

Polyelectrolyte Behavior of Chemically Modified Cotton Cellulose

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Synopsis

Ion exchange and sorption of charged molecules such as dyes, crosslinking agents, etc., by cotton cellulose very much depend on the charge on cellulose, which in turn is known to depend on the external pH of the medium. In order to understand the role of various fixed groups in cellulose in its polyelectrolyte behavior, the standard cellulose was deliberately oxidized with nitrogen dioxide and sodium periodate, and the sorption of formaldehyde and dimethylol dihydroxyethylene urea by these oxycelluloses as well as by alkali-treated nitrogen dioxide-oxycellulose was investigated. The results obtained are interpreted in terms of polyampholyte behavior of oxycellulose. The nitrogen dioxide-oxycellulose is positively charged and is a polycation in acidic medium due to protonation of aldehyde groups while it is negatively charged and acts as a polyanion in slightly acidic to alkaline medium due to dissociation of carboxyl groups.

INTRODUCTION

Cellulose derivatives which are either polyanions or polycations find many practical applications. Useful reviews^{1,2} of their application have been published. Several studies on the ion exchange properties of cellulosic polyanion have been reported.^{3,5} Sobue and Tabala⁴ investigated the exchange of sodium and hydronium ions on the films of carboxymethyl cellulose and calculated activity coefficient for the ions in the film. Lawton et al.⁵ studied interaction of methylene blue with cellulosic polyanions in heterogeneous system and obtained thermodynamic parameters for the ion exchange reactions on these polyanions. They later extended the study⁶ to the ion exchange of inorganic cations with sodium ions and observed that both cellulose sulfate and phosphate bind potassium ions in preference to sodium ions, whereas with oxycellulose (cell-COO⁻) and carboxymethylcellulose (cell-CH₂-COO⁻) the order is reversed.

Cotton is known to have a negatively charged surface in water. The origin of the negative charge has been attributed to ionization of surface polar groups^{7,8} and their interaction with solvent molecules.⁹ It is also known that addition of neutral salt increases absorption of dyes by cotton cellulose.¹⁰ This has been attributed to a decrease in potential barrier which prevents dye anion from reaching the negatively charged cotton surface. Studies^{9,11,12} made on cellulose-aqueous electrolyte solution interface, however, indicate that H⁺ and OH⁻ concentration in the system determine the polarity of the surface. The charge is negative at pH 2.5 and is positive below pH 2.5. We¹³ had earlier concluded that nitrogen dioxide-oxycellulose containing aldehyde groups carries a positive charge in acidic medium and that the large increase in absorption of crosslinking

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molecules by the oxycellulose in the presence of neutral salt was due to a decrease in electrostatic repulsion between fixed polycation and mobile coions.

Ion exchange and sorption of charged molecules by cotton cellulose very much depend on the charge of cellulose molecules. This study was undertaken to understand the correlation between the pH and the ionization of various fixed groups in cellulose. The article describes further study on sorption of formaldehyde and dimethylol dihydroxyethylene urea (DMDHEU) by chemically modified cellulose. The cotton cellulose seems to behave both as polyacid and polybase depending on the pH and the nature of fixed ionizable groups in cellulose. It is believed that the results obtained may be of value in developing better understanding of various reactions of cellulose leading to its better utilization and improved end use properties of cotton.

EXPERIMENTAL

Chemically Modified Celluloses

Various oxycelluloses were prepared from the purified cotton fabric by standard procedures.^{14,15} The details were given earlier.^{13,16} The specifications of various oxycelluloses used in this investigation are described below.

Oxycellulose OC1 is a nitrogen dioxide-oxidized cellulose. The primary hydroxyl group in the β -glucose unit is oxidized to carboxyl group. It also contains 0.35 mol aldehyde groups per mol of carboxyl groups. The sample OC1 has a carboxyl content of 20 m mol/100 g cellulose and an aldehyde content of 7 mmol/100 g cellulose.

Oxycellulose OC1-Na is a sodium salt of carboxycellulose. It was prepared by treating the oxycellulose OC1 with sodium hydroxide solution.

Oxycellulose OC2 is a periodate-oxidized cellulose. The secondary hydroxyl group in the β -glucose units are oxidized to aldehyde groups giving 2:3 dialdehyde-cellulose. The OC2 sample contains 61 mmol aldehyde per 100 g cellulose.

Equilibrium Sorption of Formaldehyde

Cotton cellulose samples (1 g) were treated at 28°C with 100 ml aqueous solution of formaldehyde of varying concentrations in the presence of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, the catalyst. At the end of 48 h, which was adequate to attain equilibrium, samples were washed thoroughly with distilled water to remove free formaldehyde. The amount of formaldehyde bound to cellulose was determined by hydrolysis¹⁷ followed by colorimetric determination with Schiff's reagent. The results are expressed as g formaldehyde bound to 100 g cellulose (% formaldehyde). The experiments were also carried out in the presence of added 0.001M and 0.1m NaCl.

Treatment of Cellulose with DMDHEU

Cotton cellulose samples of known weight were padded with DMDHEU solution together with velustrol, a wetting agent, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ catalyst to give 70% wet pickup. Samples were then dried at 110°C for 4 min and cured at 150°C

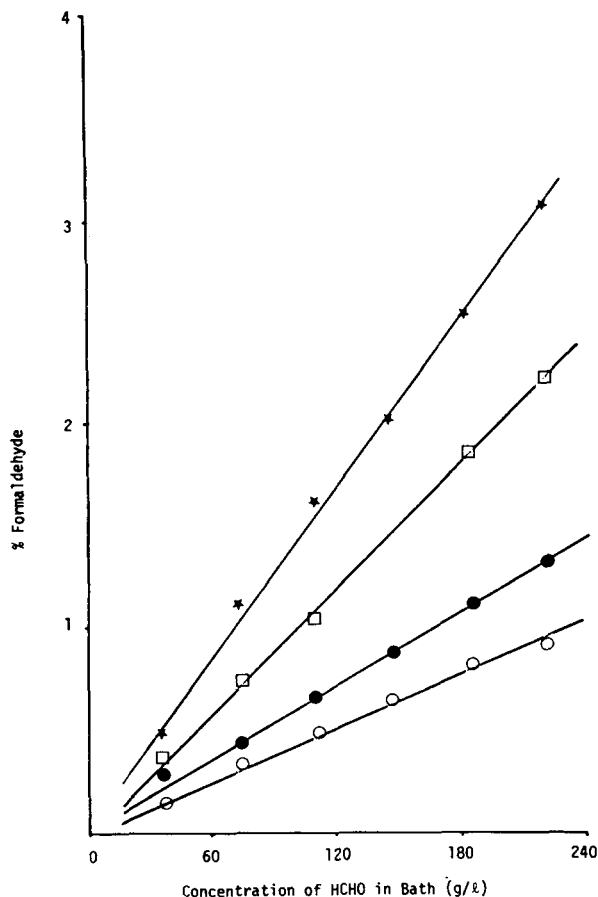


Fig. 1. Equilibrium adsorption of formaldehyde by standard cellulose and nitrogen dioxide-oxycellulose: (●) standard cellulose; (○) oxycellulose; (□) oxycellulose (0.001M NaCl); (*) oxycellulose (0.1M NaCl).

for 3 min. They were then washed with neutral soap. The amount of DMDHEU sorbed by cellulose was determined from the nitrogen content in the fiber by the Kjeldhal method. The results are expressed as N%.

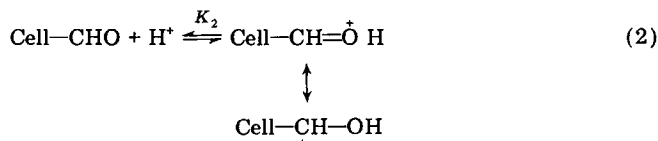
RESULTS AND DISCUSSION

Figure 1 shows the variation of equilibrium sorption of formaldehyde by the standard and oxycellulose OC1 with concentration of formaldehyde in the reaction bath. In the concentration range investigated, % formaldehyde increases with increase in concentration of formaldehyde in the reaction bath. The uptake of formaldehyde by the oxycellulose OC1 is, however, less than that by the standard cellulose, and, further, it increases sharply in the presence of added neutral salt such as sodium chloride. We¹³ had earlier explained this behavior as due to electrostatic interaction between oxycellulose and formaldehyde as outlined below.

In acidic solution, hydrated formaldehyde acquires a proton:



Likewise, oxycellulose acquires proton in acidic solution and is resonance stabilized:



Thus, we now have a situation in which the fixed ions in the oxycellulose molecule as well as the mobile formaldehyde molecule are both positively charged in acidic medium. This will give rise to high electrostatic repulsion resulting in decrease in formaldehyde uptake. When a neutral salt such as sodium chloride is added to the reaction bath, the counterions, in this case Cl^- , shield the positively charged fixed ions in cellulose from the approaching positively charged protonated formaldehyde thereby reducing electrostatic repulsion and thus facilitating sorption of formaldehyde by the oxycellulose. It can be seen from Figure 1 that % formaldehyde is markedly increased in the presence of even as low as 0.001M NaCl. Increasing the concentration of sodium chloride further decreases electrostatic repulsion, causing further increase in the sorption of formaldehyde.

The sorption of formaldehyde by periodate oxycellulose OC2 is shown in Table I. It is not surprising that the % formaldehyde values are extremely small. The oxycellulose OC2 has a very high aldehyde content and hence a much higher charge density than oxycellulose OC1. It will therefore suffer greater electrostatic repulsion thereby retarding sorption of formaldehyde.

We have seen above that the polycationic nature of oxycellulose accounts for large decrease in the sorption of formaldehyde. It is worthwhile to see how the sorption of positively charged crosslinking molecules would be affected if the charge on cellulose is changed to negative. Oxycellulose OC1, which contains aldehyde as well as carboxyl groups, was treated with sodium hydroxide solution so that the carboxyl groups are dissociated. Oxycellulose OC1-Na can therefore be considered as a solid polyanion. DMDHEU rather than formaldehyde was used as a probe to investigate the polyanionic behavior of OC1-Na for the following reasons: Unlike DMDHEU, formaldehyde reacts with cellulose in highly acidic medium only.¹⁸ Under this condition, the oxycellulose will not exhibit

TABLE I
Sorption of Formaldehyde by Periodate-Oxycellulose

Formaldehyde concentration in the reaction bath, g/dL	% Formaldehyde
3.7	0.03
6.4	0.03
11.1	0.02
14.8	0.03
18.5	0.04
22.2	0.06

TABLE II
Sorption of DMDHEU by Nitrogen dioxide-Oxycellulose

Type	Polyion	N%
Standard cellulose	neutral	0.84
Oxycellulose OCl (Cell-CH=ÖH)	polycation	0.62
Oxycellulose OCl (in presence of 0.1M NaCl)	polycation	1.78
Oxycellulose OCl-Na (Cell-COO ⁻)	polyanion	2.08

polyanionic character since its carboxyl groups will be undissociated. Hydrated formaldehyde or methylol compounds such as DMDHEU can be considered as stronger bases than dialdehyde cellulose since the equilibrium constant K_1 for reaction (1) is greater than K_2 for reaction (2). DMDHEU will therefore acquire a proton in preference to oxycellulose OCl and will be positively charged even though the oxycellulose is either neutral or negatively charged.

The sorption of DMDHEU by nitrogen dioxide-oxycellulose, under different conditions, is shown in Table II. The results clearly demonstrate the polyelectrolyte behavior of nitrogen dioxide-oxycellulose. In acidic medium, the net positive charge or polycationic character of oxycellulose suppresses the sorption of DMDHEU, while in slightly acidic medium, the net charge is negative and the oxycellulose behaves as a solid polyanion facilitating sorption of DMDHEU. The N% for standard cellulose (very close to no charge) is 0.84. It drops to 0.62 for polycationic oxycellulose and increases sharply to 2.08 when the oxycellulose is converted to polyanion.

Nitrogen dioxide oxycellulose can therefore be considered as a solid polyampholyte. It is positively charged in acidic medium due to protonation of aldehyde groups, and the charge changes to negative value as the dissociation of carboxyl groups takes place on the addition of alkali. The pK_a value of carboxyl group in oxycellulose is 3.6,¹⁹ and hence it will behave as a polyanion in slightly acidic to alkaline medium. It has been reported by Madan²⁰ that surface charge of cotton is zero at pH 2.8, negative above this pH, and positive at pH lower than 2.8. Neale and Strandling have also observed a change in potential in cellophane going from neutral to acidic solution. These workers have not attributed the changes in charge to any specific groups in cellulose. Cotton and cellophane used in their investigations are most likely to contain a small but definite amount of aldehyde and carboxyl groups formed during purification processes such as scouring, bleaching, etc.

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