sample no.	Duration of oxidation, hr	Oxygen consumption, milliatoms/100 g cellulose	Copper number				Carboxyl value, meq/100 g		
			Oxycellulose	Chlorous acid-treated oxycellulose	Borohydride-treated oxycellulose	Oxycellulose	Chlorous acid-treated oxycellulose	Borohydride-treated oxycellulose	
1	4	9.3	4.42	0.31	0.11	1.80	10.86	0.45	
2	24	24.8	10.00	0.60	0.12	2.25	30.89	0.67	
3	2	7.7	Potassium Dichromate-Sulfuric Acid Oxycellulose	2.65	0.65	0.05	1.07	1.96	0.54
4	24	34.0	Potassium Dichromate-Oxalic Acid Oxycellulose	17.8	2.36	0.82	5.25	15.03	3.86
5	4 <sup>a</sup>	—	Potassium Metaperiodate Oxycellulose	2.60	0.27	0.05	1.38	6.80	0.35
6	4 <sup>b</sup>	—	Potassium Metaperiodate Oxycellulose	9.82	0.98	0.82	6.53	23.07	1.84

<sup>a</sup> With 10 ml 2N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

<sup>b</sup> With 50 ml 2N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

oxycelluloses and further modified oxycelluloses were determined, and the results are given in Table I.

When reducing types of oxycellulose are treated with chlorous acid, the reducing groups (aldehydes) are converted to carboxyl groups. It is seen from Table I that chlorous acid oxidizes most of the reducing groups (assessed in terms of copper number), producing a substantial amount of carboxyl groups. The oxidation takes place to a greater extent in the case of periodate oxycellulose than in other cases.

Sodium borohydride treatment is found to remove the reducing groups almost completely (96–98% decrease in copper number is found after the borohydride treatment). This treatment also brings about a substantial decrease in the iodometric carboxyl value of the different oxycelluloses. The decrease may be due to the presence of enediol and/or lactones in the oxycellulose, and the residual iodometric carboxyl value after the borohydride treatment may be taken as free carboxyl groups present in the oxycellulose.<sup>14</sup>

The different chemically modified celluloses selected for the study on the affinity of direct dyes for these fiber substances were as follows: (1) some were of predominantly reducing type (periodate oxycelluloses and potassium dichromate–sulfuric acid oxycelluloses); (2) some were of predominantly acidic type with fairly low reducing properties (chlorous acid-treated oxycelluloses); and (3) the rest were of fairly low acidic type with practically no reducing properties (borohydride-treated oxycelluloses).

### Affinity of Direct Dyes

In calculating the affinity of direct dyes for cellulose and chemically modified celluloses, the same theoretical treatment was followed as that used by Shenai and Veeramani<sup>4</sup> for calculating the affinity of vat dyes for the same substrates, except that in the present system, sodium hydroxide and sodium hydrosulfite are not present. All the concentrations of different ions in the fiber are expressed in terms of g. ion/l. of internal volume, taking a value of 0.3 l./kg for this volume.

The affinity ( $-\Delta\mu^0_D$ ) was calculated using the equations

$$-\Delta\mu^0_D = RT \ln \frac{[D]_f [Na]_f^z}{[D]_s [Na]_s^z} \quad (1)$$

$$[Na]_f = \left[ [D]_f + \frac{[ACOO]_f}{z} \right] \left[ \frac{z}{2} + \left\{ \frac{z^2}{4} + \frac{[Na]_s [Cl]_s}{\left( [D]_f + \frac{[ACOO]_f}{z} \right)^2} \right\}^{1/2} \right] \quad (2)$$

where  $[D]_f$  and  $[D]_s$  are the concentrations of the dye in the fiber and the solution at equilibrium,  $[Na]_f$  and  $[Na]_s$  are the sodium ion concentrations in the fiber and the solution,  $[Cl]_s$  is the chloride ion concentration in the solution,  $[ACOO]_f$  is the carboxyl value (mEq/l. of internal volume of fiber),  $z$  is the anionic change in the dye anion,  $R$  is the gas constant, and  $T$  is the absolute temperature.

The affinity values were calculated from the adsorption isotherms obtained at equilibrium. The results for the different oxycelluloses at higher level of oxidation are given in Table II.

TABLE II  
Affinity of Chrysophenine G for Different Oxycelluloses

Starting concentration of the dye, mg/l.	$[D]_f$ , (moles/l.) $\times 10^4$	$[Na]_f$ , (g ions/l.) $\times 10^4$		$[D]_s$ , (g ions/l.) $\times 10^5$		Affinity, cal/mole		
		0% <sup>b</sup>	100% <sup>b</sup>	Interpolated <sup>b</sup>	Interpolated <sup>b</sup>	0% <sup>b</sup>	100% <sup>b</sup>	Interpolated <sup>b</sup>
Periodate Oxycellulose (HOL) <sup>a</sup>								
100	29.41	884.9	1350.3	1280.1	129.4	-2323	-2939	-2861
150	41.97	898.2	1368.1	1296.9	195.4	-2304	-2916	-2839
200	54.90	911.9	1386.9	1315.6	261.2	-2310	-2920	-2843
250	70.60	921.9	1409.4	1337.5	325.1	-2349	-2967	-2891
					Mean	-2321	-2936	-2858
$K_2Cr_2O_7-H_2SO_4$ Oxycellulose (HOL)								
100	26.08	881.5	2142.8	1502.4	130.8	-2223	-3515	-2998
150	37.27	893.4	2162.1	1518.9	198.2	-2199	-3485	-2972
200	50.00	906.0	2183.9	1538.6	264.1	-2224	-3505	-2997
250	64.50	922.4	2209.7	1560.4	328.9	-2276	-3548	-3041
					Mean	-2230	-3513	-3123
$K_2Cr_2O_7$ -Oxalic Acid Oxycellulose (HOL)								
100	25.00	880.5	2517.3	1540.9	132.06	-2182	-3712	-2998
150	34.31	890.0	2533.8	1555.3	200.0	-2127	-3650	-2939
200	44.90	901.1	2553.2	1571.2	267.2	-2130	-3646	-2939
250	56.07	912.8	2572.7	1588.8	334.0	-2148	-3656	-2955
					Mean	-2147	-3666	-2958

<sup>a</sup> HOL = High oxidation level.

<sup>b</sup> Degree of ionization.

TABLE III

Slopes of Plots of Log of Ionic Product of the Dye on the Fiber Against that of Ionic Product of the Dye in the Solution for Different Dyes and for Different Degrees of Ionization of Carboxyl Groups

Substrate	Slope					
	Chrysophenine G			Chlorazol Sky Blue FF		
	0% Ionization	100% Ionization	Interpolated	0% Ionization	100% Ionization	Interpolated
Standard cellulose	0.99	0.97	0.98	1.0	0.97	1.0
KIO <sub>4</sub> oxycellulose I	1.00	0.97	1.0	0.97	0.96	0.94
KIO <sub>4</sub> oxycellulose II	1.00	0.95	1.0	1.01	0.95	0.96
NaBH <sub>4</sub> -treated oxycellulose I	1.00	1.02	1.04	0.97	0.94	0.93
NaBH <sub>4</sub> -treated oxycellulose II	1.03	1.04	1.01	0.99	0.94	0.96
Chlorous acid-treated oxycellulose I	0.90	0.90	0.97	1.02	0.90	0.94
Chlorous acid-treated oxycellulose II	0.90	0.89	—	0.94	0.89	—
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + (COOH) <sub>2</sub> oxycellulose I	0.95	0.94	0.96	1.02	0.95	0.97
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + (COOH) <sub>2</sub> oxycellulose II	1.04	0.92	1.0	1.01	0.91	0.95
NaBH <sub>4</sub> -treated oxycellulose I	1.04	1.02	1.03	0.97	0.96	0.93
NaBH <sub>4</sub> -treated oxycellulose II	1.0	1.0	0.96	1.03	0.95	0.94
Chlorous acid-treated oxycellulose I	1.04	1.0	1.0	1.02	0.91	0.93
Chlorous acid-treated oxycellulose II	0.90	0.94	0.94	1.03	0.97	0.98
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> SO <sub>4</sub> oxycellulose I	0.95	0.96	0.92	1.02	0.97	0.96
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> SO <sub>4</sub> oxycellulose II	1.02	1.00	0.94	1.00	0.90	0.98
NaBH <sub>4</sub> -treated oxycellulose I	0.98	0.97	1.02	1.00	1.01	0.92
NaBH <sub>4</sub> -treated oxycellulose II	1.00	1.00	0.98	0.95	0.90	0.91
Chlorous acid-treated oxycellulose I	1.04	0.90	0.92	1.01	0.95	0.96
Chlorous acid-treated oxycellulose II	0.94	0.90	0.92	1.03	0.94	1.00

In order to see whether the present dyeing system behaves in accordance with the theory described earlier,<sup>4</sup>  $\log [Na]_f^z[D]_f$  was plotted against  $\log [Na]_s^z[D]_s$  for all the chemically modified celluloses studied in the present investigation, and the slopes of the straight lines obtained were determined. The slopes are expected to be 1.0 if the theory described earlier is applicable to the present system. The results are given in Table III.

While calculating  $[Na]_f$ , three cases were considered: (1) where the carboxyl groups of chemically modified celluloses are not ionized, (2) where the carboxyl groups are completely ionized, and (3) where carboxyl values are partially ionized (interpolated values).

The affinity values of the direct dyes for standard cellulose and the different chemically modified celluloses are given in Table IV. Copper number and iodometric carboxyl values of the samples are also given in the table. A value of  $-5820 \pm 70$  cal/mole has been reported<sup>15</sup> for the affinity of Chlorazol Sky Blue FF for cotton at 90°C where the ionization of the carboxyl groups present in cotton was not considered. In the present investigation, also this has been found to be  $-5866 \pm 35$  cal/mole (at 95°C) for 0% ionization of carboxyl groups (Table IV).

It is seen that for all the oxycelluloses studied, the affinity of both the dyes decreases with increasing degree of oxidation, if all the carboxyl groups are assumed to be un-ionized. The affinity values decreased further on treatment with





$K_2Cr_2O_7 + (COOH)_2$ oxycellulose I	2.60	1.38	1.34	1.28	-2713 ± 24	-3095 ± 26	-3082 ± 22	-4931 ± 37	-5630 ± 32	-5582 ± 31
$K_2Cr_2O_7 + (COOH)_2$ oxycellulose II	9.82	6.53	3.05	3.28	-2147 ± 35	-3666 ± 46	-2958 ± 40	-4209 ± 53	-6953 ± 57	-5807 ± 49
$NaBH_4$ -treated oxycellulose I	0.05	0.35	0.35	0.35	-3601 ± 31	-3687 ± 16	-3687 ± 16	-5612 ± 50	-5808 ± 45	-5808 ± 45
$NaBH_4$ -treated oxycellulose II	0.07	1.84	1.70	1.68	-2595 ± 23	-3097 ± 13	-3063 ± 21	-4905 ± 45	-5821 ± 48	-5745 ± 47
Chlorous acid-treated oxycellulose I	0.27	6.80	3.10	3.35	-2127 ± 44	-3692 ± 55	-2950 ± 48	-4170 ± 57	-7005 ± 53	-5802 ± 44
Chlorous acid-treated oxycellulose II	0.98	23.7	4.68	4.81	-1243 ± 24	-4527 ± 30	-2476 ± 30	-3022 ± 18	-9267 ± 53	-5352 ± 28
$K_2Cr_2O_7 + H_2SO_4$ oxycellulose I	2.65	1.07	1.03	1.03	-2838 ± 36	-3135 ± 23	-3123 ± 34	-4955 ± 24	-5504 ± 16	-5480 ± 15
$K_2Cr_2O_7 + H_2SO_4$ oxycellulose II	17.80	5.25	2.89	3.03	-2230 ± 46	-3513 ± 35	-3002 ± 39	-4279 ± 54	-6598 ± 50	-5764 ± 46
$NaBH_4$ -treated oxycellulose I	0.05	0.54	0.54	0.54	-3229 ± 37	-3379 ± 38	-3378 ± 44	-5350 ± 24	-5607 ± 50	-5607 ± 50
$NaBH_4$ -treated oxycellulose II	0.82	3.86	2.56	2.63	-2560 ± 33	-3548 ± 30	-3242 ± 35	-4660 ± 38	-6470 ± 58	-5935 ± 63
Chlorous acid-treated oxycellulose I	0.65	1.96	1.81	1.75	-2408 ± 17	-2944 ± 18	-2906 ± 18	-4478 ± 31	-5472 ± 33	-5372 ± 32
Chlorous acid-treated oxycellulose II	2.36	15.03	4.17	4.44	-1476 ± 41	-4070 ± 47	-2550 ± 42	-8494 ± 63	-8371 ± 57	-5633 ± 12

TABLE V  
Affinity of Congo Red W S and C.I. Direct Brown 86 for Standard Cellulose and Hypobromite Oxycelluloses<sup>5</sup>

Sample	Carboxyl content, mmoles/100 g	Affinity, cal/mole					
		Congo Red W S			C.I. Direct Brown 86		
		0% Ionization	100% Ionization	Interpolated	0% Ionization	100% Ionization	Interpolated
Cellulose	0.60	-6850	-7739	—	-3948	-4818	—
Hypobromite oxycellulose A	6.63	-5046	-8925	-6872	-2745	-5250	-4150
Hypobromite oxycellulose B	17.51	-3866	-9676	-6748	-2441	-5629	-4114

chlorous acid treatment. When the oxycelluloses were treated with sodium borohydride solutions, the affinity values increased, though not to those for standard cellulose.

In the case of the assumption of complete ionization of carboxyl groups, the affinity values apparently increased with the carboxyl content. Similar behavior has been reported by Johnson et al.<sup>5</sup> in the case of hypobromite oxycelluloses. Some of their values are given in Table V.

It is seen that the affinity values fell with increasing carboxyl content if the carboxyl groups are assumed to be un-ionized and rose with increasing carboxyl content if assumed to be fully ionized. They suggested that the true state of affairs may be that the carboxyl groups may be partly ionized. They further suggested that the ionization of the carboxyl groups may be influenced by the adsorbed dye.

The dye anions are assumed to be adsorbed by the fiber. When the fiber contains carboxyl groups, some of which are in the ionized form, the negative charge on the carboxylate ion is likely to repel the the anion, and as a result, the amount of the dye adsorbed ( $[D]_f$ ) at equilibrium decreases. Further, some of the primary and secondary hydroxy groups, which are supposed to be the sites at which the dye anion is held by hydrogen bonds, are oxidized, the available sites are also reduced in number, and hence  $[D]_f$  is further decreased. The number of carboxyl groups interfering with the equilibrium dye uptake (i.e., the number of ionized carboxyl groups) may be less than the total number of carboxyl groups determined by the iodometric method, which estimates lactones, in addition to free carboxyl groups present in the cellulose. Under the conditions of dyeing direct dyes, these lactones are unlikely to be cleaved and hence do not become ionized. This may be the reason why all the iodometric carboxyl value does not interfere with the equilibrium dye uptake and only the ionized carboxyl value does. Thus, the affinity values of the dyes for the various chemically modified celluloses calculated from the interpolated carboxyl value may be taken as the true affinity values of the dyes for these fiber substances.

Work on the effect of lactonization on the equilibrium dye uptake in the dyeing of direct dyes on chemically modified celluloses is under progress and will be reported later.

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