The Alcoholysis of Cellulose

J. E. HEATH and R. JEFFRIES,

The Cotton Silk and Man-made Fibres Research Association,
Shirley Institute, Manchester, England

Synopsis

The alcoholysis of cellulose in solutions of sulfuric acid in ethanol and *n*-butanol is described; emphasis is placed on the reactions of a cellulose that is 97% disordered, as measured by an infrared-deuteration technique, but the reactions of several partially ordered celluloses are also investigated.   Alcoholysis produces only very slight increases in hydrogen-bond order, and the rate of reaction is roughly related to the degree of hydrogen-bond disorder in the starting material.   The reactivity of the 97% disordered cellulose is dependent upon the method of freeing the film from the non-aqueous media used in its preparation.   This variable reactivity is not associated with differences in hydrogen-bond order or in the surface area of internal voids, capillaries, etc., as measured by nitrogen sorption and a nonswelling oxidation technique, but could be due to the existence of a very fine pore structure in some of the films.

INTRODUCTION

The reactions of cellulose with alcoholic solutions of mineral acids[1-7] have provided information on the fraction of disordered material present.[1,2] The method is essentially similar to the well-known acid hydrolysis technique but is thought to have the advantage that crystallization of the cellulose during the reaction is probably less.[1,2,3,5]   The main aims of the present work were to investigate the nature of any tendency of cellulose to crystallize during alcoholysis, the relation between the rate of alcoholysis and the hydrogen-bond disorder in the cellulose, and the relation between alcoholysis and the internal surface area of the cellulose.   Much of this work was done with films of a cellulose prepared in such a way as to be practically completely (at least 97%) hydrogen-bond disordered.[8]

EXPERIMENTAL

Preparation of Disordered Cellulose

Films of a commercial secondary cellulose acetate (acetic acid yield, 53.8%) were saponified in a 1% solution of sodium hydroxide in absolute ethanol for at least 5 hr. and then washed for several days in absolute ethanol.   In one instance the film was prepared and washed in methanol. Samples were removed from the final ethanol wash as required, blotted,

and dried, first in air and then in an oven at 105°C., before alcoholysis. In many of the early experiments (before the importance of the drying technique was realized) no particular attempt was made to control the temperature and time of the air-drying, because previous work had shown[8] that the hydrogen-bond disorder in the film was not affected by varying these drying conditions. In later experiments, to confirm and clarify the importance of the drying conditions, the films were dried in two standardized ways: some films were carefully blotted free from excess ethanol and dried at 20°C. in air for about 10 min. (prior to the final drying at 105°C.), and other films, still wet with ethanol, were put directly into an oven at 105°C.

The absence of acetate groups in the samples was checked by measuring the intensity of infrared absorption in the 1725 cm.$^{-1}$ (carbonyl stretching) region of the spectrum. The dry, disordered cellulose films were 5–10 μ thick.

Preparation of Other Cellulose Samples

Cellulose of Differing Degrees of Hydrogen–Bond Order. Samples of disordered cellulose were crystallized either by boiling in water for 5–10 min. or by immersion in 18% w/w sodium hydroxide solution for 15 min. followed by boiling in water for 10 min.; these samples were approximately 25 and 22% hydrogen-bond ordered (cellulose II type), respectively.

Other samples of cellulose included in the study were Fibro rayon, scoured cotton, and cotton mercerized in 6N sodium hydroxide at 20°C. and then washed in water; these samples were 25, 58, and 37% hydrogen-bond ordered of the cellulose II, cellulose I and, mainly, cellulose II types, respectively.[8,9]

Cellulose of Differing Surface Areas. Two weighed samples of scoured cotton were mercerized in 6N sodium hydroxide solution for 30 min. at 20°C. One was then washed in water and dried, and the other was washed in water and solvent-exchanged into ethanol.

Infrared Measurements

Infrared measurements were made on a Grubb Parsons DB1 double-beam spectrophotometer. The samples were mounted in brass cells (calcium fluoride windows), which could be evacuated. Two types of measurement were made. The first, with a sodium chloride prism, was to confirm the complete saponification of disordered cellulose film. The second was to investigate the deuteration of disordered cellulose after alcoholysis, for which a lithium fluoride prism was used.

Infrared-Deuteration Technique

After being dried by evacuation through a cold trap the mounted films were exposed to the saturated vapor of a reservoir of 99.7% deuterium oxide in the absence of air for about 12 min. at room temperature and were then freed from deuterium oxide by re-evacuation. This deuteration exchanges the hydroxyl groups in the hydrogen-bond disordered parts of the

structure to OD groups. The fraction of hydrogen-bond disordered material was calculated from the relative intensities of the OH, OD, and CH bands in the infrared spectra of this partially deuterated cellulose.

Nitrogen Sorption

The surface areas (external plus internal) of certain of the cellulose samples were measured by the nitrogen-sorption technique. The apparatus, method of measurement, and method of calculation of surface areas from nitrogen-sorption values were similar to those described by Haselton[10] and Bugge and Kerlogue.[11]

Oxidation with Chromium Trioxide in a Non-Aqueous Solvent

In this method[12] the sample is oxidized for various times with a solution of chromium trioxide in a 4:1 v/v mixture of acetic acid and acetic anhydride. The rate of reaction is initially rapid and then decreases to a slow value; extrapolation of the slow rate curve back to zero time gives a measure of the fraction of readily-oxidized material. The solvent mixture has very little, if any, swelling effect on cellulose, and thus the readily oxidized fraction is probably a measure of the surface area (external plus internal) of the cellulose rather than of any molecular disorder. This method of measuring surface area has the advantage over nitrogen sorption that it can be applied to "never-dried" cellulose.

Alcoholysis Procedure

Ethanolysis measurements were made in 30% w/w sulfuric acid, analytical reagent quality, in absolute ethanol at 80°C. Ether did not appear to be generated to any significant extent at this comparatively low temperature; because of the low temperature a high concentration of acid was necessary to effect a convenient rate of reaction. The system chosen for studies of butanolysis was 10% w/w sulfuric acid in n-butanol at 95°C.; there was no indication of any significant production of dibutyl ether under these conditions. For both ethanolysis and butanolysis about 0.1 g. of cellulose, dried at 105°C., was treated with about 40 ml. of reaction mixture. The tubes were shaken at intervals, and after the required reaction time the samples were filtered in sintered-glass crucibles and washed for at least 90 min. in ethanol. The residues were then dried to constant weight at 105°, and the loss of weight was determined.

RESULTS AND DISCUSSION

Nature of Disordered Cellulose

The properties of the disordered celluloses used in the present work have been described fully by Jeffries,[8] and similar disordered celluloses have been described by other workers,[13-18] but for a full appreciation of some of the results presented in this paper it is helpful to summarize these properties.

For clarity it is first necessary to describe briefly the infrared-deuteration technique as applied to cellulose.[9,19]   In this method the cellulose is immersed in an excess of deuterium oxide; the absorbed deuterium oxide converts OH groups to OD groups in the accessible parts of the structure. With normal, partially crystalline types of cellulose the exchange reaction is in two stages, i.e. a rapid stage followed by a slow one.   A fraction of the OH groups remains unexchanged even after prolonged treatment; i.e., these OH groups are inaccessible to deuterium oxide, at least on any practicable time scale.   Infrared study of the OH-stretching and OD-stretching bands of the dried, partially deuterated product at the end of the initial rapid exchange enables the proportion of readily accessible cellulose to be measured.   As regards hydrogen bonding, cellulose can be divided into two components.   In the first, which comprises the rapidly exchanged portion of the cellulose, the hydrogen bonding is disordered in character; the hydroxyl band of this component is thus broad and featureless.   In the second component, which comprises the slowly accessible and inaccessible portions of the cellulose, the hydrogen bonding is regular and ordered in character and gives rise to a hydroxyl band showing characteristic peaks and shoulders.[9,19,20]   In undeuterated cellulose, therefore, the hydroxyl band is a combination of these two components.

In cotton about 40% of the hydroxyl groups are "hydrogen-bond disordered" and readily accessible (i.e., deuterate within about 15 min. in saturated D_2O vapor at 20°C.);[21] and in textile viscose rayons, about 75%. The important feature of the disordered cellulose film used in the present study is that it is at least 97%, and often as much as 99%, hydrogen-bond disordered.   The infrared hydroxyl-stretching band of this material is broad and featureless, with virtually no ordered component.   On deuteration this hydroxyl band rapidly disappears, leaving at most a very weak residual band.   This weak band sometimes has the shape characteristic of cellulose II ordered regions but is more often broad and poorly defined, with a peak in the 3400 cm.$^{-1}$ region.   The material is, therefore, practically completely accessible to deuterium oxide.   So far as the infrared-deuteration technique is concerned, in fact, this type of cellulose has all the properties of the hydrogen-bond disordered components of normal types of cellulose.

These highly disordered celluloses are produced by regeneration of films or fibers of cellulose derivatives in non-aqueous solutions, followed by washing in non-aqueous solvent and drying in air.   The method outlined above, namely the saponification of secondary cellulose acetate in ethanolic solutions of sodium hydroxide, is very satisfactory, but it is emphasized that other derivatives and non-aqueous regenerating systems give similar results.

Effect of Alcoholysis on Hydrogen-Bond Order

Samples of disordered cellulose film were treated with boiling methanol, ethanol, n-propanol, and n-butanol for periods of up to 1 hr.   Infrared-
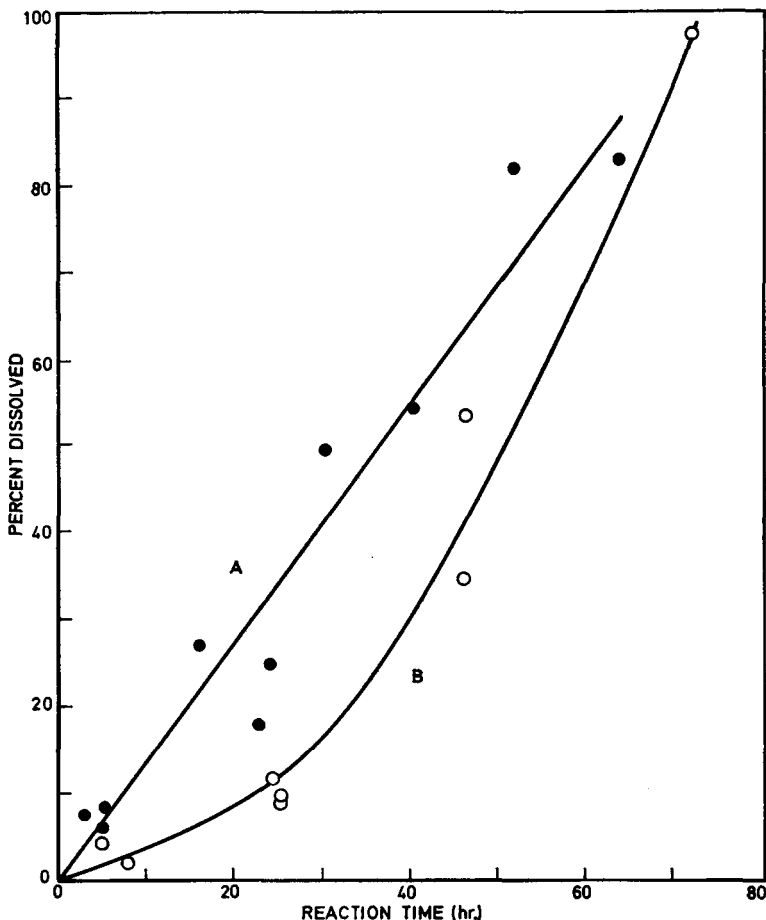
Fig. 1. Alcoholysis of disordered cellulose with 10% w./w. sulfuric acid in n-butanol at
95°C. Disordered cellulose prepared in: (A) ethanol; (B) methanol.

deuteration measurements of the film after drying showed that none of the
treatments produced any significant increase in hydrogen-bond order.

Samples of dried, disordered cellulose film reacted with 10% sulfuric
acid in n-butanol at 95°C. for lengths of time up to that at which the film
became too disintegrated for infrared study; other samples reacted with
30% sulfuric acid in ethanol at 80°C. for the maximum possible time.
After reaction the films were washed in ethanol for several hours and dried
in air. Infrared-deuteration measurements of these films showed that the
residual hydroxyl band, after deuteration of the rapidly exchangeable
fraction, was in general broad and featureless, although in a few cases there
was some evidence of peaks and shoulders characteristic of cellulose II;
this residual band was weak but, in general, more intense than that of the
original cellulose; i.e., both types of alcoholysis reaction produced a slight
increase in the hydrogen-bond order in the cellulose. This increase in the

fraction of hydrogen-bond ordered cellulose varied from 0 to 9% (average, 3%) with butanolysis and from 1 to 4% (average, 3%) with ethanolysis; it showed no systematic variation with time of alcoholysis, any effect probably being masked by the considerable scatter of results in the longer treatments, owing to the films being broken up and thus difficult to handle and study quantitatively.

The increase in order on alcoholysis is, therefore, very small (at least for the levels of reaction involved in these experiments) and would probably be negligible with ordinary celluloses, which already contain a high proportion of ordered regions.   A few results were obtained on the degree of order after alcoholysis of disordered cellulose that had been boiled in water and dried before alcoholysis to give about 25% hydrogen-bond ordered material of the cellulose II type.   These results showed considerable scatter, again prob-
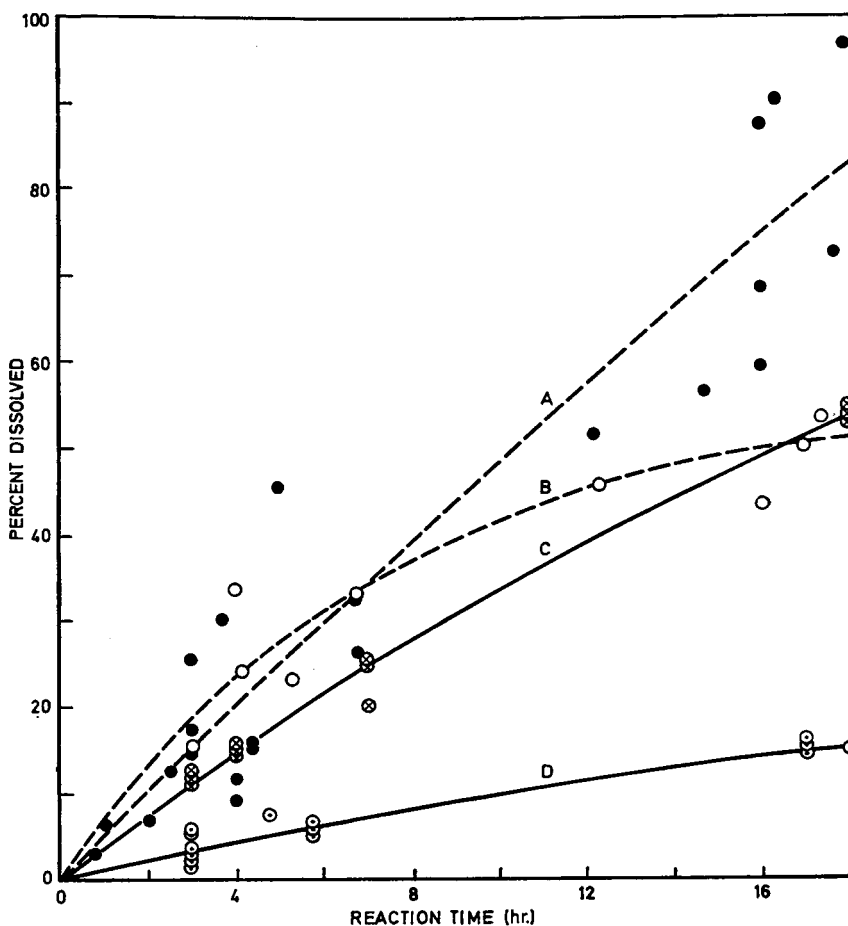

Fig. 2. Alcoholysis of cellulose in 30% w./w. sulfuric acid in ethanol at 80°C.: $(A, \bullet)$ disordered cellulose film; $(B, \bigcirc)$ disordered cellulose film boiled in water; $(C, \otimes)$ Fibro rayon; $(D, \odot)$ scoured cotton.

ably the result of the difficulties in handling badly disintegrated specimens, but gave no indication of any significant effect of alcoholysis on hydrogen-bond order.

Relation Between Hydrogen-Bond Disorder and Rate and Extent of Alcoholysis

The rates of butanolysis of disordered cellulose prepared in ethanol and methanol are shown in Figure 1; the difference in these rates was not due to differences in hydrogen-bond disorder, since both films were at least 97% disordered, as measured by the infrared-deuteration technique. The rate of ethanolysis of disordered cellulose and partially ordered cellulose is illustrated in Figure 2. An attempt was made to analyze these results in a way similar to that used for hydrolysis.[22] However, no satisfactory resolution into a fast and a slow reaction could be inferred from either linear plots or "first order" plots (log weight loss against time) derived from them.

In view of these difficulties it was not found possible to obtain from the present results any clear indication of a "readily accessible" fraction as distinct from an inaccessible fraction. Comparing the results for various types of cellulose, the rates of reaction lie in roughly the same order as the fractions of disordered cellulose, as determined by infrared-deuteration
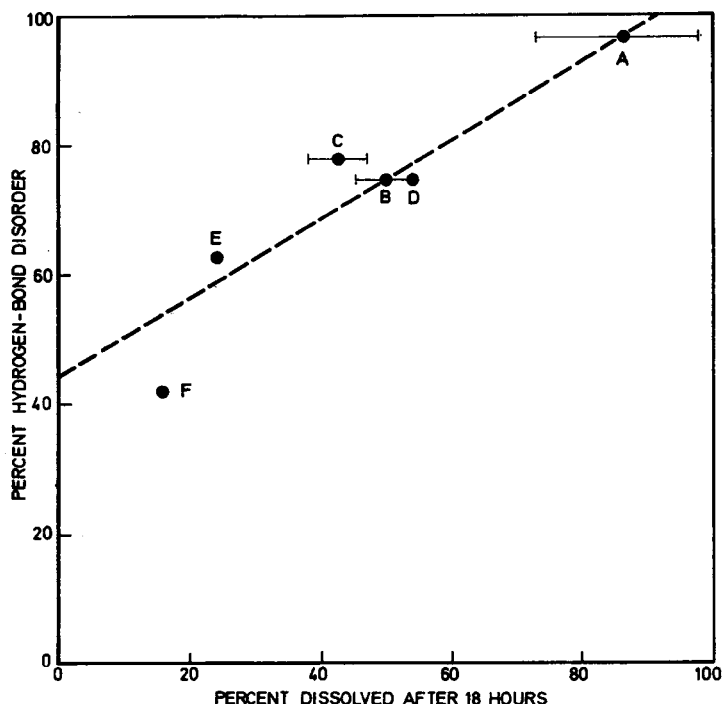

Fig. 3. Relation between initial hydrogen-bond disorder and rate of ethanolysis: (*A*) disordered cellulose film; (*B*) boiled disordered cellulose film; (*C*) alkali-treated disordered cellulose film; (*D*) Fibro rayon; (*E*) mercerized cotton; (*F*) scoured cotton.

measurements.   This relation between disorder and rate of alcoholysis is shown in Figure 3, where the loss in weight on reaction in 30% w./w. sulfuric acid in ethanol at 80°C. for 18 hr. is plotted against initial hydrogen-bond disorder.   Alcoholysis measurements, therefore, provide a method of grading celluloses in terms of order and disorder.

In these measurements of rates of alcoholysis the scatter of experimental results was much greater with disordered cellulose than with partially crystalline samples (see Figs. 1, 2, and 4); this scatter was subsequently traced to genuine sample variability, which arose in the early work from the freeing of disordered samples from ethanol in a nonstandard manner. The effect of the conditions of drying on the subsequent rate of alcoholysis of disordered cellulose is described in the next section.

Effect of Drying Conditions on Alcoholysis of Disordered Cellulose

The rate of alcoholysis of disordered cellulose depended greatly upon the way in which the ethanol used in the preparation of the film was evaporated. Film dried at 105°C. (see Experimental section) was much more reactive in the early stages than that dried at room temperature (Table I);   this

TABLE I

Time of ethanolysis,[a] hr.	Dissolved % (±2)		
	Hot-dried	Cold-dried	Never-dried
3	37.9	2.4	35.1
	44.9	3.6	40.5
	44.6	9.1	
	40.6		
	33.3		
	43.8		
	43.3		
16	85.6	83.5	

[a] 30% w./w. sulfuric acid in ethanol at 80°C.

TABLE II

Pretreatment of disordered cellulose	Time of ethanolysis[a]	Dissolved, %
Never-dried, refluxed 90 min.		
"hot-dried"	3 hr. 20 min.	36.7 ± 2.0
"cold-dried"	3 hr. 20 min.	0–3.8
Cold-dried, refluxed 30 min.		
"never-dried"	3 hr.	5.4 ± 3.0
"cold-dried"	3 hr.	3.3 ± 3.0
Cold-dried, refluxed 20 min.		
"hot-dried"	3 hr.	3.5 ± 3.0
Cold-dried, refluxed 2 hr.		
"hot-dried"	3 hr.	1–5

[a] Conditions as in Table 1.

"hot-dried" film was, in fact, similar in reactivity to the never-dried film (Table I), suggesting that "hot-drying" retains the film in an "open" form, with the highly reactive character typical of never-dried material. It should be emphasized that the temperature of drying had no effect on the infrared-deuteration behavior; i.e., all films were highly hydrogen-bond disordered (at least 97%) before alcoholysis.

Since pretreatment of disordered cellulose (both dried and never-dried) with boiling ethanol had no effect on the subsequent reactivity to alcoholysis (Table II), the effect of hot-drying in producing highly reactive films is clearly associated with the actual *evaporation* of solvent. Nonstandardization of the initial drying process before alcoholysis in the earlier work almost certainly accounts for the scatter of results for disordered cellulose shown in Figures 1 and 2 and for differences observed between the disordered celluloses prepared in methanol and in ethanol (Fig. 1). The drying conditions also affected the reactivity of disordered cellulose that had been solvent-exchanged from ethanol to benzene and then dried; in this case, however, the film dried at room temperature was more reactive than the hot-dried film (21% dissolved after 3 hr. of ethanolysis, compared with 11%).

Relation Between Rate of Alcoholysis and Surface Area of Cellulose

The importance of the initial drying conditions suggested that the rate of alcoholysis of disordered cellulose may be controlled to some extent by the "surface area" of the material (the external surface and the surface of internal voids and capillary structures) as well as by disorder in the molecular arrangement. The surface areas of various celluloses were, therefore, studied in relation to the rate of alcoholysis.

Nitrogen-sorption measurements showed, however, that the surface area of "hot-dried" (i.e. reactive) disordered cellulose (0.29 m.^{2}/g.) is little larger than the external surface of the film, so the high rate of alcoholysis cannot be accounted for in terms of a high "internal surface" (at least of a type measurable by this technique). Results for chromium trioxide oxidation, which gives a measure of "surface area," also showed a lack of correlation with the alcoholysis results: "hot-dried" disordered cellulose was only about one-tenth as reactive as never-dried disordered cellulose that had first been solvent-exchanged to acetic acid, consuming 0.01 moles of chromium trioxide per anhydroglucose unit at "zero time" compared with 0.15 moles, although the materials had similar rates of alcoholysis.

This lack of correlation between surface area and rates of alcoholysis was illustrated still further by ethanolysis of mercerized cottons. Some samples of cotton, swelled in caustic soda solutions of mercerizing strength, were washed in water, solvent-exchanged to ethanol without intermediate drying, and treated in this never-dried condition; there is strong evidence[23] that never-dried samples of this type have a high internal surface, probably as a result of the high degree of interfibrillar separation that is maintained
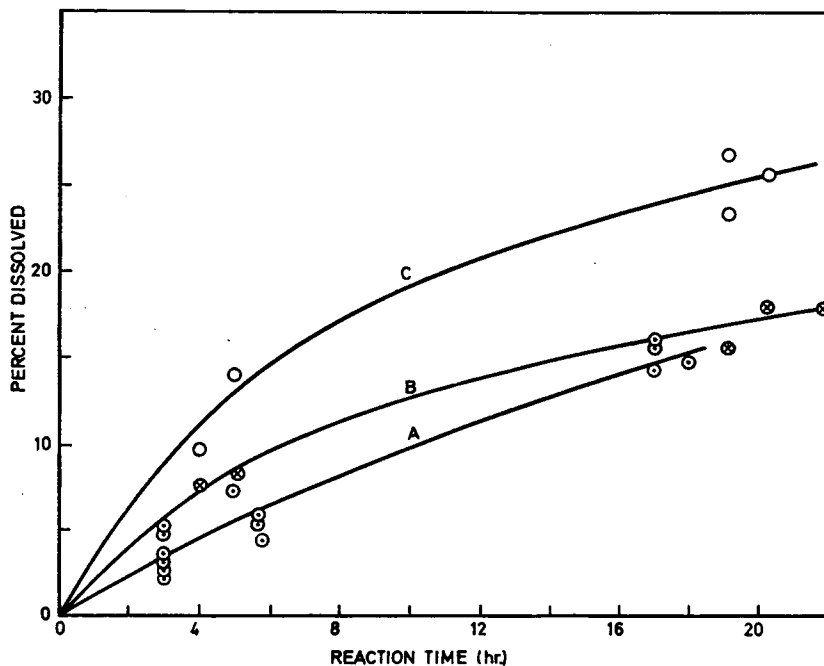
Fig. 4. Ethanolysis of celluloses of differing surface areas in 30% w./w. sulfuric acid in ethanol at 80°C.: (A) scoured cotton; (B) mercerized cotton, washed in water, solvent-exchanged to ethanol; (C) mercerized cotton, washed in water, dried.

in the alkali-swollen material during the solvent-exchange treatments. Other alkali-swollen samples were dried from water; these samples have a very low internal surface, as measured by nitrogen sorption and chemical techniques, as a result of the sealing up of voids and capillaries during the drying from the water.[23]   The ethanolysis results (Fig. 4) show that mercerized and dried cotton is considerably more reactive than untreated cotton (in agreement with other results,[23] and as expected from the increase in disorder on mercerization) but that the mercerized and never-dried sample is only slightly more reactive than untreated cotton.   This result is difficult to explain, but it does emphasize that there appears to be no direct relation between internal surface area, as generally understood, and rate of ethanolysis of cellulose.

It may be that the reactive structural arrangement in hot-dried disordered cellulose film involves a pore system that is too fine to be penetrated by nonswelling reagents.   The existence of a pore structure in certain types of secondary cellulose acetate film has been postulated by Meares,[24] the mean pore diameter being suggested as 6–9 A.   In the preparation of disordered cellulose such a structure could well be maintained throughout the saponification, the washing in ethanol, and the hot, rapid evaporation of the ethanol; a slower rate of removal of ethanol would allow a greater degree of collapse of the pore system.

The first stages of the subsequent alcoholysis would tend to increase the diameter of the pores as a result of a general swelling of the structure and thus facilitate subsequent penetration of reagent.

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