

Epichlorohydrin-Triethanolamine Reaction in the Preparation of Quaternary Cellulose Anion Exchangers

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Synopsis

The reactions between cotton cellulose and a mixture of triethanolamine and epichlorohydrin in the presence of aqueous NaOH have been studied. It has been shown that cotton fabric pretreated with aqueous base and then reacted with a 3:1 mole ratio of epichlorohydrin to triethanolamine forms a strong base anion exchanger. Resultant properties differed from those of the product made by the conventional method of preparing ECTEOLA cellulose, a commercial product of the same reactants. Titration curves of the strong base cellulose exchangers were similar to that obtained with the product of the reaction between cotton and trimethylglycidylammonium chloride. Substitution of triethylamine for the triethanolamine also resulted in a quaternary base cellulose anion exchanger. A cyclic diquaternary salt, [2,5-*p*-dioxanylenebismethylene]bis[tris(2-hydroxyethyl)ammonium chloride], has been isolated from the triethanolamine-epichlorohydrin mixture and a mechanism of the reaction has been proposed.

INTRODUCTION

Some interesting observations were reported rather recently¹⁻⁴ on the nature of ECTEOLA cellulose, a commercially available anion exchanger of unknown composition prepared by reacting alkali cellulose with triethanolamine and epichlorohydrin. It has had wide application in the fractionation of such polymeric substances as nucleotides, polynucleotides, and polysaccharides^{5,6} since its introduction by Peterson and Sober.⁷ It has been suggested, among other possibilities, that the epichlorohydrin reacts with the hydroxyl groups of the triethanolamine. Jakubovic^{3,4} suggested that the alkali cellulose is crosslinked by epichlorohydrin or its reaction product with the alkylol amine. No evidence for the formation of a quaternary ammonium group on ECTEOLA cellulose has been reported. In our research program concerned with the preparation of glycidyl-substituted amines^{8,9} and quaternary ammonium compounds for use in the chemical modification of cotton, we have studied the reaction products of tertiary amines and epichlorohydrin.¹⁰ We have shown that when epichlorohydrin and triethanolamine in the 3:1 mole ratio, used by Peterson and Sober, are

reacted at room temperature in the absence of alkali and cotton, a waxy product identified as a quaternary [2,5-*p*-dioxanylenebismethylene]bis-[tris(2-hydroxyethyl)ammonium chloride] can be isolated.¹⁰ While the simple glycidyltriethanolammonium chloride was not isolated, evidence for its initial formation is shown by the production of the cyclic diquaternary mentioned. It is believed that addition of the glycidyltriethanolammonium chloride or graft polymers of it to cotton accounts for the anion exchange properties of the quaternary-base product. It has been demonstrated that chemicals used for preparation of ECTEOA cellulose can be applied to cotton in the fabric form under certain conditions such that the resultant product is a quaternary cellulose anion exchanger. These products have been compared with those formed by use of the conventional method for preparation of ECTEOA celluloses^{1,7} which utilizes wood pulp under more severe reaction conditions.

EXPERIMENTAL

Cellulose

An 80 × 80 cotton print cloth weighing 3.12 oz./yd.² was desized, scoured, and then processed in commercial peroxide bleaching equipment. All preparations of anion exchangers were with cellulose in this form rather than with pulp. The reason for this procedure is that fabric properties of the finished cloth may be measured and used as an indication of type of reaction product formed. For example, the crease recovery angles of the fabrics as measured by use of the Monsanto wrinkle recovery tester¹¹ can be used to compare fabrics finished with the reactants under consideration with those treated with epichlorohydrin alone. The latter imparts to cottons pretreated with aqueous alkali of all strengths only high wet crease recovery.¹²

Chemical Treatment

Fabric samples measuring approximately 13 × 13 in. and weighing 10–12 g. were padded to approximately 100% wet pickup with 8, 23, or 28% aqueous NaOH and then immersed in stoppered cylinders containing a 3:1 mole ratio mixture of epichlorohydrin and triethanolamine at room temperature for various lengths of time.

In a few instances, fabrics pretreated with aqueous base were padded through the 3:1 epichlorohydrin–triethanolamine mixture and then heated in a forced-draft oven at 100°C. for 10 min.

Testing

All fabrics were acidified, thoroughly washed with distilled water, ironed dry, and air-equilibrated for 24 hr. before being tested for fabric properties, weight gains, and nitrogen analyses.

Potentiometric Titrations

The cotton anion exchangers in the salt form were ground in a Wiley mill and regenerated to the base form with 0.05*N* NaOH according to procedures described previously.¹³ Exchangers in base form were dried over P₂O₅ under vacuum to constant weight before elemental analyses, and anion-exchange capacities on a dry weight basis were determined. An accurately weighed sample of sufficient weight to give approximately 0.6 meq. of replaceable anion was placed in a specially designed titration flask containing exactly 50.00 ml. of 1*M* NaCl solution prepared with conductivity water, kept in a nitrogen atmosphere, and titrated as described previously.¹³ All pH measurements were made with either a Beckman Model GS or a Model 101900 pH meter to ± 0.05 pH units.

RESULTS AND DISCUSSION

For fabrics pretreated with dilute aqueous base and then reacted with the 3:1 mole ratio of epichlorohydrin-triethanolamine for intervals of 1-3 days at 25°C., the weight gains varied only slightly, with a maximum add-on of 6%. The amount of bound nitrogen was always 0.2% by weight. Finished fabrics had wet crease recovery angles of approximately 240 (W + F)^o which were much lower than the 300 (W + F)^o angles obtained

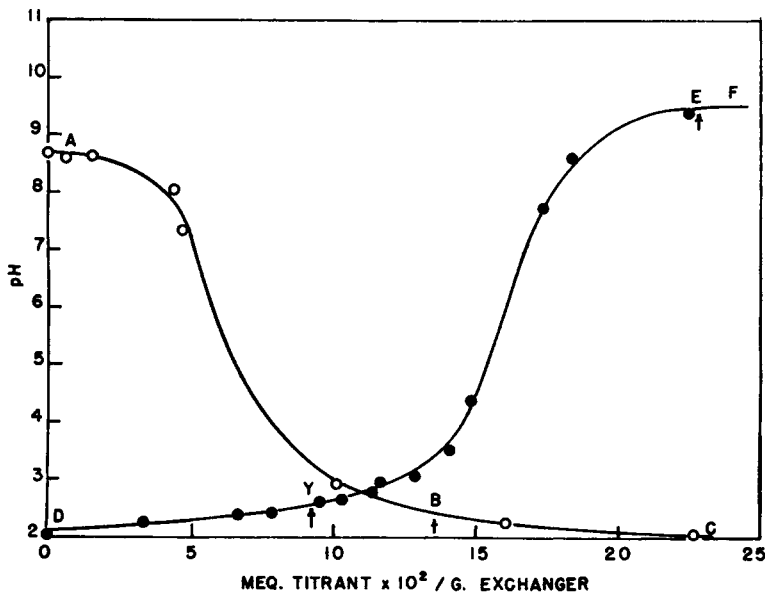


Fig. 1. Potentiometric titration curve of cellulose anion exchanger formed by padding fabric with 8% aqueous NaOH and then reacting it in a 3:1 mole ratio mixture of epichlorohydrin and triethanolamine at 25°C.: (O) titration of the regenerated base equilibrated with 0.5*M* NaCl vs. standardized 0.1*M* HCl; (●) is the titration curve of excess HCl and salt form vs. standardized 0.1*M* NaOH. AB and YE correspond to theoretical capacities of exchangers. (Sample weight 0.7988 g., 0.19% N, 3.8% add-on.)

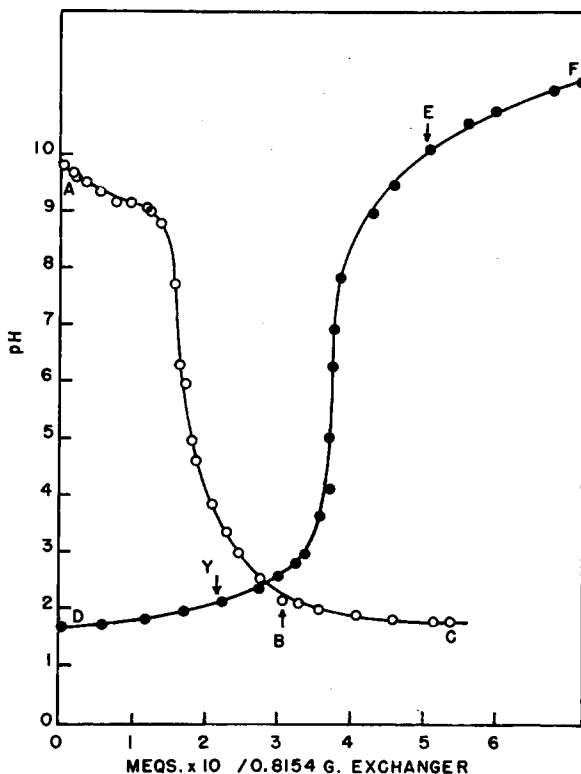


Fig. 2. Potentiometric titration curves of cellulose anion exchanger formed by padding fabric with 28% aqueous NaOH and then reacting it in a 3:1 mole ratio mixture of epichlorohydrin and triethanolamine at 25°C.: (O) titration of the regenerated base equilibrated with 0.5M NaCl vs. standardized 0.1M HCl; (●) titration curve of excess HCl and salt form vs. standardized 0.1M NaOH. AB and YE correspond to theoretical capacity of exchanger. (Sample weight 0.8154 g., 0.52% N, 12.6% add-on.)

when epichlorohydrin alone is added to fabric pretreated with dilute base. The dry crease recovery angles of only 200 (W + F)° were equivalent to those of the epichlorohydrin controls. All of these fabrics titrated as strong-base anion exchangers. Typical curves are shown in Figure 1.

In order to increase the nitrogen content and resultant capacity of the exchanger, it was necessary to increase the concentration of alkali used in the pretreatment. Use of 23–28% aqueous NaOH resulted in add-ons of epichlorohydrin–triethanolamine reaction product as high as 20% by weight after a reaction interval of 1 day at 25°C. Bound nitrogen contents as high as 0.62% by weight resulted. All finished fabrics had wet crease recovery angles higher than 250 (W + F)°, but these values were approximately 30 (W + F)° lower than those obtained at like add-ons of epichlorohydrin in the presence of only NaOH. At the higher nitrogen contents, the dry crease recovery angles increased to approximately 240 (W + F)°, indicating that some crosslinking of the cellulose chains oc-

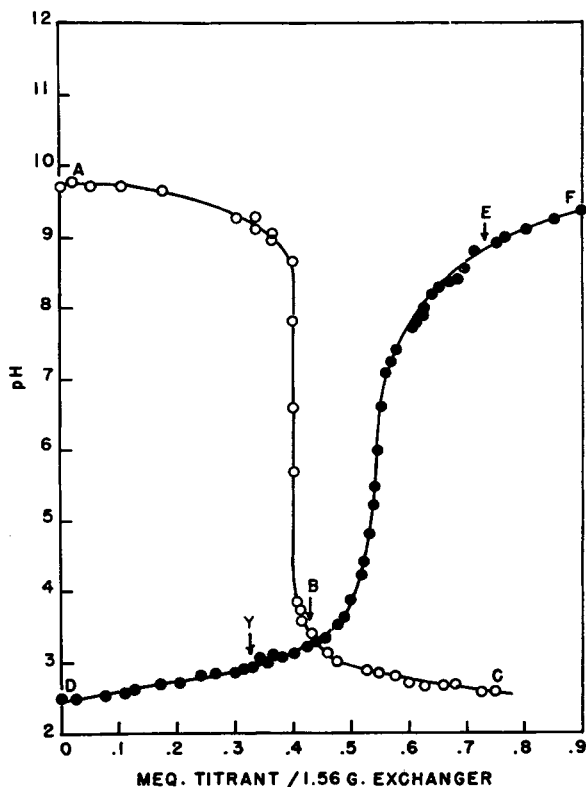


Fig. 3. Potentiometric titration curves of a cellulose anion exchanger formed by reacting pieces of cotton fabric previously soaked in 28% aqueous NaOH at 0°C. with a 3:1 mole ratio mixture of epichlorohydrin-triethanolamine: (O) regenerated base equilibrated with 0.5M NaCl vs. standardized 0.1M HCl; (●) titration of excess HCl and salt form vs. standardized 0.1M NaOH. AB and YE correspond to theoretical capacity of exchanger. (Sample weight 1.5592 g., 0.37% N, 9.0% add-on.)

curred. These angles were comparable to those obtained with like add-ons of nitrogen from a similar mixture of epichlorohydrin with triethylamine rather than triethanolamine. Again, all finished fabrics titrated as strong-base anion exchangers. Typical curves for a fabric which had been padded with aqueous 28% NaOH and then reacted in a 3:1 mole ratio mixture of epichlorohydrin-triethanolamine are shown in Figure 2. A fabric which had been cut into small pieces and then reacted exactly according to procedure of Peterson and Sober⁷ also resulted in a strong-base anion exchanger. In this instance, the fabric pieces were soaked in the concentrated aqueous base and then immersed in an ice bath before being treated with the 3:1 mole ratio of epichlorohydrin-triethanolamine mixture. Titration curves for such a sample having 0.37% nitrogen content are illustrated in Figure 3.

For comparative purposes, titration curves for commercially available samples of ECTEOLA cellulose and of DEAE cellulose obtained from the

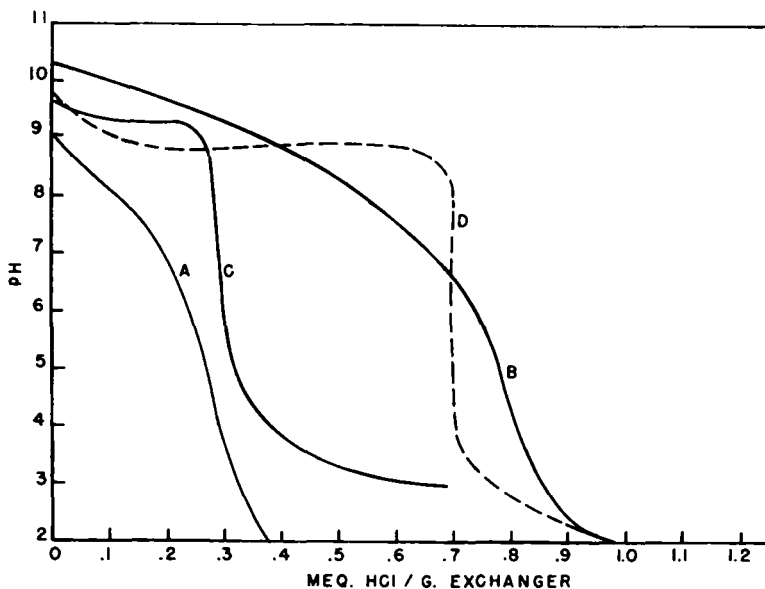


Fig. 4. Potentiometric titration curves of regenerated base forms of exchangers equilibrated with $0.5M$ NaCl vs. standardized $0.1M$ NaOH: (A) 1.7419 g. of a commercially available ECTEOLA cellulose of 0.21% N; (B) 0.5015 g. of a commercially available DEAE cellulose of 1.14% N; (C) represents 1.060 g. of a quaternary cellulose anion exchanger prepared by reacting alkali cellulose with glycidyltrimethylammonium chloride to a 0.40% N; (D) represents 0.5005 g. of a quaternary cellulose anion exchanger prepared by reacting a cotton fabric prepadded with 23% aqueous NaOH with a 3:1 molar ratio of epichlorohydrin-triethylamine at $25^{\circ}C$. to a 1.01% N content.

Bio-Rad Co., and a quaternary cellulose prepared by reacting alkali-treated cotton with glycidyltrimethylammonium chloride are illustrated in Figure 4. Included in Figure 4 is a titration curve for a cellulose exchanger prepared in the fabric form when triethylamine was substituted for triethanolamine. This example is included to show that the quaternary sites can be introduced into cotton with a tertiary amine not containing alkylol groups. It is noteworthy that even higher dry crease recovery angles were obtained with the triethylamine-epichlorohydrin reaction than with the triethanolamine-epichlorohydrin reaction in the presence of dilute aqueous NaOH. Triethylamine ($pK_B = 3.3$) is much more basic than triethanolamine ($pK_B = 6.2$).

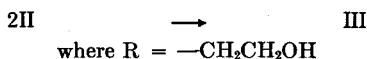
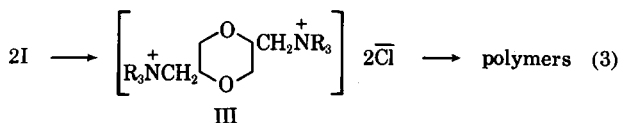
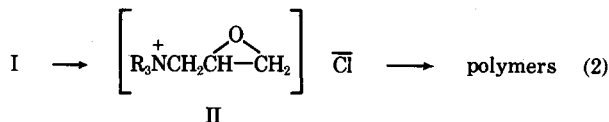
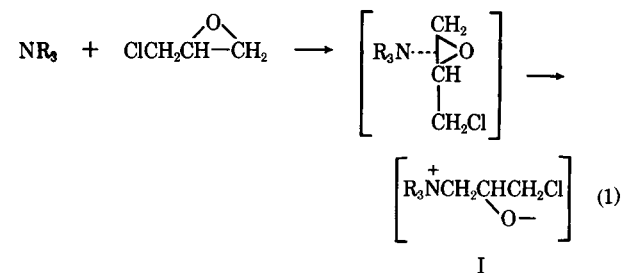
Fabrics which were only padded with the 3:1 epichlorohydrin-triethanolamine mixture and then heated to $100^{\circ}C$. for 10 min. had add-ons of approximately 2% by weight and nitrogen contents less than 0.1% by weight. Fabrics thus finished showed no increase in dry crease recovery angles, but had wet crease recovery angles approaching $300 (W + F)^{\circ}$. The latter value is usually obtained when cotton is reacted with epichlorohydrin in the presence of concentrated aqueous bases.

With ECTEOLA celluloses made in the presence of excess concentrated base, such as those reported in the studies of Veder,¹ the titration curves

indicate that the resultant product may have been a mixture of weak-base and quaternary-base anion-exchange sites. Veder noted the very low exchange capacity of his ECTEOLA celluloses in the pH range 5.5–8. In these experiments, the amount of NaOH used was in large excess over that used by our padding technique of fabric with even the most concentrated base solution investigated. Such excesses of base favor resin deposition within cellulose fibers.

The solution which was in contact with alkali cotton fabric for 16–24 hr. separated into two layers. The top layer was a yellowish, thick liquid. The lower portion was a balsam-like substance. In the absence of NaOH and cellulose, a diquaternary salt, [2,5-*p*-dioxanylenebismethylene]bis-[tris(2-hydroxyethyl)ammonium chloride], separated within 20 hr. at room temperature in high yield. Addition of 23% NaOH to a similar mixture of 3:1 epichlorohydrin-triethanolamine caused a resin formation after 12–16 hr. at 25°C. and precipitation after a few days of a granular product containing 4.4% chlorine and 2.2% nitrogen. The granular powder was highly swollen in water and acid washes. After dehydration with alcohol and ether, a dry, white powder was obtained. The deposition of the resins in or on the cellulose may well furnish the desirable properties of ECTEOLA celluloses.

As a result of spectroscopic studies,¹⁰ we have found that an intermediate is formed immediately between the tertiary amine acting as an electron donor and the oxirane ring acting as an electron acceptor. The result is in effect equivalent to a quaternization of the tertiary amine. The quaternary compound can then rearrange, dimerize, or even polymerize, or react with cellulose, depending on experimental conditions. The reactions which can occur are numerous, and those given in eqs. (1)–(3) are illustrative:



Cellulose, alkali, and epichlorohydrin also react in a number of ways.¹² Since the latter reactions are not concerned with the presence of nitrogen in the product, and hence would not impart anion exchange properties to cellulose, they are omitted here. Nevertheless, it should be noted that these reactions are important factors in determining the degree of cross-linking of the polymeric chains and hence influence the resultant properties of the exchangers prepared with tertiary amines. Although the simple glycidyl quaternary (II) has never been isolated with triethanolamine, it is known that glycidyltrimethylammonium chloride reacts with cotton in the presence of alkali to form a strong anion exchanger (Fig. 4). The diquaternary III, which has been isolated from the epichlorohydrin-triethanolamine reaction mixture, does not react with cotton. However, its formation requires the presence of II or a precursor of it, either of which is capable of reacting with cellulose.

SUMMARY

Cellulose anion exchangers have been prepared by padding cotton fabric with aqueous NaOH varying in concentration from 8 to 28% and then reacting the pretreated fabric with a 3:1 molar ratio mixture of epichlorohydrin and triethanolamine. While the glycidyltriethanolammonium chloride has not been isolated, evidence for its formation is shown by the isolation of a cyclic diquaternary, [2,5-*p*-dioxanylenebismethylene]bis[tris(2-hydroxyethyl)ammonium chloride]. Potentiometric titration curve for the strong-base anion exchangers have been compared with those of a weak-base cellulose exchanger, with the conventional ECTEOLA-cellulose exchanger, with a quaternary-base exchanger prepared by reacting alkali cellulose with glycidyltrimethylammonium chloride, and with an exchanger prepared by use of triethylamine rather than triethanolamine. A mechanism for the probable reaction is suggested.

Mention of a company and/or product by the Department does not imply approval or recommendation of the company or product to the exclusion of others which may also be suitable.

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Résumé

Les réactions entre la cellulose de coton et un mélange de triéthanolamine et d'épichlorhydrine en présence de soude caustique aqueuse ont été étudiées. On a montré que les tissus de coton prétraités avec une base aqueuse et ensuite traités avec un mélange à rapport molaire 3:1 d'épichlorhydrine et de triéthanolamine formaient un échangeur anionique de base forte. Les propriétés résultantes différaient de celles du produit préparé par la méthode conventionnelle de préparation de cellulose ECTEOLA, produit commercial des mêmes réactifs. Des courbes de titration des échangeurs cellulose de base forte étaient semblables à celles obtenues avec le produit de la réaction avec le coton et le chlorure de triméthylglycidylammonium. La substitution de la triéthylamine par la triéthanolamine a également comme conséquence la formation d'un échangeur anionique cellulose de base quaternaire. Un sel cyclique diquaternaire, le chlorure de [2,5-*p*-dioxanylènebisméthylène]bis[tris(2-hydroxyéthyl)ammonium] a été isolé au départ du mélange triéthanolamine-épichlorhydrine et un mécanisme de la réaction a été proposé.

Zusammenfassung

Die Reaktionen zwischen Baumwollcellulose und einem Triäthanolamin-Epichlorhydrin-Gemisch in Gegenwart von wässrigem NaOH wurden untersucht. Es wurde gezeigt, dass Baumwollgewebe bei Vorbehandlung mit wässriger Base und darauffolgender Reaktion mit einem 3:1-Gemisch von Epichlorhydrin und Triäthanolamin starke Basen mit Anionenaustauschereigenschaften bilden. Diese Eigenschaften unterschieden sich von denjenigen des nach der konventionellen Methode der ECTEOLA-Cellulose-Herstellung, eines handelsüblichen Produktes aus den gleichen Ausgangsprodukten, erhaltenen Produkten. Die Titrationskurven der starken Celluloseaustauscher-Basen waren den mit dem Reaktionsprodukt aus Baumwolle und Trimethylglycidylammoniumchlorid erhaltenen ähnlich. Substitution von Triäthylamin für das Triäthanolamin führte ebenfalls zu einer quaternären Celluloseanionenaustauscher-Base. Ein zyklisches diquaternäres Salz, [2,5-*p*-Dioxanylenbismethylen]bis[tris(2-hydroxyäthyl)ammoniumchlorid], wurde aus der Triäthanolamin-Epichlorhydrinmischung isoliert und ein Reaktionsmechanismus vorgeschlagen.

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