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Polyethylenimine-Containing Cotton Fabrics

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ABSTRACT

Polyethylenimine-containing cotton fabrics were prepared by reaction of 1-epoxyethyl-3, 4-epoxycyclohexane with cotton fabric impregnated with polyethylenimine of a moderately high molecular weight. Fabrics with a high unremovable polyethylenimine content and with a different degree of cross-linking were obtained. Adsorption of several heavy metal salts such as mercuric chloride and cupric sulfate by the fabrics was investigated. Adsorption was controlled by polyethylenimine content of the fabric, extent of cross-linking, and the pH of the solution.

INTRODUCTION

Amine-containing cellulose derivatives are well known for their ion-exchange properties and their ability to form stable complexes with heavy metal salts [1, 2]. Among many cellulose derivatives containing

nitrogen, the possibility of utilizing ethylenimine and its polymer for introduction of amine groups to cellulose was also reported. Thus, for example, on heating cellulose in the presence of ethylenimine and acetic acid in benzene, cellulose derivatives containing 1.5 and 2.7% N were obtained with cotton and rayon cellulose [3]. Cotton fabrics with a much higher nitrogen content were prepared by cross-linking polyethylenimine prepolymer within the fabric [4]. These fabrics were obtained by impregnating cotton fabric with ethylenimine prepolymer which was subsequently converted to an insoluble network polymer by reaction with 1,2-dichloroethane which was also used to prepare the ethylenimine prepolymer. Polyethylenimine can be adsorbed by cellulose. Its use in this form for the introduction of amine groups to cellulose is limited since the adsorbed polymer can be removed by repeated treatments in water [5]. The cotton fabrics containing unremovable polyethylenimine showed high complexing capacity for several heavy metal salts, among them mercuric and cupric salts [4]. Roberts and Rowland [6] compared the effectiveness of four chemically modified cotton cellulose-containing amine groups in adsorbing mercuric salt from aqueous solutions. The modified cellulose derivatives were ethylenimine network polymer formed in the fiber (2.75% N), polyethylenimine adsorbed on filters (1.11% N), 2-diethylaminoethyl-substituted cellulose (0.29% N), and 2-aminoethyl-substituted cellulose (0.64% N). It was found that cotton cellulose containing ethylenimine network polymer was the most effective cotton derivative on the basis of the weight of the cellulosic composition.

This paper describes another possibility of preparation of unremovable polyethylenimine containing-cotton fabric. This fabric can be prepared by impregnation with polyethylenimine of a moderately high molecular weight (30,000 to 40,000) and cross-linking it with a diepoxide. The diepoxide used was 1-epoxyethyl-3,4-epoxycyclohexane. The use of a moderately high molecular weight polymer will prevent the polyethylenimine from diffusing into the cellulose fiber. Therefore, the cross-linked polyethylenimine should be found only outside the fibers. Nevertheless, a lower extent of reaction will be needed in order to obtain high nitrogen content fabrics. It was also interesting to investigate the complexing capacity of these type of cellulose derivatives with some heavy metal salts.

EXPERIMENTAL

Materials

Polyethylenimine (50% in water, MW 30,000 to 40,000), 1-epoxyethyl-3,4-epoxycyclohexane (Fluka), cupric sulfate, mercuric

chloride (Riedel de Hoën), silver nitrate, uranyl chloride (B.D.H.), cobalt chloride (Merke), and nickel chloride (AnalaR) were used.

Preparation of Polyethylenimine-Containing Fabric

Cotton print cloth, purified according to a known procedure [7], was swelled in 20% NaOH under nitrogen atmosphere for 15 min at room temperature. The fabric was washed with water and impregnated in 35% polyethylenimine water solution to a pick-up of 0.8 g dry polyethylenimine/1 g cotton. The fabric was dried in an oven at 100°C and was transferred to a solution of 1-epoxyethyl-3, 4-epoxycyclohexane in dimethylformamide of the required concentration and was kept for 3 hr at 110°C. The fabric was washed with 2% acetic acid solution and was Soxhlet extracted with water for 15 hr in order to remove any unreacted polyethylenimine. The fabric was dried in vacuum on P_2O_5 and weighed.

Adsorption Experiments

Polyethylenimine-containing fabric (0.1 to 0.2 g) was kept in salt solution (10 ml) with cupric, nickel, cobalt, and uranium salts, and (20 ml) mercuric chloride solution. The required time for complete adsorption was 50 hr for cupric sulfate, 100 hr for nickel, cobalt, silver, and uranium salts, and 150 hr for mercuric salt. The extent of adsorption of cupric sulfate, nickel chloride, and cobalt chloride was determined with a Fisher electrophotometer using calibration curves. Silver nitrate adsorption was determined by sodium chloride titration. Mercuric chloride and uranyl chloride adsorption was determined by the weight increase of the fabric after vacuum drying.

RESULTS AND DISCUSSION

Cotton fabrics containing unremovable polyethylenimine were prepared by impregnation of the fabrics with polyethylenimine (MW 30,000 to 40,000) water solution, and then reacting them with 1-epoxyethyl-3, 4-epoxycyclohexane in DMF solution. The results are reported in Table 1.

Three different reactions can be expected between the diepoxide and the polyethylenimine-impregnated fabric. The diepoxide may react with the hydroxyl groups of the cellulose, thus leading to cross-linking of the cellulose molecules. The diepoxide may react

TABLE 1. Reaction of 1-Epoxyethyl-3, 4-epoxycyclohexane with Polyethylenimine Impregnated Cotton Fabric[a]

1-Epoxyethyl-3, 4-epoxycyclohexane [M]	Cotton fabric (g)	Weight increase[b] (%)	Nitrogen content (%)	Polyethylene imine in the fabric[c] (%)	Reacted diepoxide[d] (%)
0.60	7.51	63.5	7.12	21.9	16.7
0.64	4.16	73.5	7.48	23.0	19.5
0.92	4.12	87.0	7.37	22.6	23.5
1.28	4.09	93.8	7.43	22.8	25.7
1.56	4.06	92.5	6.94	21.3	26.8

[a]Cotton fabric was swelled in 20% NaOH and was impregnated with 35% polyethylenimine water solution to weight increase of 0.8 g polyethylenimine/1 g cellulose. Reaction was carried in DMF at 110°C for 3 hr.

[b]Determined after Soxhlet extraction with water.

[c]Calculated from % N.

[d]Calculated from nitrogen analysis and weight increase.

with both cellulose hydroxyls and polyethylenimine amine groups, thus grafting the polyethylenimine on the cellulose. The diepoxide may also react only with amine groups of the polyethylenimine impregnated in the fabric, thus cross-linking the polyethylenimine itself. Both grafting and cross-linking of the polyethylenimine will lead to insolubility of the polyethylenimine in the fabric due to chemical bonding to the cellulose molecules or to the conversion of the polyethylenimine to a three-dimensional network. Since moderately high molecular weight polyethylenimine was used, it is most likely that the insoluble polyethylenimine network formed within the fabric did not penetrate the cellulosic fibers.

The impregnated fabric was allowed to react with the diepoxide at different concentrations. Unreacted polyethylenimine was removed by Soxhlet extraction with water. The extent of reaction was determined from nitrogen analysis and the weight increase of the fabric. Cotton fabrics with a high nitrogen content (6.94 to 7.48% N), corresponding to more than 20% polyethylenimine content, were obtained. An increase in the extent of the diepoxide reaction did not lead to any significant change in the polyethylenimine content of the fabric. It may be concluded that an increase in the extent of reaction led mainly to an increase in the extent of cross-linking of the polyethylenimine that had already reacted.

Figure 1 describes the time dependence of adsorption by complexation of mercuric chloride, cupric sulfate, and silver nitrate by polyethylenimine-containing fabric.

The complexing capacity of polyethylenimine-containing fabric with several heavy metal salts at different salt concentrations is reported in Table 2. All adsorption experiments were carried in aqueous solutions except adsorption with uranyl chloride which was carried in ethanol. Adsorption should be attributed only to complexation by the polyethylenimine amine groups since under similar reaction conditions adsorption by cellulose alone is negligible. Among the heavy metal salts investigated, good results were obtained with mercuric chloride, cupric sulfate, and silver nitrate. Though the complexing capacity of the polyethylenimine was high, not all amine groups in the polymer participated in complexation. An increase in the heavy metal salt solution concentration led to an increase in the polyethylenimine complexing capacity, but the maximum theoretical value was never obtained. Limited excessibility should be the reason for that phenomenon. All adsorption experiments reported so far were conducted with polyethylenimine-containing fabric of the same nitrogen and cross-linking agent content. The extent of cross-linking should influence accessibility and the extent of adsorption. Figure 2 described the complexation capacity of cupric sulfate by cotton fabrics of similar polyethylenimine content reported in Table 1 but containing different amounts of cross-linking agent.

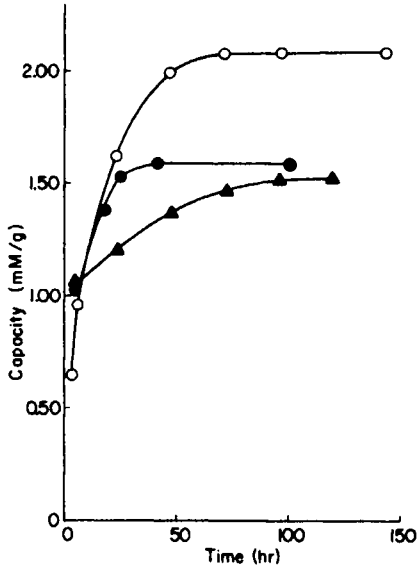

FIG. 1. Adsorption of heavy metal salts by polyethylenimine-containing cotton fabric, time dependence. Fabric of 7.12% N containing 16.7% cross-linking agent was used. Adsorption was carried out in water. (●) Cupric sulfate, (○) mercuric chloride, and (▲) silver nitrate.

It can be seen that the complexation capacity dropped from 3.20 mmole/g for a fabric containing 16.7% cross-linking agent to 1.74 mmole/g for a fabric containing 26.8% cross-linking agent.

The extent of complexation by polyethylenimine-containing fabrics is also limited by solution pH. An increase in free amine groups concentration in the fabric leads to a decrease in the polyethylenimine complexing capacity. Figure 3 describes the pH dependence of the polyethylenimine-containing fabric adsorption capacity of cupric sulfate and mercuric chloride. A decrease in solution pH leads to a decrease in adsorption capacity; nevertheless, even at low pH values the fabric still adsorbed heavy metal salts. In an adsorption experiment with cupric sulfate in 1 $\underline{N}$ H_2SO_4 solution, under similar conditions and using the same fabric, a capacity of 0.05 mmole/g was determined. From the adsorption pH dependence it can be seen that adsorption and desorption of the heavy metal salts can be controlled by changing the solution pH.

TABLE 2. Adsorption of Heavy Metal Salts by Polyethylenimine-Containing Fabric[a]

Salt solution	[M]	Polyethylenimine-containing fabric (g)	Fabric complexing capacity (mmole/g)	Polyethylenimine capacity (mmole/g)
Cupric sulfate	0.025	0.106	0.56	2.60
	0.050	0.113	0.70	3.20
	0.100	0.120	1.59	7.30
	0.250	0.115	1.73	7.90
	0.500	0.415	1.86	8.50
Mercuric chloride	0.001	0.137	0.11	0.48
	0.010	0.168	0.75	3.40
	0.040	0.197	1.45	6.60
	0.070	0.203	1.90	8.65
	0.100	0.206	2.08	9.45
Nickel chloride	0.500	0.134	1.31	5.95
Cobalt chloride	0.500	0.123	0.64	2.90
Silver nitrate	0.100	0.102	1.52	6.86
Uranyl chloride	0.050	0.108	0.45	2.05

[a]Polyethylenimine-containing fabric of 7.12% N and 16.7% cross-linking agent was used. Adsorption was carried out in water solution except for uranyl chloride which was adsorbed from ethanol.

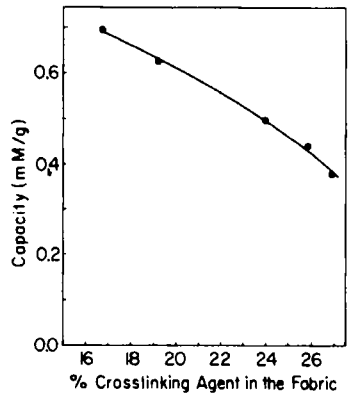

FIG. 2. Adsorption of cupric sulfate by polyethylenimine-containing cotton fabric at different degrees of cross-linking. Adsorption was carried in water. The fabrics used are reported in Table 1.

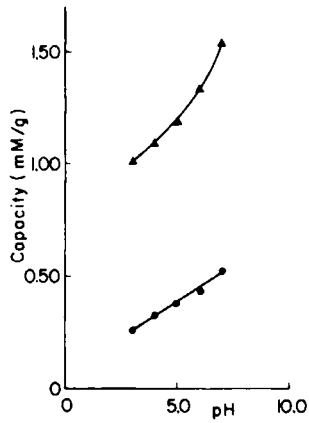

FIG. 3. Adsorption of mercuric chloride and cupric sulfate by polyethylenimine-containing cotton fabric, pH dependence. Fabric of 7.12% N containing 16.7% cross-linking agent was used. Adsorption was carried out in water. (●) Cupric sulfate and (▲) mercuric chloride.

Since the polyethylenimine in the fabric is alone responsible for complexation of the heavy metal salts, by controlling the amount of polyethylenimine in the fabric, the extent of cross-linking, and the solution pH, fabrics with the desired complexation capacity can be prepared. Such fabrics may be of interest for removal of heavy metal salts from their water solutions.

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