

Electrical Conductivity of γ -Irradiated Native and Mercerized Cotton Celluloses

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Synopsis

In the present study the electrical conductivity (σ) of ball-milled and NaOH-treated cotton fibers were measured in vacuum. The induced electrical conductivity and the activation energy ΔE of γ -irradiated samples were measured as a function of radiation doses and at various temperatures. It was found that γ -irradiation of cotton fibers either decreases or increases its electrical conductivity. Thus, it was found that γ -irradiation of cotton reduces the conductivity of the samples having particle sizes ranging from 0.07 to 0.11 mm and the magnitude of the reduction diminishes as the particle size increases. The results have also shown that, for any given concentration, γ -irradiation of NaOH-treated samples causes an increase of the measured electrical conductivity.

INTRODUCTION

The electrical conductivity of textile fibers has been previously investigated by several workers.¹⁻⁸ Electrical conductivity is of concern because build up of the static charges on textile fibers causes a variety of problems in the textile industry. Most of the earlier investigators have been principally concerned with the effect of humidity on the electrical properties of cotton fibers¹⁻⁸ and express the view that moisture is the most important factor in determining the electrical conductivity of textile materials and causes a 10 magnitude variation in electrical conductivity. Actually moisture content, moisture distribution, ion concentration, chain length, ash, density, and species are all important factors influencing the dc resistance of textile fibers. However, the effect of high-energy ionizing radiation on the electrical properties of textile fibers has not yet been fully investigated.

The present study is undertaken to study the electrical conductivity of γ -irradiated native and mercerized cotton celluloses.

EXPERIMENTAL

Fibers of Giza 66 were first washed with hot ethanol, then boiled for 25 h in a solution of 1% NaOH, washed with distilled water and dilute acetic acid, neutralized with dilute NaOH, and finally washed several times with distilled water.

The dried fibers were cut into small pieces and then ground in a hardened steel vial containing two hardened steel balls. The vial was fitted to a spex-Mixer mill which was rotated several times for short periods. The obtained powder was then sieved to particle fractions of different particle sizes.

The powder was immersed in NaOH solution of various concentrations at room temperature (27°C) for 12 min. The material:liquor ratio was 1:50 (w/w). The powder was then washed with distilled water and then treated with 1% acetic acid solution for 5 min.

The conductivity measurements were carried out on the samples using dc electrometer of type TR-150 I Orion-K.T.V. (Budapest). A sample holder or conductivity cell, made of Pyrex tubing was used. The Pyrex was provided with a ground joint to be connected to a detachable head through which one electrical lead passed by way of a tungsten rod to the glass seals. In a diametrically opposite side of the tube, the second lead was spot welded and sealed in glass via a tungsten rod. The two electrodes were made of platinum. The conductivity cell with the specimen inside could be evacuated very well by means of an upper tube designed in the ground joint.

The samples used in the measurements were pressed into cylindrical pellets of 16 mm diameter and 3 mm thickness, at a pressure of about 200 kg/cm². This pressure was chosen as the electrical conductivity was independent of load.

The X-ray diffraction patterns were obtained on a Siemens U 500 diffractometer. The powder was filled in the specimen holder and all the samples were subjected to the same pressure.

The samples were irradiated at room temperature in a ⁶⁰Co γ -radiation cell with a dose rate of 67 rad/s.

RESULTS AND DISCUSSION

Measurements of electrical conductivity σ were carried out on samples of cotton powder of particle diameter ranging from 0.07 to 0.46 mm in the form of compressed discs. Values of σ were measured at different temperatures from 476°K down to 333°K and in vacuum. The variation of $\log \sigma$ for the various samples with the reciprocal of absolute temperature $\left(\frac{1000}{T}\right)$ is shown in Figure 1.

It will be seen from Figure 1 that conductivity increases with decreasing particle size. The conductivity of the sample of largest particle size, for example, assumes value of the order ($-11.5 \Omega^{-1} \text{ cm}^{-1}$) at the temperature 373°K whereas, that of the smallest particle size is of the order of $-10.7 \Omega^{-1} \text{ cm}^{-1}$ at the same temperature.

Since there is a positive temperature coefficient of electrical conductivity $\left(\frac{d\sigma}{dT}\right)$ for all lines, all the specimens investigated have a semiconducting character in the investigated temperature range. The conductivity varies exponentially with the absolute temperature according to the well-known relation.⁸

$$\sigma = \sigma_0 e^{\frac{-\Delta E}{2KT}}$$

From this linear relationship the activation energy ΔE was calculated.

Where σ is the electrical conductivity at a given temperature T , σ_0 is the initial conductivity, ΔE is the activation energy, and K is the Boltzmann constant.

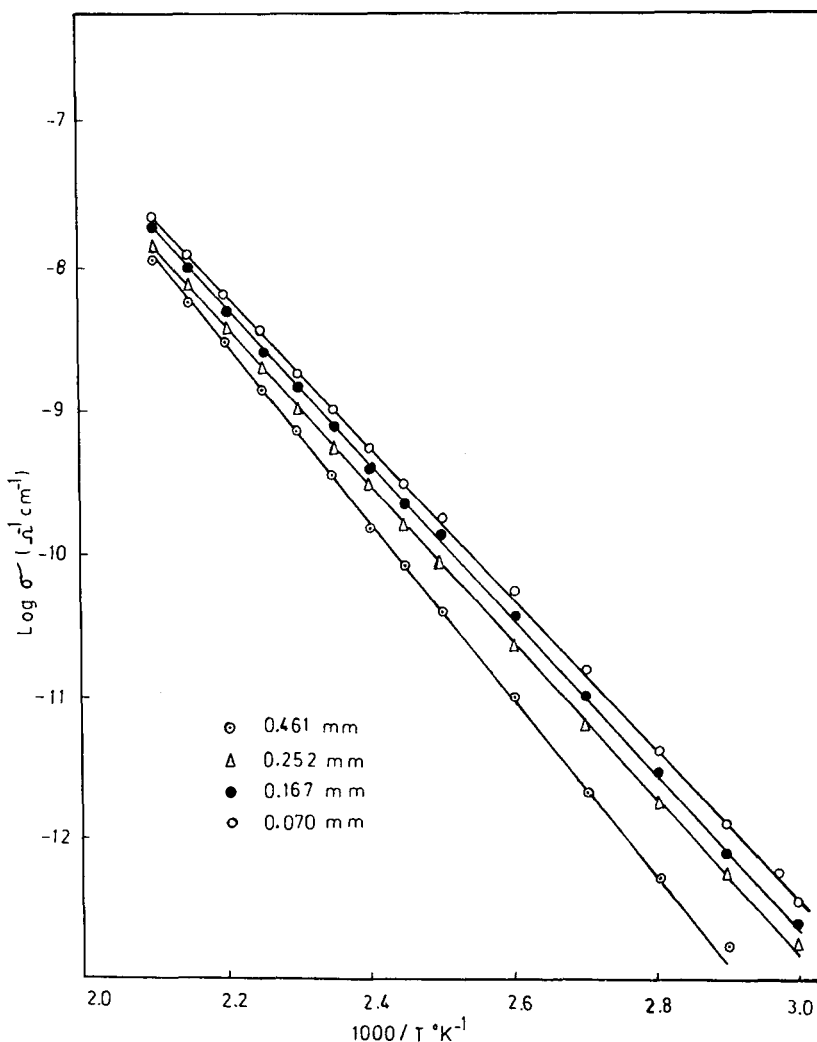
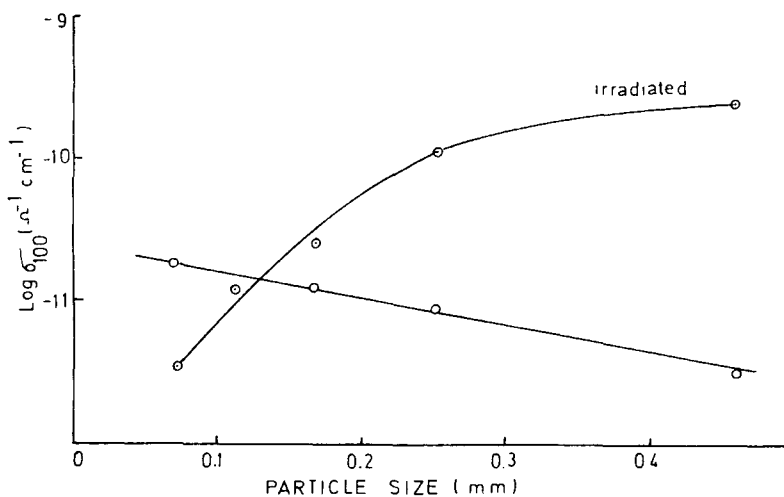


Fig. 1. Variation of the electrical conductivity of the ball-milled cotton fibers with temperature.

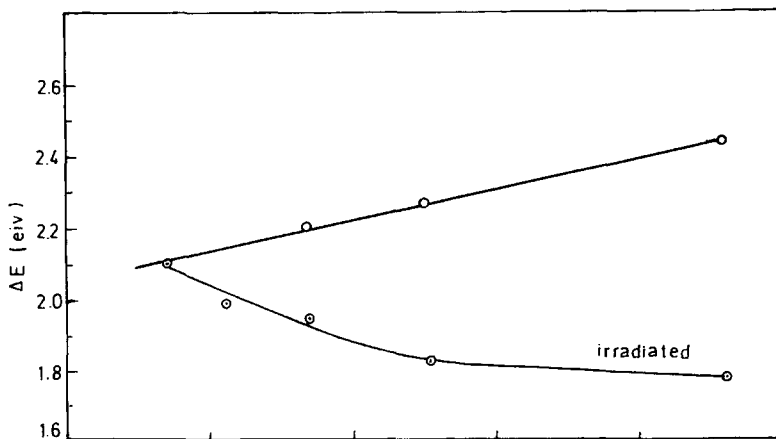
The relatively slight response of σ with temperature involving ΔE values which can be interpreted by a small single band model. The ΔE values are assumed to correspond to the activation energies of conduction.

The variation of $\log \sigma_{100}$ (measured at 100°C) and ΔE with the particle size is represented graphically in Figure 2 (A) and (B) respectively. It is evident from this figure that $\log \sigma$ decreases while ΔE increases linearly with the increase of particle size.

The variation of σ and ΔE with particle size could be attributed to a decrease in the degree of crystallinity or an extension and formation of amorphous regions in crystalline cotton. As a consequence, there is an increased freedom of movement of the side groups and of portions of the cellulose molecules. This is in agreement with the fact that the current will be



(a)



(b)

Fig. 2. (A) Variation of electrical conductivity of ball-milled cotton fibers with particle size before γ -irradiation. (B) Variation of the activation energy with particle size of cotton fibers after γ -irradiation.

flowing in the noncrystalline regions of the fibers.¹⁻³ Indeed, the ordered arrangement of cellulose materials in a crystalline region would be expected to be highly insulating.

The samples under investigation were then exposed to γ -radiation to a dosage level of 4×10^7 rad in an atmosphere of air at room temperature. Figure 3 indicates that $\log \sigma$ for the exposed samples decreases also linearly as the temperature is decreased. The variation of $\log \sigma_{100}$ and ΔE as a function of particle size of the exposed samples is represented graphically in Figure 2. It appears from Figure 2 that $\log \sigma_{100}$ increases while ΔE decreases with the

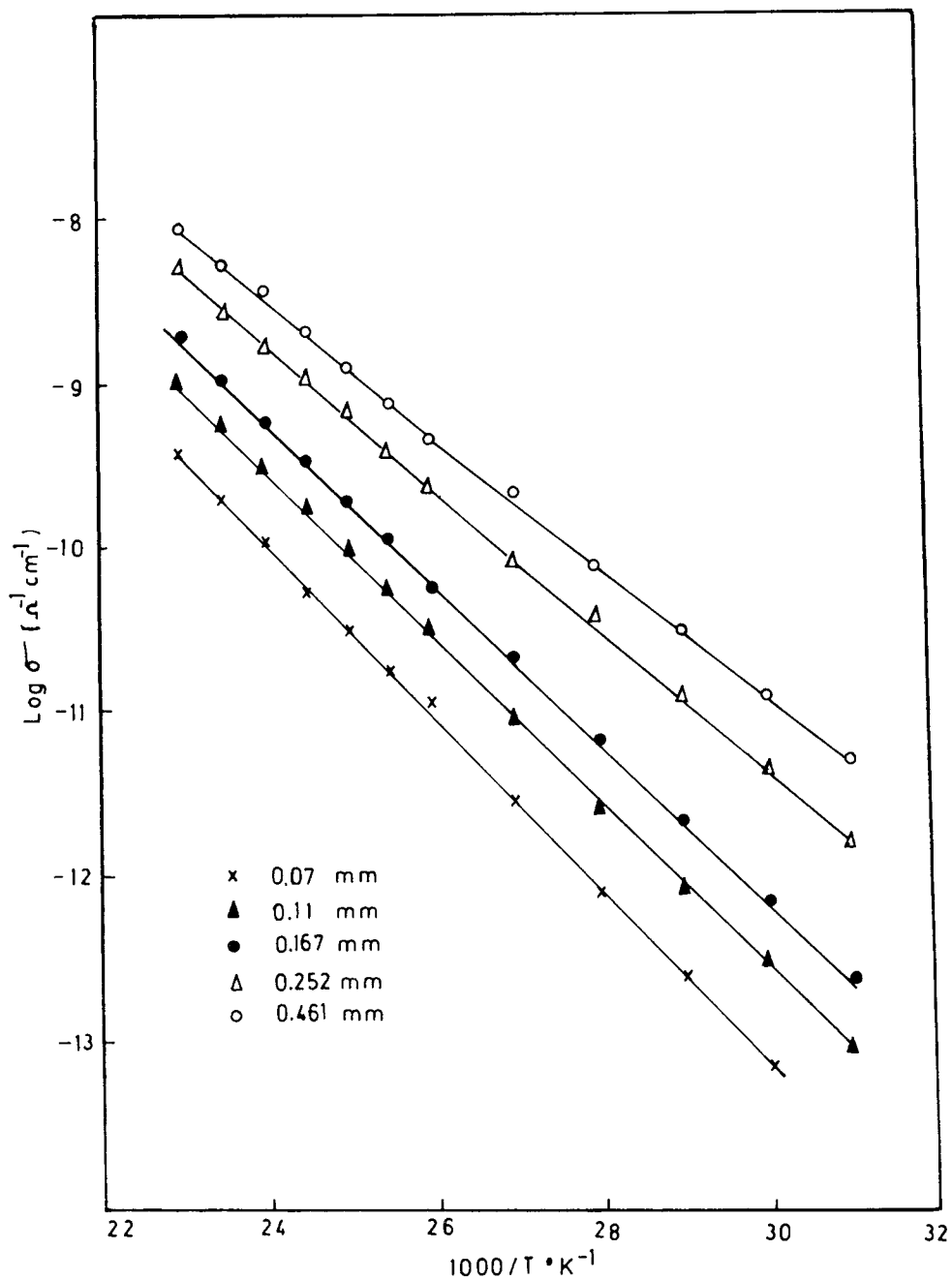


Fig. 3. Variation of the electrical conductivity of the γ -irradiated ball-milled cotton fibers with temperature.

increase of particle size. But it seems very interesting to mention here that γ -irradiation of cotton powder either decreases or increases its electrical conductivity, and consequently, either increases or decreases the correspond-

ing ΔE values of the test samples, depending on their degree of crystallinity with respect to their values before irradiation.

Thus, it appears from Figure 2 that γ -irradiation of cotton reduces the conductivity of the samples having particle sizes ranging from 0.07 to 0.11 mm, and the magnitude of this reduction diminishes as the particle size increases. γ -irradiation of the samples having a particle size higher than 0.11 mm in diameter increases their conductivity over those of the unexposed ones. It appears from Figure 2 that γ -irradiation affects the values of ΔE , but in the opposite direction to that of $\log \sigma_{100}$. That is to say, the curves representing the behavior of $\log \sigma_{100}$ values as a function of degree of crystallinity for the unirradiated and γ -irradiated samples are mirror images to those constructed for the ΔE values displaying a plane of symmetry.

This could be easily explained on the basis that γ -irradiation highly affects cotton with small particle size, since these have originally more lattice defects than cotton with large particle size. Thus, γ -irradiation of the lower particle size sample may induce further lattice defects and these lattice defects may act as scattering centers and barrier energy for the flow of electrical current. This may be reflected in the decrease of the obtained values of the electrical conductivity and the subsequent increase of activation energy values. This was in accordance with the previous findings of Viadiminski and Niki-tinshaya⁹ and Ibrahim et al.¹⁰

An explanation of this behavior includes the stepwise mechanism of γ -radiation damage. This takes place via particle dissociation of macromolecular cellulose polymer giving rise to a free radicals. The generated free radicals may recombine with other molecules and/or remain unchanged. This in turn may produce long-chain or cross-linked copolymer and the electrical conductivity increases, therefore, the corresponding activation energy increases progressively in the same direction.

The increase of conductivity of the coarse sample after γ -irradiation could be attributed to the increase of the number and mobility of charge carriers present. These charge carriers are created as a result of the ionizing effects of γ -radiation damage (γ -radiolysis) which provides mobile-free charge carriers capable of conduction of the electric current.

The subsequent decrease in values of $\log \sigma$ of γ -irradiated samples with decreasing particle size may be considered to be associated with irradiation damage and the formation of color centers (impurity centers). The latter is caused by the creation of trapping centers and/or rearrangement in fiber structure as a result of irradiation of the less-ordered samples. However, it was generally accepted that the type and number of free radicals generated from cellulose after γ -irradiation depends on the fine structure of cellulose.^{11,12}

Samples of cotton powder of the same particle size (0.167 mm in diameter) were immersed in an aqueous solution of NaOH under various concentrations, namely, 10%, 14%, 18%, 22%, 26%, and 30% (w/w) for 12 minutes at room temperature (27°C). The electrical conductivity was then measured at different temperatures.

Values of $\log \sigma$ are plotted against the reciprocal of T in Figure 4. The variation of $\log \sigma_{100}$ values with NaOH concentrations is represented graphically in Figure 5. It appears from this relation that $\log \sigma_{100}$ initially decreases after treating with 10% NaOH and then increases as the concentration of

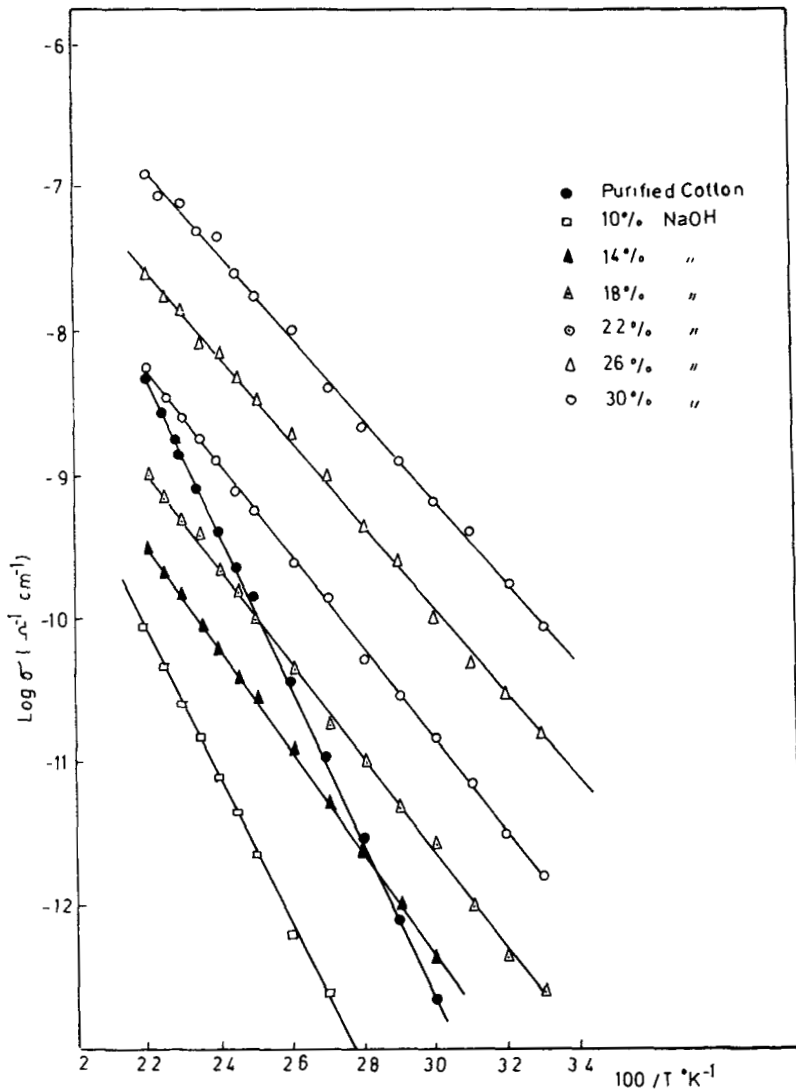


Fig. 4. Relationship between the electrical conductivity of the mercerized cotton fibers and temperature.

NaOH treatment is increased to 14%, but its value is still lower than that for native celluloses. Continued increases in the concentration result in progressive increase in $\log \sigma$.

The variation of ΔE values of the treated samples with the NaOH concentration is illustrated in Figure 6 where it is easily seen that treatment of cotton cellulose with 10% NaOH solution produces no change in its activation energy, while treatment with 14% causes considerable decrease in ΔE values. Continued increase of NaOH solution up to 30% still decreases the ΔE values.

The X-ray diffraction patterns (XRD) of these samples are given in Figure 7. As can be clearly seen, the diffractogram of purified cotton displays the (101), (10 $\bar{1}$) and (002) diffraction peaks at 2θ values = 14.80, 16.25, and 22.6,

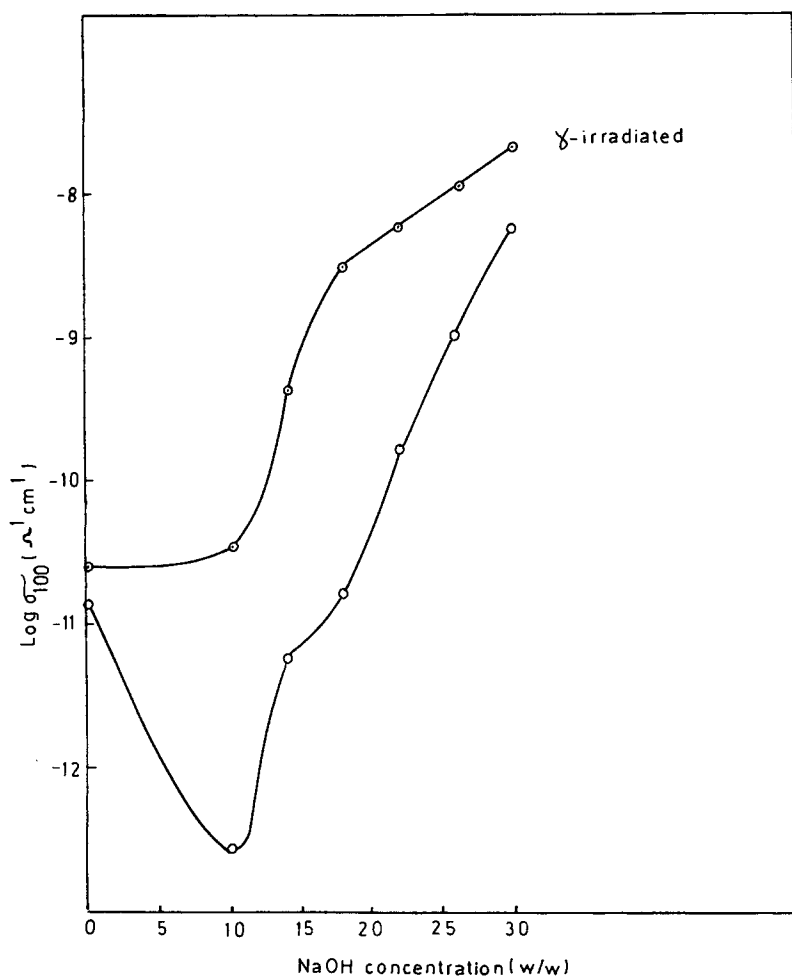


Fig. 5. Variation of $\log \sigma_{100}$ for the mercerized cotton fibers with the concentration of NaOH: (A) Before γ -irradiation. (B) After γ -irradiation.

respectively, which are the characteristics of cellulose I lattice type.^{13,14} On the other hand, X-ray diffractograms of each sample pretreated with 14%, 18%, 22%, 26%, and 30% NaOH solutions show the above-mentioned peaks at 2θ values 12° , 20.2° , and 21.8° which are the characteristics of cellulose II lattice.^{13,14} It can be seen from Figure 7 that the sample treated with 10% NaOH solution indicates the presence of cellulose I in addition to a small fraction of cellulose II. The peaks in the X-ray diffraction pattern of the sample treated with 14% indicate that this sample is a mixture of cellulose lattice types I and II.

The resolution (R) of the (101) and (101) peaks of the XRD scan of cellulose I and that of (101) and (002) peaks of cellulose II were determined for the samples under investigation by using the relation¹⁵

$$R = \frac{h_1 + h_3}{h_2}$$

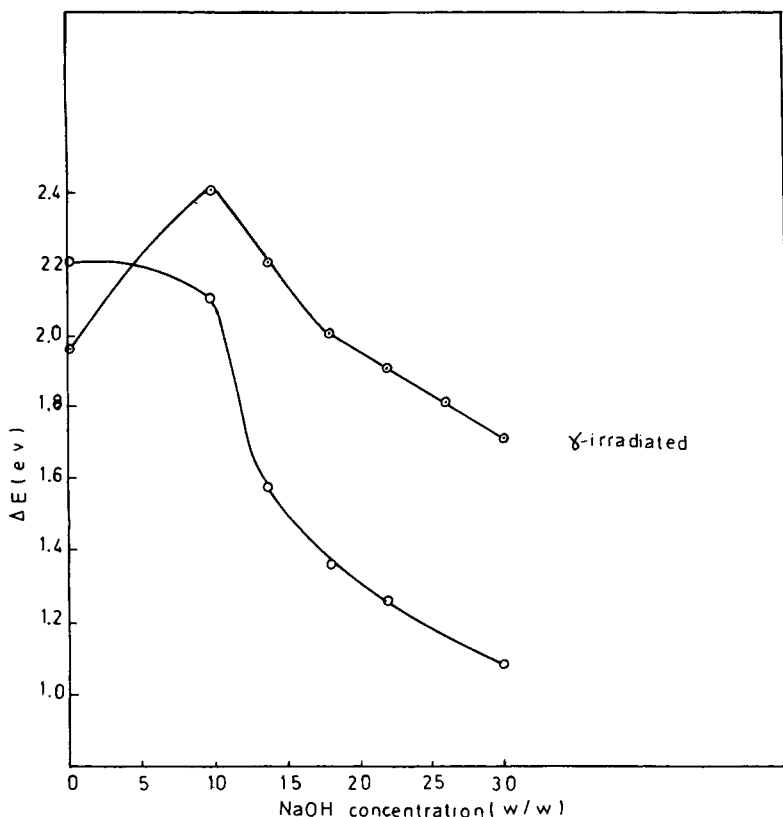


Fig. 6. Variation of the activation energies of the mercerized cotton fibers with NaOH concentration: (a) Before γ -irradiation. (b) After γ -irradiation.

Where for cellulose I, h , h_2 , and h_3 are heights at 2θ values of 16.5° , 15.8° , and 14.8°C , respectively, in the scan above a background line drawn connecting the points in the scan at 2θ values of 10° and 18°C , for cellulose II, h_1 , h_2 , and h_3 are the heights at 2θ values of 21.8° , 20.9° , and 20.2°C , respectively, in the scan above a background line drawn connecting the points in the scan at 2θ values of 8° and 28°C (Fig. 7).

The R values of the samples under investigation are plotted against their ΔE values in Figure 8. It is evident that ΔE increases linearly as R values increase, and this means that ΔE correlates well with R .

It is generally accepted that in mercerization varying degrees of structural changes take place in phase transformation of cellulose I to cellulose II molecular orientation and in the degree of crystallinity. Pandey and Iyengar¹⁶ stated that cellulose crystallinity was reduced to a certain extent by treatment with NaOH solution. Patil, Dweltz, and Radhakushnan¹⁷ pointed out that NaOH in aqueous solution acts as a decrystallizing agent at all concentrations in excess of 20%. Shenouda and Jappy¹⁸ observed that treatment of cotton fibers with 10% NaOH solution brings about a small increase in the amorphous fraction in the sample without formation of cellulose II. Furthermore, they pointed out that the 13.4% decrease of cellulose I resulting from

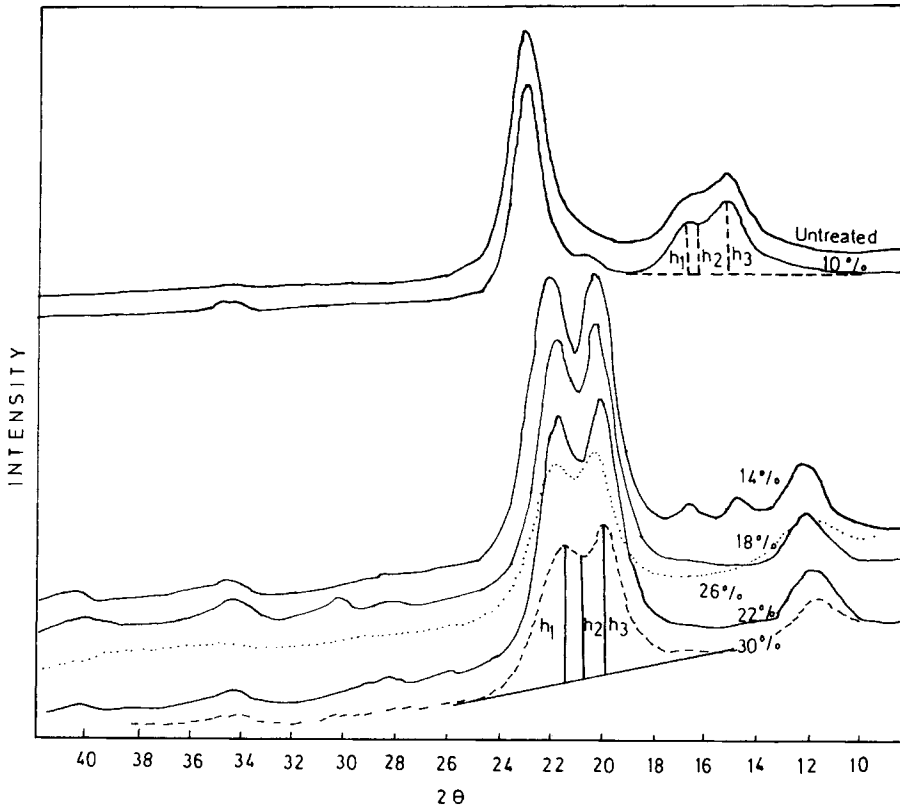


Fig. 7. XRD patterns of NaOH-treated cotton fibers.

treating the control with 11% NaOH solution is made up of a 7.9% increase of the amorphous materials and an increase of only 5.5% of cellulose II fraction, indicating that the conversion of cellulose I fraction into amorphous regions predominates over the transformation to cellulose II fraction. They further stated that this order is reversed for higher concentrations.

Besides these considerations, different authors have shown that strong hydrogen bonds are formed as a result of alkali treatment if the fiber is surrounded by an outer layer strong enough to exert a restrictive influence on the swelling of the fiber, and since the cotton fiber has a comparatively strong outerlayer, these strong hydrogen bonds should be mainly intermolecular.

The NaOH-treated samples were also exposed to the same dosage of γ -radiation under the same prementioned conditions. $\log \sigma_{100}$ and ΔE were calculated. Figures 5 and 6 indicate the variation of $\log \sigma_{100}$ and ΔE with NaOH concentration, respectively.

It is clear that, for any given concentration, γ -irradiation of NaOH-treated samples causes an increase of the measured electrical conductivity. This could be attributed to the increase of the number and mobility of charge carriers in the same direction and/or that the increase of molecular weight through cross linkage acting as bridge for electron motion appreciably increases their conductivity. The rate of increase is not constant for the different concentrations of NaOH. It varies from one concentration to another. As has been stated

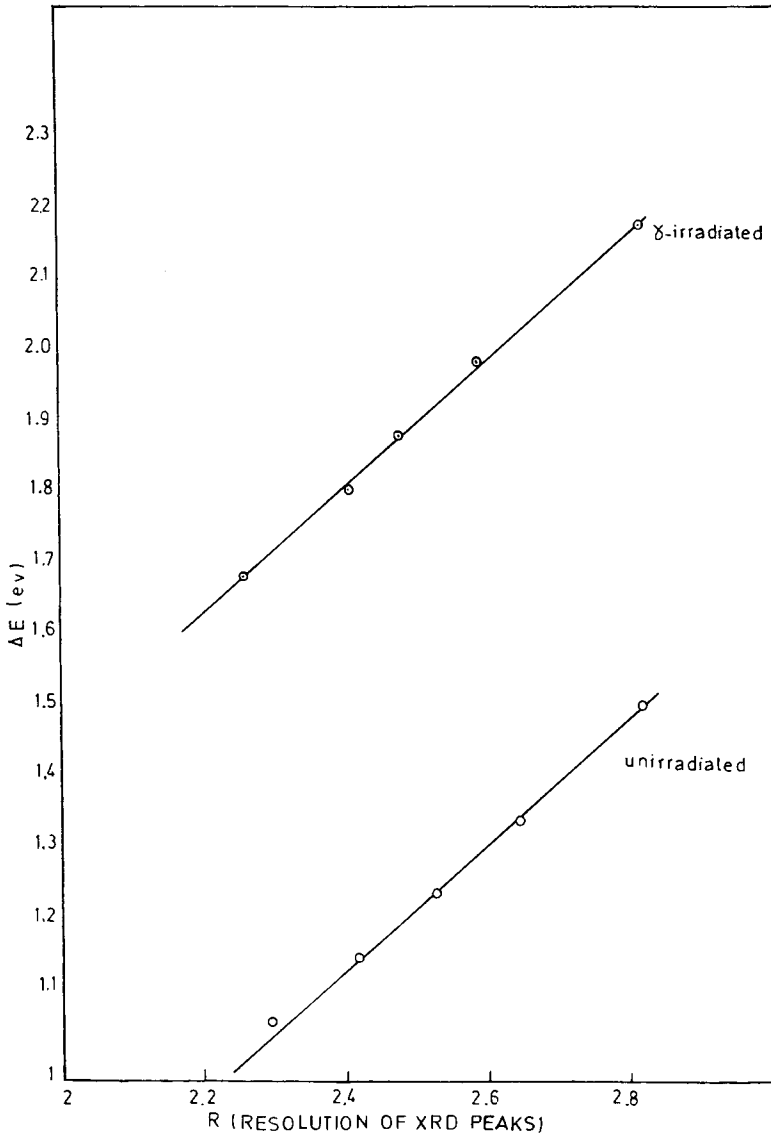


Fig. 8. Variation of the activation energy with the resolution of the XRD patterns for the mercerized cotton fibers before and after γ -irradiation.

before^{16,17} treatment of cotton fibers with NaOH solution results in changes in the degree of crystallinity and causes a phase transformation from cellulose I lattice type to cellulose II lattice type. On the other hand, several authors have claimed that the type and number of free radicals produced by γ -irradiation of cotton cellulose depends on the crystalline structure of the fiber (order and degree of crystallinity^{11,12}). Thus, it could be concluded that the extent of the increase of σ value due to γ -irradiation is originally due to the variation in the crystalline structure of each other. Figure 6 indicates that γ -irradiation of cotton cellulose increases its activation energy and the rate of increase depends on the concentration of NaOH solution.

From the above-mentioned data it could be concluded that the measurement of the electrical properties of cotton celluloses could be considered as a precise and rapid method of following small changes in crystalline structures resulting from mechanical or chemical treatments.

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