Synthesis of Cotton-Bearing DEAE, Carbamoyethyl, Carboxyethyl, and Poly(acrylamide) Graft for Utilization in Dye Removal

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ABSTRACT: Cotton cellulose in the fabric form was subjected to etherification and grafting reactions with the purpose of obtaining cotton with ionic properties. Thus, cottons bearing DEAE, carbamoylethyl, and carboxyethyl groups, along with partially hydrolyzed poly(Aam) graft, were synthesized. The ability of these cotton substrates to function as ion exchangers, particularly for removal of direct, basic, acid, and reactive dyes from aqueous solution was examined. The obtained results reveal that such modifications increase the ability of cotton to remove these dyes to about 150 times. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1007–1014, 1999

INTRODUCTION

Chemical modification of polymers with the aim of imparting specific, desirable properties is one of the main directions of development in modern macromolecular chemistry.¹ Chemical modification lies essentially in introducing functional groups into the cellulose molecules, which confer new properties on the cellulose without destroying its many desirable intrinsic properties. Among the modified cotton celluloses that constitute examples of this were partially carboxymethylated cotton,² cyanoethylated cotton,³ carbamoylethylated cotton,⁴ cellulose carbamate,^{5,6} and cellulose copolymerized with various vinyl monomers.¹

In a very recent study,⁷ we have reported on the preparation of DEAE cotton-*g*-poly(methacrylic acid) for use as an ion exchanger. A potassium permanganate–citric acid redox system was used for initiation of grafting. Ability of the synthesized poly(methacrylic acid)–DEAE cotton graft copolymers to remove dyes and metal ions from aqueous solutions was also reported.

Journal of Applied Polymer Science, Vol. 73, 1007–1014 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/061007-08 With the above in mind, the present work aims at synthesizing cotton cellulose bearing different substituents. The latter are selected in a way that cotton will be rendered ionic exchanger. Hence cotton, alkali-treated cotton, and DEAE cottons were subjected to carbamoethylation with a view to introduce carbamoyethyl groups in the molecular structure of cellulose in addition to the DEAE groups in the modified cotton. The carbamoyethylated products are further modified by subjecting them to grafting with acrylamide. Investigation into the ability of the carbamoyethylated products-g-poly(Aam) before and after saponification to remove different dyes from aqueous solutions are then made.

EXPERIMENTAL

Materials

Mill-desized, scoured, and bleached cotton fabric (popline) was supplied by Misr Company for spinning and weaving, Mehala Elkubra, Egypt. The fabric was purified in the laboratory by scouring at 100°C for 60 min using solution containing Na₂CO₃ (2 g/L). It was then thoroughly washed with water and dried at ambient conditions.

Chemicals

B-Chloroethyldiethylamine hydrochloride, sodium hydroxide, acrylamide, potassium permanganate, citric acid, glacial acetic acid, and other chemicals were of laboratory-grade chemicals.

The dyes used included direct dye, Solophenyl Orange TGL, basic dye, Maxilon Blue TL; acid dye, Remalan Fast Red EGG; and reactive dye, Remazol Blue R. These dyes were kindly supplied by Ciba-Giegy, Switzerland.

Preparation of DEAE Cotton

Diethylaminoethyl (DEAE) cotton was prepared according to reported modification of Hartman Process.⁸ The fabric was added twice to approximately 100% wet pick up with aqueous solution of *B*-chloroethyldiethylamine hydrochloride and dried at 60°C for 10 min. The fabric was then immersed in 8% sodium hydroxide solution for 10 min at 95°C, washed in dilute acetic acid and then under tap water, followed by drying at ambient conditions.

Preparation of Alkali-Treated Cotton

The fabric is immersed in 8% aqueous sodium hydroxide at 95°C for 10 min. The excess alkali is removed by washing the fabric with dilute acetic acid and then under tap water, followed by drying, as above.

Preparation of Carbamoylethylation

Cellulose reacts with acrylamide (Aam) in alkaline medium to give carbamoylethylated cotton cellulose.⁹ The reaction involved may be represented as follows:

Cell-OH +
$$H_2C \approx CH \cdot C - NH_2 \longrightarrow Cell-O-CH_2-CH_2 - C - NH_2$$

Untreated cotton, alkali-treated cotton, and DEAE cottons having different %N were treated with acrylamide at different concentrations, along with 3.8% sodium hydroxide. After being squeezed to a wet pick up of approximately 85%, the fabric was heated in an oven at 125°C for 6 min. At this end, the fabric was thoroughly washed and air-dried at room temperature.

Grafting Process

Treatment with Potassium Permanganate

Unless otherwise indicated, grafting of cotton, alkali-treated cotton, and DEAE cotton was carried out as per the following procedure. The sample was treated with a solution containing $\rm KMnO_4$ (0.25 g/L) at 30°C for 30 min using a material-toliquor ratio of 1 : 30 with continuous shaking to avoid the heterogeneity of $\rm MnO_2$ deposition on the fabric surface. After this treatment, the fabric was thoroughly washed with water and squeezed between two filter papers, then immersed in polymerization solution.¹⁰

Graft Polymerization

The so-obtained KMnO₄-treated sample was introduced in 100-mL stoppered conical flask containing an aqueous solution of Aam at a concentration of 100% based on fabric-weight (0.25 g/L) citric acid (pH 3). Polymerization was allowed to proceed at 80°C for 60 min. At the end of reaction the sample was removed, thoroughly washed several times with cold and boiled water, and dried at 105°C for 180 min.¹¹

Saponification Process¹¹

Samples of these modified cotton were immersed in (IN) NaOH at 80°C for 2 h. A material-to-liquor ratio (L : R) 1 : 50 was employed. The sample was washed repeatedly with water and dried at room temperature.

TESTING AND ANALYSIS

Percentage graft yield (Y_g) was calculated as follows [eq. (1)]:

$$Y_g = \frac{(W_2 - W_1)}{W_1} \times 100 \tag{1}$$

where W_1 is the dry weight of original sample, and W_2 is the dry weight of the grafted sample.

The carboxyl content was determined according to reported method.¹² The nitrogen content was determined by kjeldhal method.¹³

Evaluation of ion exchange as a dye absorbant was carried out using a photoelectric colorimeter Model 528.

RESULTS AND DISCUSSION

Carbamoyethylation of DEAE Cottons

When cotton cellulose is treated with *B*-chloroethyldiethylamine hydrochloride in the presence of

	Un C	treated otton	Alkal C	i-Treated otton	DEA with	E Cotton 0.109 <i>N%</i>	DEA with	E Cotton 0.211 <i>N%</i>	DEA with	E Cotton 0.43 <i>N%</i>
[Acrylamide] (g/L)	N%	Carboxyl Content	N%	Carboxyl Content	N%	Carboxyl Content	N%	Carboxyl Content	N%	Carboxyl Content
80	0.782	10.90	0.731	10.70	0.811	10.70	1.100	10.70	1.292	10.93
100	0.913	16.80	0.965	16.71	9.890	16.71	1.351	16.71	1.401	16.71
120	1.083	18.91	1.114	18.91	1.201	18.91	1.410	18.91	1.439	18.91
240	1.450	19.99	1.312	19.99	1.540	19.99	1.622	19.99	1.885	19.99
350	2.010	22.12	2.030	22.12	2.090	22.12	2.050	22.12	2.390	22.12

Table I Effect of Acrylamide Concentration on the Extent of Carbamoylethylation (Expressed as N%)

Variations of nitrogen content and carboxyl content meq-COOH/100 g fabric of acrylamidomethylated products with the concentration of acrylamide.

alkali, DEAE-cotton is formed via aminization,⁷ as shown by following the reaction suggested by eq. (2):



The extent of aminization is usually expressed as N%. DEAE cottons having different N%, namely, 0.109, 0.211, and 0.43%N, which are shown in Table I, were obtained by changing the concentration of *B*-chloroethyldiethylamine hydrochloride whereas, alkali-treated cotton represents a control for DEAE cotton, as detailed in our previous work.⁷ These DEAE cottons, along with untreated cotton and alkali-treated cotton, were subjected to carbamoylethylation. The latter involves treatment of the cotton substrate with acrylamide in presence of alkali, as described in the experimental section. Carbamoyethylation takes place according to the following reaction suggested by eq. (3):

Cell—OH + CH₂—CHCONH₂ \rightarrow CellOCH₂CH₂CONH₂ (3)

Table I shows the dependence of carbamoylethylation of the aforementioned substrates, namely, untreated cotton, alkali-treated cotton, and DEAE cottons on the concentration of acrylamide. It is seen that increasing the amount of DEAE groups expressed as %N in the molecular structure of cotton cellulose significantly enhances the susceptibility of the latter towards carbamoyethylation. This is rather a direct consequence of extra nitrogen due to the introduction of carbamoylethyl groups in additional to DEAE groups.

It is also seen that the extent of carbamoylethylation (expressed as %N) increases by increasing the acrylamide concentration, irrespective of the substrate used, within the range studied. This reflects the dependence of the magnitude of the carbamoylethylation reaction on the availability of acrylamide molecules in the proximity of cellulose hydroxyl groups, which are themselves immobile.¹⁴

Graft Polymerization

Untreated cotton fabric, alkali-treated cotton, and DEAE cottons having different degrees of aminization, expressed as %N, were graft-polymerized under different conditions with Aam, as described in the experimental section. Results of the graft yield obtained with these five substrates are summarized in Tables II and III. It is seen that the graft yield increases by increasing the concentration of the initiator, that is, $KMnO_4$ and citric acid, within the range studied, regardless of the substrate used. Nevertheless, the nature of the substrate determines the magnitude of grafting for a given condition. The DEAE cottons exhibit greater grafting than does the untreated cotton, whereas alkali-treated cotton stands in a midway position.

		Graft	Yield	ł (%) ^k)			Graf	t Yiel	d (%)				Graf	't Yiel	d (%)	
[KMnO4] (g/L) ^a	Ι	II	III	IV	V	[Citric Acid] (g/L) ^c	Ι	II	III	IV	V	[Aam] (% ows) ^d	Ι	II	III	IV	V
0.05	5	8	10	12	15	0.05	4	10	15	18	21	20	5	7	10	19	22
0.10	9	12	15	18	20	0.10	6	14	18	20	25	40	13	15	17	20	25
0.15	11	14	17	19	24	0.15	10	15	19	21	27	60	14	18	20	26	29
0.20	15	19	25	28	26	0.20	13	20	21	29	31	80	16	21	25	28	31
0.25	22	27	29	30	37	0.25	20	25	30	32	36	100	18	22	27	30	37

Table II Effect of Initiator and Monomer Concentrations on Grafting of Acrylamide onto Untreated and Alkali-Treated Cottons and DEAE Cottons

^a [Aam], 100% ows; [citric acid], 0.25 g/L (temperature, 80°C; time, 60 min; material-to-liquor ratio, 1 : 20; pH 3). ^b I represents untreated cotton; II, alkali-treated cotton; III, IV, and V, DEAE cottons having 0.109, 0.211, 0.43%N, respectively.

^c [Aam], 100% ows; [KMnO₄], 0.25 g/L (temperature, 80°C; time, 60 min; material-to-liquor ratio, 1 : 20; pH 3).

^d [KMnO₄], 0.25 g/L; (citric acid), 0.25 g/L (temperature, 80°C; time, 60 min; material-to-liquor ratio, 1 : 20; pH 3).

According to previous report,¹⁵ the creation of primary free radicals in the permanganate-citric acid (HR) system occurs presumably as follows:

$$Mn^{IV} + HR \rightarrow Mn^{III} + H + R^{\circ}$$
 (4)

$$R^{\circ} + H_2 O \rightarrow HR + HO^{\circ}$$
 (5)

$$Mn^{IV} + H_2 \rightarrow Mn^{II} + H + HO^{\circ}$$
 (6)

These free radical species attack the cellulose molecule (cell-OH) and results in cellulose macroradical via abstraction of hydrogen atom, as exemplified by the reaction suggested by eq. (7).

$$Cell - OH + R^{\circ} \rightarrow Cell - O^{\circ} + HR$$
(7)

The cellulose macroradical may also be formed via direct attack of Mn^{IV} , as shown by eq. (8).

$$Cell - OH + Mn^{IV} \rightarrow Cell - O^{\circ} + Mn^{III} + H^{+} \quad (8)$$

Addition of the cellulose radical to the double bond of Aam initiates grafting through formation of the chemical bond between the cellulose and (Aam) molecule with creation of free radical on the latter, as suggested by eq. (9).

Cell—O° + CH₂=CH—CONH₂
$$\rightarrow$$

Cell—O—CH₂C°HR (9)

This is followed by subsequent addition of Aam molecules, thereby propagating the graft chain, which will be terminated by combination, disproportionation, or other means.

The above reaction mechanism explains the dependence of the graft yield on the initiator concentration. Both the initiator components, that is,

	Gra	aft Yield ((%) ^b				Gr	aft Yield	(%)	
Ι	II	III	IV	v	Time ^e (min)	Ι	II	III	IV	v
8	12	17	19	20	30	5	8	21	18	20
13	14	19	22	29	45	12	15	24	24	24
21	25	30	32	36	60	19	22	29	29	30
					75 90	$\frac{21}{22}$	$\frac{23}{25}$	30 36	30 36	$35 \\ 37$
	I 8 13 21	Gra I II 8 12 13 14 21 25	Graft Yield (I II III 8 12 17 13 14 19 21 25 30	Graft Yield (%) ^b I II III IV 8 12 17 19 13 14 19 22 21 25 30 32	$\begin{tabular}{ c c c c c } \hline & Graft Yield (\%)^b \\ \hline I & II & III & IV & V \\ \hline & 8 & 12 & 17 & 19 & 20 \\ 13 & 14 & 19 & 22 & 29 \\ 21 & 25 & 30 & 32 & 36 \\ \hline \end{tabular}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

Table III Effect of Time and Temperature of Polymerization on Grafting of Acrylamide onto Untreated Cotton and Alkali-Treated Cottons as Well as on DEAE Cottons

[Aam], 100% ows; [KMnO₄], 0.25 g/L; [citric acid], 0.25 g/L; pH 3; material-to-liquor ratio, 1 : 20.

^b I represents untreated cotton; II, alkali-treated cotton; III, IV, and V, DEAE cottons having 0.109, 0.211, and 0.43 %N.

^a Time: 60 min.

^c Temperature: 80°C.

 Mn^{4+} and citric acid, participate in the production of the primary free radical, which reacts with cellulose to form cellulose macroradicals capable of initiating grafting. Mn^{4+} can also directly attack the cellulose to form similar cellulose macroradicals. It is logical, therefore, that increasing the concentration of the KMnO₄ and citric acid in the polymerization medium favors grafting.

Enhancement of the susceptibility of cotton towards grafting by prior alkali treatment (Table II) suggests that cotton undergoes physical changes, which act in favor of grafting. Most probably, cotton is rendered more accessible, and, therefore, more cellulose hydroxyls will be available for reaction. Enhanced accessibility facilitates diffusion and adsorption of monomer and initiator, thereby providing a better environment for grafting to proceed. The same holds true for modified cotton with the additional effect of the DEAE groups. Introduction of these groups in the molecular structure of cotton cellulose in presence of alkali holds the structure open. This, in combination with increased accessibility, would make the DEAE cotton a better candidate for grafting. Grafting seems to be affected by the presence of DEAE groups as a chemical moiety. It is likely that these groups act as additional sites⁷ for grafting, as shown by eq. (10).

Cell-O-CH₂-CH₂-N + R^o
$$\longrightarrow$$
 Cell-O-CH₂-C-N + HR (10)
C₂H₅ C_2H_5 O C_2H_5

It is also possible that citric acid molecule is attached to the DEAE groups by virtue of the basicity of the latter and, in so doing, favors formation of free radicals in the proximity of the cellulose, thereby promoting grafting over homopolymerization.⁷

Table II shows that the graft yield increases significantly as the acrylamide concentration increases from 20 to 100% ows. This is observed regardless of the substrate used, but with the certainty that DEAE cottons acquire the highest graft yields and the untreated cotton the least, while the alkali treated cotton lies in between.

The favorable effect of monomer concentration on the graft yield could be associated with greater availability of Aam molecules in the vicinity of the cellulosic substrate at higher monomer concentrations. The substrate macroradicals are immobile, and their reaction with Aam molecules would rely on presence of the latter in their proximity. It is also possible to interpret this enhancement in graft yield in terms of the gel effect. The latter creates a viscous environment through dissolution of poly(Aam) in its own monomer and, in so doing, impedes termination of the graft. As a result, the molecular weight of the molecular weight of the graft and, therefore, the graft yield increases.

Table III shows the effect of duration and temperature on the graft yield. Obviously, the extent and rate of grafting increases as the temperature and duration increases within the range studied. This is rather a direct consequence of the favorable effect of both factors on the following:

- 1. decomposition of the redox system in question, giving rise to more free radicals;
- 2. swellability of substrate;
- 3. mobility of the monomer molecules;
- 4. diffusion of monomer from aqueous phase to fiber phase;
- 5. rate of initiation and propagation of the graft.

Table IV contains results of synthesis and characterization of modified cottons obtained through grafting of acrylamide onto the carbamoylethylated products of cotton, alkalitreated cotton, and DEAE cottons. Grafting was carried using different concentrations of acrylamide (100–300% ows), KMnO₄, and citric acid (0.25 g/L each); pH 3; and a material-to-liquor ratio of 1 : 20 at 80°C for 60 min. As is evident, the graft yield increases substantially by increasing the acrylamide concentration within the range studied. The same holds true for the nitrogen content and carboxyl content. Nevertheless, the magnitudes of the graft yield and nitrogen are determined by the nature of the substrate.

By virtue of having two types of additional groups for grafting, namely, the DEAE groups⁷ and the carbamoylethyl groups,¹⁶ DEAE cottons display higher graft yield and nitrogen content than cotton and alkali-treated cotton bearing only carbamoylethyl groups.

It is understandable that the nitrogen content is the total nitrogen of the sample representing the DEAE groups, plus the carbamoyethyl groups, plus the poly(Aam) in DEAE cottons, with only the latter two grouping in case of the untreated and alkali treated cottons. On the other hand, the carboxyl content expresses the magnitude of carboxyethylation occurring simultaneously during the carbamoyethylation as a re-

						Carba	moylethyl	ated Produ	act Derive	d from					
Substrate		Uni	treated Co	tton			Alkali	-Treated C	Jotton			DEAE C	otton with	$0.43 \ \%N$	
Acrylamide (g/L)	100	150	200	250	300	100	150	200	250	300	100	150	200	250	300
Graft yield (%)	35	39	47	49	52	39	42	51	56	64	42	48	59	63	71
	(41)	(44)	(53)	(56)	(58)	(45)	(48)	(55)	(61)	(69)	(47)	(53)	(92)	(68)	(20)
Nitrogen content	7.5	8.9	10.3	11.4	13.5	7.7	8.9	10.3	11.3	13.5	8.1	9.5	11.2	12.1	14
(%)	(4.5)	(7.1)	(8.2)	(8.9)	(10.9)	(4.6)	(7.3)	(8.4)	(8.8)	(10.8)	(5.1)	(7.8)	(8.9)	(9.2)	(11.2)
Carboxyl	20.4	32.1	34.6	45.5	51.9	20.1	33.5	34.1	45.5	51.5	20.4	32.1	34.6	45.5	51.9
(m eq/100 g S)	(40)	(63)	(75)	(89)	(10.5)	(40)	(63)	(75)	(89)	(105)	(40)	(63)	(22)	(88)	(105)
The values in ps cotton having 0.43 3: material-to-liquo	rentheses %N were g	represent 1 graft-polym 20 Alkali	the results the results terized using the hydroly	after sapon ig the indic	iffication, t cated amor	hat is, alki int of Aar	aline hydro 1, along wii	lysis. The th [KMnO	carbamoyl 4], 0.25 g/I	ethylated] .: [citric ac	broducts of id], 0.25 g/	cotton, alk L; tempera	tali-treated ature, 80°C	l cotton, ar C; time, 60	nd DEAE min; pH

sult of partial alkaline hydrolysis of the -CONH₂ groups of the carbamoylethyl cotton to carboxyethyl ethyl groups. This is rather an inevitable reaction, usually accompanying the carbamoylethylation, and, as evidenced by current data, it is independent of the nature of the substrate. The magnitude of the carboxyl contents is also not affected by grafting since their values remain constant after grafting.

Saponification

Results given in parenthesis in Table IV show the effect of saponification on the acrylamide moieties present as a group or in the form of polymer (graft) in the aforementioned carbamoyethylated products-g-poly(Aam). Obviously, the graft yield increases after saponification and so does the carboxyl content. The nitrogen content, on the other hand, decreases. This is rather a direct consequence of the conversion of the -CONH₂ grouping in the acrylamide moieties to -COOH groups.^{17,18} At any event, however, we are now dealing with different modified cottons. While those derived from cotton and alkali-treated cotton bear carbamoyl and carboxyethyl in the form of a group, as well as in the polymer form, DEAE cottons possess additional DEAE groups. This indeed imparts ionic exchange properties to these cottons and makes them a suitable candidate for dye adsorption, as shown below.

Dye Adsorption

The ability of the aforementioned carbamoylethyl cotton products grafted with poly(acrylamide) before and after saponification to adsorb different dyestuffs from aqueous solution was studied. This is done to feature the ionic properties of these substrates and to figure out their suitability to serve as ionic exchangers.

Table V contains the amount of dye adsorbed by the said different modified cottons. Evidently, substrates prepared from DEAE cotton exhibit the highest ability to adsorb and, therefore, to remove different dyes from aqueous solutions; whereas those prepared from cotton exhibit the least. On the other hand, substrate prepared from alkali-treated cotton stand in a midway position. The ability to remove different dyes from aqueous solutions is directly related to the graft yield.

Table V also shows the dependence of dve adsorption on the substrate (i.e., dye removal from solution) on the type and nature of the dye. Dyes

Graft Yield, Nitrogen Content, and Carboxyl Content of the Carbamoyethylated Products-g-Poly(Aam) Before

Table IV

Graft Yield (%)	$\begin{array}{c} \mbox{Acid Dye Adsorption} \\ \mbox{(mg/1 g S)} \end{array}$	Direct Dye Adsorption $(mg/1 \ g \ S)$	Reactive Dye Adsorption (mg/1 g S)	$\begin{array}{c} Basic \ Dye \ Adsorption \\ (mg\!/\!1 \ g \ S) \end{array}$
32	115	102	123	124
(39)	(121)	(105)	(125)	(127)
39	130	109	127	128
(44)	(135)	(111)	(129)	(130)
47	133	115	134	130
(53)	(136)	(118)	(136)	(133)
49	135	120	138	132
(56)	(138)	(125)	(140)	(135)
52	137	130	138	135
(58)	(140)	(135)	(142)	(138)
31	120	111	124	123
(42)	(123)	(127)	(126)	(128)
42	135	117	127	132
(48)	(138)	(131)	(129)	(133)
51	137	127	134	135
(55)	(139)	(137)	(138)	(137)
56	139	131	140	136
(61)	(145)	(138)	(142)	(139)
64	141	134	140	140
(69)	(145)	(140)	(145)	(146)
40	121	113	127	128
(45)	(122)	(128)	(138)	(143)
48	134	122	131	131
(53)	(146)	(130)	(132)	(130)
59	142	129	135	137
(65)	(147)	(135)	(138)	(135)
63	143	133	144	140
(68)	(148)	(138)	(146)	(138)
71	145	139	144	143
(76)	(148)	(141)	(148)	(148)
0	1.02	1.4	2.52	1.5
	(1.05)	(1.62)	(2.7)	(1.7)

 Table V
 Ability of the Carbamoyethylated Products-g-Poly(Aam) Before and After Saponification to Remove Dyestuffs from Aqueous Solution

The values in parentheses represent the results obtained with the saponified products of the modified cottons under investigation. Dye adsorption is expressed as mg dye/g substrate. Conditions for dye adsorption: Time, 3 h; temperature, 80°C; pH 3; dye concentration, 200 mg/L.

used encompass direct, reactive, acid, and basic dyes. The extent of dye removal is determined by nature of both the substrate and the dye. The ability of the substrate to hold the direct dye is a manifestation of the ability of the amino and hydroxyl groups of the substrate, along with the pore size of its physical structure, to trap the dye via physical association. The greater ability for acid dye removal seems to be in conformation with the basicity of the copolymer. The higher the basicity, the greater the interaction with the acid dye. It goes without saying that the basicity of the amino groups in substrates based on DEAE cotton is the highest, and it is the least with those based on cotton. For basic dye (Table V), adsorption on the substrate and removal from the aqueous phase of the dyeing system occur mainly through interactions involving the carboxyl groups of the substrate and the dye molecule. The dye is held to the substrate via ionic forces.

With the reactive dye, on the other hand, the extent of dye removal would be expected to rely on (1) the ability of the substrate to react chemically with the dye and (2) the ability of the substrate to hold the dye via ionic or other forces. While the cellulose hydroxyls of the substrates in question act as sites for dye sorption, they also act as a reactive center for reaction of the dye under the influence of the amino groups, which act as a built-in catalyst in

the case of substrates derived from DEAE cotton. Meanwhile, the amino groups themselves interact with the dye via formation of salt linkage.

Dependence of the extent of dye removal upon the nature of the dye is rather expected. The nature of the dyes is expected to decide the affinity of the dye for the exchanger, which, in turn, is governed by as many factors as penetration, availability, selectivity, and accessibility. The extent of dye removal and the ability of the substrate to remove the dye increases after the saponification treatment. Nevertheless, this increment is not so striking.

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