Chemically Modified Celluloses. XII. Affinities of Azoic Coupling Components for Chemically Modified Celluloses

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Synopsis

Three azoic coupling components were purified and applied at different concentrations on standard cellulose and a series of chemically modified celluloses, involving oxidation with potassium periodate and potassium dichromate, as well as further borohydride reduction or chlorous acid oxidation of the oxycelluloses. Thermodynamic affinities of the azoic coupling components for all the chemically modified celluloses were determined from the adsorption data. As shown in the earlier studies on the affinity of vat and direct dyes for chemically modified celluloses, the affinity of the azoic coupling components also decreased with increasing degree of oxidation and increased after the oxycelluloses were reduced with sodium borohydride, though not to the extent of that for standard cellulose.

INTRODUCTION

Dyeing of cellulosic fibers with ionic dyes involves diffusion of the dye through the dye solution to the fiber surface, adsorption of the dye on the fiber surface, and diffusion of the dye from the fiber surface into the interior of the fiber. In this system the mechanism of dye adsorption is based on an electrochemical approach to the equilibrium distribution of all the ions present in the system between the fiber and the dyebath under a given set of conditions. An electrolyte is known to affect the dyeing behavior. Donnan equilibrium has been extensively used[1-3] in evolving a dyeing theory, the main postulates of which may be summarized as follows:

1. Donnan equilibrium exists between the ions in the internal cellulose phase and the ions in the bulk external solution phase.

2. Electrical neutrality is maintained in the internal cellulose phase and the bulk external solution phase.

3. The adsorption of the dye on the fiber is directly proportional to the concentration of the free dye ions in the internal solution phase.

4. Since the activities of the dye ions are not known, the activity coefficients of all the ions involved in the dyeing equilibrium are considered to be equal to unity.

5. The volume used for the internal cellulose phase, the volume term V, is constant for a given fiber (a value of 0.22 l./kg of dry fiber has been extensively used for cotton).

In applying thermodynamics to the dyeing of cellulosic fiber with anionic dyes, the fiber is considered as a homogeneous phase of a certain volume V in which the dye is evenly distributed. The affinities have been determined by applying these concepts in the cases of direct dyes,[4,5] vat dyes,[6] azoic coupling compo-

nents,[7] etc. In the earlier work,[4-7] the affinities were determined without taking into consideration the adsorption of sodium ions on the carboxyl and hydroxyl groups of cellulose. These have been taken into consideration in the cases of affinity of reactive dyes[8] for cellulose, of vat[9] and direct[10] dyes for cellulose, and a series of chemically modified celluloses. Affinities have been shown to decrease with increasing degree of oxidation. When these oxycelluloses were reduced with sodium borohydride, the affinities increased, though not to the same extent as in the case of unoxidized cellulose. This study has been extended to the determination of the affinities of three azoic coupling components for standard cellulose and a series of chemically modified celluloses, and the results are given in the present communication.

EXPERIMENTAL

Standard Cellulose. Standard cellulose was prepared by carefully purifying 20s single yarn made from Indian cotton. It had the following properties: copper number,[11,12] 0.05; iodometric carboxyl value,[13] 0.78 mEq COOH/100 g bone-dry cellulose.

Periodate Oxycelluloses. Oxidation of standard solution was carried out using $0.01M$ 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 treated with $0.1N$ potassium dichromate and $0.2N$ sulfuric acid at 30°C for 2 and 24 hr, keeping a liquor ratio of 50:1.

Potassium Dichromate–Oxalic Acid Oxycelluloses. These were prepared by treating 60 g standard cellulose with 1500 ml $2N$ oxalic acid solution, followed by addition of 20 ml and 100 ml of $1N$ potassium dichromate solution (finally diluting to 3000 ml) and keeping at 30°C for 4 hr.

Sodium Borohydride Treatment of Oxycelluloses. The differently prepared oxycellulose were treated with unbuffered sodium borohydride solutions ($0.01\ M$) at 30°C for 24 hr, keeping a liquor ratio of 50:1.

Chlorous Acid Treatment[15] of Oxycelluloses. The various oxycellulose samples were treated with $0.2N$ sodium chlorite in the presence of $1M$ acetic acid at 30°C for 72 hr, keeping a liquor ratio of 50:1.

After the above treatments were completed, the various modified cellulosic samples were washed with distilled water till free from the impurities and were dried at 30°C before analyzing.

Analysis of Chemically Modified Celluloses. The copper number[11,12] and iodometric carboxyl value[13] of the chemically modified celluloses were determined by standard methods.

Azoic Coupling Components. Amarthol AS, Amarthol AS-D, and Amarthol AS-TR (CI Azoic Coupling Components 2, 18, and 8, respectively) were selected for the study. These were purified by the method of Spiegler,[16] involving repeated treatment of the commercial azoic coupling components with boiling water, followed by filtering, treatment with 2% aqueous sodium carbonate solution (to dissolve and remove the uncondensed β-oxynaphthoic acid), dissolving in 40% aqueous sodium hydroxide, filtering, acidifying the filtrate to get the free azoic coupling component, and finally crystallizing successively from ethyl alcohol. The purity was ascertained by the melting points.

Affinity of Azoic Coupling Components for Cellulose and Chemically Modified Celluloses. The affinity values of the three azoic coupling components for standard cellulose and the various chemically modified cellulose were calculated from the equilibrium dyeing data. The initial concentration of the azoic coupling components was varied in the range 1.5–7.5 g/l., and the dyeing was carried out for 30 min in the presence of sodium chloride (50 g/l.) at $30 \pm 1°C$ at a constant alkali-to-azoic coupling component mole ratio of 4:1. The liquor ratio was kept at 40:1. Sodium chloride was not added to the dyebath containing Amarthol AS-TR, since it precipitated in the dyebath in the presence of 50 g/l. sodium chloride.

At the end of the dyeing, the azoic coupling component present in the dyebath was estimated by the volumetric method of Daruwalla and Desai.[17] The amount taken up by the fiber was then calculated from the decrease in the concentration. The method of estimation of azoic coupling component involved separate titrations in aqueous medium with phenolphthalein indicator and in 95% aqueous ethanol medium using Alkali Blue 6B indicator against standard ($0.05N$) hydrochloric acid solution. The former neutralized the total alkali and the latter free alkali, the difference giving the amount of the bound alkali, which is equivalent to the amount of the azoic coupling component present.

RESULTS AND DISCUSSION

Oxidation of Cellulose

Sodium borohydride treatment and chlorous acid treatment have been widely used to further modify oxycelluloses, since the former reduces the aldehyde, enediol, and lactone groups, while the latter selectively oxidizes the free aldehyde groups to carboxyl groups. These treatments have been used in the present investigation also on different oxycelluloses prepared by treating standard cellulose with potassium periodate, potassium dichromate–sulfuric acid, and potassium dichromate–oxalic acid. The copper number and the iodometric carboxyl value of all the modified and further modified cellulosic fibers were determined. The results are given in Table I.

It is seen that some of the fiber samples were of predominantly reducing type (periodate oxycelluloses and potassium dichromate–sulfuric acid oxycelluloses), some were of predominantly acidic type (chlorous acid-treated oxycelluloses), and others were of fairly low acidic type with practically no reducing properties (borohydride-treated oxycelluloses).

Affinity of Azoic Coupling Components

For calculating the affinity of azoic coupling components for standard cellulose and various chemically modified celluloses, the same theoretical treatment was followed as that used by Shenai and Veeramani[9] for calculating the affinities of vat dyes for these substrates, except that in the present system sodium hydrosulfite is not present. All the concentrations of the different ions in the fiber are expressed in terms of g ions/l. internal volume, taking value of 0.22 l./kg for this volume.

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
Potassium Periodate Oxycellulose								
1	4	12.95	4.76	0.21	0.02	1.94	17.14	0.97
2	24	31.50	13.96	0.51	0.12	3.88	46.15	1.47
Potassium Dichromate–Sulfuric Acid Oxycellulose								
3	2	5.78	1.52	0.21	0.07	1.66	3.99	0.92
4	24	36.10	13.08	1.86		9.80	20.74	3.77
Potassium Dichromate–Oxalic Acid Oxycellulose								
5	4[a]	···	2.89	0.19	0.05	1.14	6.08	0.57
6	4[b]	—	11.87	0.96	0.09	5.89	20.52	1.90

[a] With 20 ml $1N$ $K_2Cr_2O_7$.
[b] With 100 ml $1N$ $K_2Cr_2O_7$.

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

$$\Delta\mu_D^0 = RT \ln \frac{[D]_f [Na]_f^z}{[D]_s [Na]_s^z} \tag{1}$$

$$[Na]_f = \left[[D]_f + \frac{[ACOO]_f}{z}\right]\left\{\frac{z}{2} + \left(\frac{z^2}{4} + \frac{[Na]_s \,(K[OH]_s + [C]_s)}{[D]_f + \dfrac{[ACOO]_f}{z}}\right)^{1/2}\right\} \tag{2}$$

where $[D]_f$ and $[D]_s$ are the concentrations of azoic coupling component in the fiber and the solution at equilibrium, $[Na]_f$ and $[Na]_s$ are the sodium ion concentrations in the fiber and the solution, $[ACOO]_f$ is the carboxyl value (mEq/l. of internal volume of the fiber), z is the anionic charge on the azoic coupling component, R is the gas constant, T is the absolute temperature, $[OH]_s$ and $[Cl]_s$ are the hydroxyl ion concentration and the chloride ion concentrations in the external solution, and K is defined by

$$RT \ln K = -\Delta\mu^0_{NaOH}$$

A value of 10 had been obtained for K by Peters and Simons[18] in the case of dyeing vat dyes on cuprammonium rayon. The same value is used in the present case also.

The affinity values were calculated from the adsorption isotherms obtained at equilibrium. The affinity values of the three azoic coupling components for standard cellulose are given in Table II. The affinity values of the three azoic coupling components for standard cellulose and the variously modifed celluloses are given in Table III.

It is seen that with increasing degree of oxidation of cellulose with potassium periodate, there is a decrease in the affinity of all the three azoic coupling components, as was the case with direct dyes[10] as well as vat dyes[9] reported earlier. This leads to the conclusion that the introduction of aldehyde groups at the C-2 and C-3 positions of the anhydroglucose units of cellulose (as in periodate oxidation of cellulose) does have an adverse effect on the affinity of the azoic coupling components. Further, if the aldehyde groups are reduced by the borohydride treatment of these oxycelluloses, the affinity increases, though it does not attain the same value as that for standard cellulose. As shown in the case of vat dyes,[9] the difference in the affinity values (for standard cellulose and borohydride-treated periodate oxycellulose) may be ascribed to the residual aldehyde and acidic groups present in the borohydride-treated periodate oxycelluloses.

When cellulose is oxidized with potassium dichromate in the presence of sulfuric acid or oxalic acid, the oxidation supposedly takes place predominately, though not exclusively, at the primary hydroxy groups, with the formation of aldehyde or carboxyl group. The affinity values of the azoic coupling components are found to decrease with the increasing extent of oxidation with either of the oxidizing systems. When these oxycelluloses were reduced with sodium borohydride, the affinity values increased, through not to the value for standard cellulose. Similar behavior was reported earlier in the case of vat dyes.[9]

Chlorous acid treatment of all the oxycelluloses studied increased the carboxyl value sharply. The affinity of the azoic couping components for these samples also increased with increase in the carboxyl value. The increase in the affinity

TABLE II

Affinity of Azoic Coupling Components for Standard Cellulose at 30°C

Concn. of azoic coupling component		Azoic coupling component taken up by the fiber [D]$_f$		$[Na]_f$, g ions/l.	$[Na]_f$, g ions/l.	Affinity cal/mole	Mean affinity, cal/mole
Initial, g/l.	Final, [D]$_g$, (moles/l.) × 10³	(moles/kg) × 10²	(moles/l.) × 10²				
Amarthol AS							
1.5	4.47	4.93	22.41	0.895	0.998	−2486	−2564
2.5	7.36	8.57	38.93	0.909	1.083	−2591	
3.5	10.35	11.82	53.74	0.925	1.162	−2638	
5.0	15.53	13.93	63.32	0.946	1.269	−2540	
7.5	24.47	16.19	72.72	0.963	1.315	−2229[a]	
Amarthol AS-D							
1.5	4.13	5.15	23.43	0.873	1.025	−2529[a]	−2440
2.5	7.29	6.93	31.36	0.885	1.186	−2441	
3.5	10.35	9.14	41.55	0.898	1.301	−2447	
5.0	15.05	11.97	54.41	0.919	1.465	−2441	
7.5	23.05	16.07	73.00	0.951	1.707	−2432	
Amarthol AS-TR							
1.5	4.07	2.99	13.59	0.017	0.186	−3548	−3525
2.5	6.75	5.15	23.27	0.028	0.293	−3535	
3.5	9.18	6.91	31.39	0.040	0.385	−3492	
5.0	13.419	10.56	48.00	0.058	0.564	−3523	
7.5	20.46	14.47	65.76	0.089	0.781	−3400[a]	

[a] Values not included in the average.

TABLE III
Effect of Chemical Modification on the Affinity of Azoic Coupling Components for Cellulose

Oxidation with[a]	Subsequent treatment	Copper number	Carboxyl value mEq/1000 g	Affinity, cal/mole		
				Amarthol AS	Amarthol AS-D	Amarthol AS-TR
Nil (standard cellulose)	nil	0.05	0.78	−2564	−2440	−3525
KIO$_4$ (LOL)	nil	1.94	4.76	−2204	−2296	−3327
KIO$_4$ (LOL)	NaBH$_4$	0.02	0.97	−2409	−2355	−3428
KIO$_4$ (LOL)	HClO$_2$	0.21	17.14	−21989	−2360	−4020
KIO$_4$ (HOL)	nil	13.96	3.88	−2153	−2238	−3305
KIO$_4$ (HOL)	NaBH$_4$	0.12	1.47	−2379	−2345	−3294
KIO$_4$ (HOL)	HClO$_2$	0.51	46.15	−2387	−2501	−4044
K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (LOL)	nil	1.52	1.66	−2120	−2306	−3410
K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (LOL)	NaBH$_4$	0.07	0.92	−2395	−2340	−3459
K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (LOL)	HClO$_2$	0.21	3.99	−2090	−2179	−3375
K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (HOL)	nil	13.08	9.80	−2065	−2210	−3258
K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (HOL)	NaBH$_4$	0.35	3.77	−2257	−2406	−3470
K$_2$Cr$_2$O$_7$ + H$_2$SO$_4$ (HOL)	HClO$_2$	1.86	20.74	−2436	−2346	−3630
K$_2$Cr$_2$O$_7$ + H$_2$C$_2$O$_4$ (LOL)	nil	2.89	1.14	−2336	−2350	−3303
K$_2$Cr$_2$O$_7$ + H$_2$C$_2$O$_4$ (LOL)	NaBH$_4$	0.05	0.57	−2507	−2399	−3448
K$_2$Cr$_2$O$_7$ + H$_2$C$_2$O$_4$ (LOL)	HClO$_2$	0.19	6.08	−2227	−2330	−3492
K$_2$Cr$_2$O$_7$ + H$_2$C$_2$O$_4$ (HOL)	nil	11.87	5.89	−2252	−2329	−3320
K$_2$Cr$_2$O$_7$ + H$_2$C$_2$O$_4$ (HOL)	NaBH$_4$	0.09	1.90	−2477	−2375	−3457
K$_2$Cr$_2$O$_7$ + H$_2$C$_2$O$_4$ (HOL)	HClO$_2$	0.96	20.52	−2286	−2394	−3920

[a] LOL = Low oxidation level; HOL = high oxidation level.

values may be due to the fact that beyond a specific carboxyl value in the fiber substance, the absorption of the azoic coupling component has a tendency to remain constant. Similar behavior has been reported by Daruwalla et al.,[19] who showed that the equilibrium adsorption of two direct dyes by oxycelluloses decreased with increasing carboxyl value and that beyond a certain carboxyl value, the dye adsorption remained constant. Due to such a restricted effect on the adsorption of the azoic coupling component, the affinity value apparently increases as [Na]$_f$ values are calculated based on the total carboxyl groups present in the oxycellulose, in addition to the sodium ions present in the fiber substance due to the adsorption of the azoic coupling component, which does not increase substantially.

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