

## The Amorphous Fraction of Cellulose and its Relation to Moisture Sorption

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### Synopsis

The OH  $\rightarrow$  OD exchange reaction between deuterium oxide vapor and cellulose has been studied for thirteen different types of cellulose; the extent of exchange in a cellulose was determined by measuring the increase in the dry weight of the sample. With each cellulose the deuteration reaction was in two stages, a rapid stage followed by a slow stage; the material that exchanges during the rapid stage is the infrared-amorphous fraction of the cellulose, and therefore values for the amorphous fractions of the thirteen samples could be obtained. These amorphous fractions were found to be linearly related to the moisture regains of the samples. There is tentative evidence that the cellulose II samples absorb slightly more water into a unit amount of amorphous material than cellulose I samples.

### 1. Introduction

Hermans,<sup>1</sup> Howsmon,<sup>2,3</sup> Kast,<sup>4</sup> and Valentine<sup>5,6</sup> have noted that the moisture regain of cellulose is linearly related to the fraction of amorphous, readily accessible material in the cellulose. As Valentine<sup>5</sup> points out, this relation enables a moisture sorption value to be used as a simple and reliable measure of the amorphous fraction. The present paper describes an experimental study of this relation for thirteen different types of cellulose. The amorphous, readily accessible fractions have been measured by means of the technique of deuterium-oxide exchange; the results obtained by this method by Mark and his co-workers<sup>7</sup> and by Mann and Marrinan<sup>8</sup> were used by Howsmon<sup>2</sup> and Valentine,<sup>5</sup> respectively.

### 2. Experimental

The samples of cellulose are those used in a recent study of moisture sorption;<sup>9</sup> they are listed in Table I, together with their absorption regains at 60% R.H. and 30°C.<sup>9,10</sup>

The extent of the OH  $\rightarrow$  OD exchange in a sample as a result of a deuteration treatment was determined by measuring the increase in the dry weight of the sample.<sup>11,12</sup> Silica spiral springs were used for this purpose; the increase in the length of a spring resulting from the increase in the dry weight of the sample was measured on a calibrated scale in the eyepiece of a microscope focused on the lower end of the spring. A large excess

TABLE I

No.	Sample	Condition	Moisture regain at 60% R.H. and 30°C., g. water/ 100 g. dry sample	Amorphous fraction, %	
				"Best" value	Range
1	Tenasco Super 70	Stabilized <sup>a</sup>	13.15	77.5	73.5-80
2	Viscose film	Unstabilized <sup>b</sup>	12.7	74.5	71 -76.5
3	Saponified acetate film	Stabilized	12.7	73	70.5-75.5
4	Viscose yarn	"	11.9	71	68 -73
5	Cuprammonium yarn	"	10.95	69	66 -70.5
6	Fortisan	"	9.3	62.5	58 -65
7	Mercerized cotton	Unstabilized	9.4	53.5	51 -55.5
8	"	Stabilized	9.2	49	46.5-50.5
9	Wood pulp	"	7.3	45.5	42 -48
10	Cotton	"	6.6	42	39 -44
11	Mercerized cotton	High temperature treated <sup>c</sup>	7.0	40	37.5-41.5
12	Ramie	Stabilized	5.75	39	37 -41
13	Bacterial cellulose	"	5.1	34.5	32 -36.5

<sup>a</sup> Stabilized by several absorption-desorption cycles (saturated H<sub>2</sub>O vapor-vacuum) at 90°C.

<sup>b</sup> As first dried.

<sup>c</sup> Treated in H<sub>2</sub>O vapor at 150°C.

of 99.7% deuterium oxide was used in all the experiments. Values thus obtained for the extent of deuteration are accurate to within 1–2%; this limit to the accuracy of the values is a result of the error involved in reading the microscope scale and an occasional very slight “creep” of the springs.

### 3. Results and Discussion

In this paper, the “crystalline” regions of cellulose are defined as those regions which are hydrogen-bonded in a manner sufficiently regular and ordered to give an infrared hydroxyl-stretching band containing well defined, characteristic peaks;<sup>8,13</sup> the “amorphous” regions are those in which the hydrogen-bonding is not regular and ordered to this extent, and which thus give a broad, featureless, hydroxyl-stretching band. It may be noted that the amorphous regions, as defined in this way, contain a certain amount of material that is crystalline to x-ray diffraction,<sup>14</sup> and it has been suggested that this material is perhaps the cellulose lying in the surfaces of the crystallites;<sup>14</sup> in this paper this “intermediate-order” cellulose is not considered separately from the remainder of the infrared-amorphous material and it is emphasized, for clarity, that “crystalline” and “amorphous” are used below only as defined in the first sentence of this paragraph.

Mark and his co-workers<sup>7</sup> and Mann and Marrinan<sup>8</sup> demonstrated that, as regards the OH → OD exchange reaction, cellulose can be divided into three components: a readily accessible component, which exchanges very rapidly (less than 1 hr. in saturated deuterium oxide vapor at room temperature); a slowly accessible component, which exchanges more slowly (up to several weeks at room temperature,<sup>13</sup> though much less at high temperatures); and an inaccessible component, which does not exchange at all in any practicable length of time. Mann and Marrinan<sup>8</sup> showed that the readily accessible part can be approximately identified with the amorphous regions (as above defined), that the slowly accessible component is a part of the crystalline fraction of the cellulose, and that the inaccessible component constitutes the remainder of the crystalline fraction; there is evidence<sup>13</sup> that the regular hydrogen-bonding arrangement is less perfect in the accessible crystalline regions than in the inaccessible crystalline regions and this is probably the reason for the difference in accessibility. The size of the accessible component of the crystalline regions has been shown<sup>13</sup> to increase somewhat with increase in temperature. The relative amounts of these three components varies from cellulose to cellulose; with unstabilized viscose film (i.e., as first dried) at room temperatures, about 75% of the structure is amorphous and readily accessible,<sup>8</sup> 15% is slowly accessible crystalline material,<sup>13</sup> and 10% is inaccessible crystalline material (at higher temperatures the accessible crystalline fraction may approach 20% and the inaccessible crystalline fraction be reduced to 5%); with unstabilized bacterial cellulose film the approximate proportions are: amorphous, 30%;<sup>8</sup> accessible crystalline, 9% (at room temperature);<sup>8,13</sup> and the remainder inaccessible crystalline.

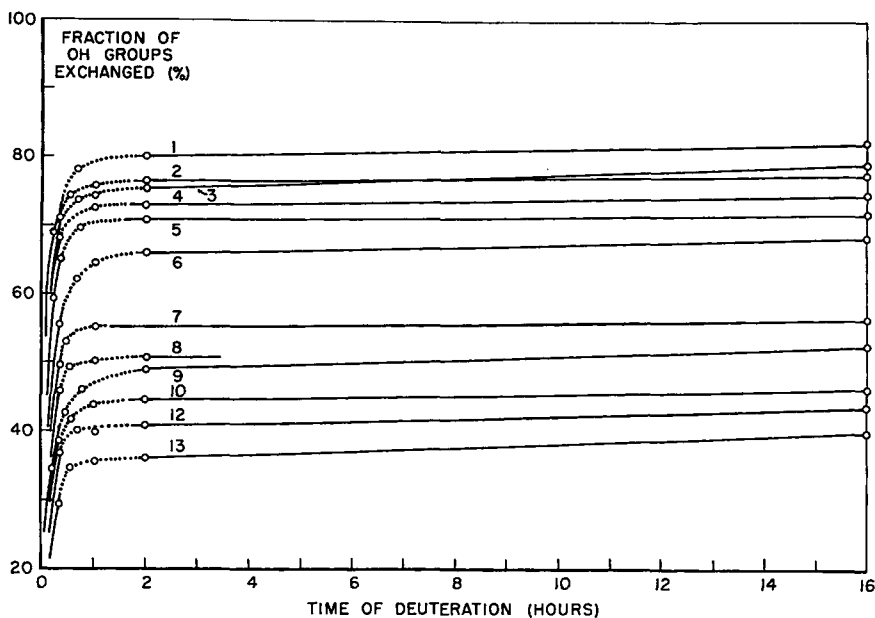


Fig. 1. The rate of OH  $\rightarrow$  OD exchange with various celluloses. Saturated deuterium oxide vapor at 25°C. The numbers refer to the samples as numbered in Table I.

The results of the present deuteration experiments are given in Figure 1; this figure shows for the various celluloses the fraction of the hydroxyl groups exchanged after various times of treatment in saturated deuterium oxide vapor at 25°C. The curves in Figure 1 show that the exchange reaction occurred in two stages: a rapid stage followed by a slow stage; the curves are, in fact, very similar in character to the rate-of-exchange plots given by Mark and his collaborators<sup>7</sup> and to plots of the absorbance of the infrared OD-stretching band against time of deuteration.<sup>8,13</sup> In accord with the generally accepted interpretation of this two-stage deuteration behavior (as outlined in the previous paragraph), the initial rapid deuteration shown in Figure 1 is attributed to the exchange of the amorphous regions and the subsequent slow deuteration is attributed to the exchange of the accessible crystalline regions. The amorphous fraction of a particular cellulose can therefore be derived from Figure 1; it is simply the fraction of the hydroxyl groups that have exchanged at the end of the rapid stage. Unfortunately, however, the changeover from the rapid stage to the slow stage is not very abrupt, and so the curves are not suitable for the precise determination of amorphous fractions: on the basis of the previous studies<sup>8,13</sup> there is little doubt that the change from "amorphous" to "crystalline" deuteration occurs at some point on the dashed parts of the curves, but it is not possible to locate the point exactly. (It may be noted that a more precise location of the changeover point is possible with infrared techniques by means of rehydrogenation procedures.<sup>8,13</sup>) The

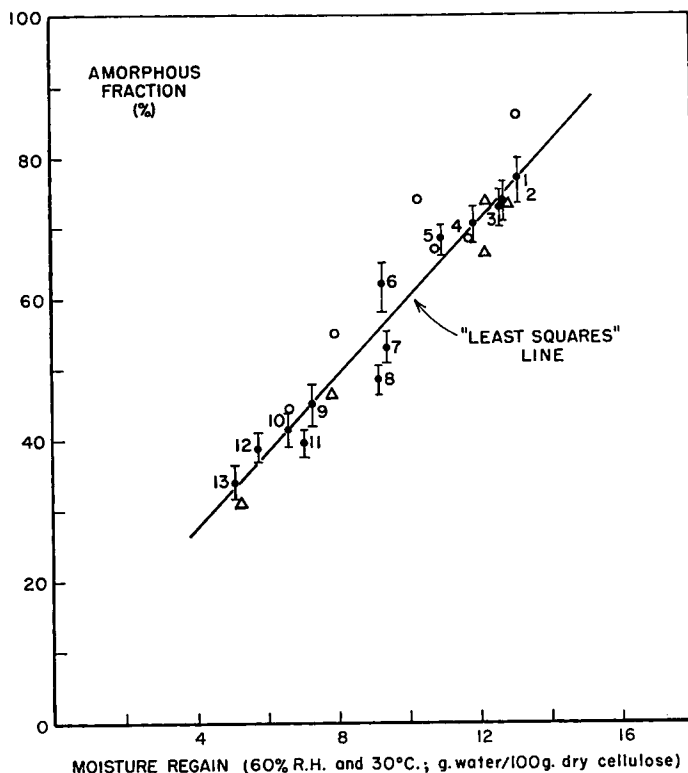


Fig. 2. The relation between the amorphous fraction and moisture regain: (O) Mark and co-workers; ( $\Delta$ ) Mann and Marrinan; ( $\bar{\Gamma}$ ) present results showing "best" values and range of possible values. The numbers refer to the samples as numbered in Table I.

estimated values for the amorphous fraction listed in the fifth column of Table I (described as the "best" values) are therefore merely the points on the curves in Figure 1 at which the rate of deuteration changes most rapidly, these points corresponding to about 30–40 min. treatment. This length of time is somewhat longer than that usually required to deuterate the amorphous regions of the cellulose films in the infrared studies,<sup>13</sup> but it should be remembered that the present samples are, in general, considerably thicker than those used in the infrared work. The sixth column in Table I lists the ranges of values covered by the dashed parts of the curves, i.e., the ranges of possible values for the amorphous fractions.

In Figure 2 the values for the amorphous fractions are plotted against the moisture regains of the samples. Though the scatter of results is considerable, there is little doubt that an approximately linear relation exists between the two quantities; the findings of the previous workers<sup>1–6</sup> to this effect are thus amply confirmed. This linear relation, it may be noted, was one of the facts contributing to the now generally accepted conclusion<sup>1–6,8,13</sup> that the sorption of water and of deuterium oxide by cel-

lulose takes place mainly, if not entirely, in the amorphous regions (as defined in this paper) and that the crystalline regions absorb at most a small amount of water. This amount is thought to be particularly small for the crystalline regions of cellulose I samples; the crystalline regions of cellulose II samples probably absorb rather more, but even here the amount must be small compared with the absorption by the amorphous regions. Any large differences in the amount of water absorbed per unit amount of amorphous material can therefore only be the result of differences in the character of the amorphous material; one aim of the present work was, in fact, to see whether any differences of this kind could be detected with certainty in the range of celluloses studied.

Figure 2 also includes the deuteration results of Mark and his co-workers<sup>7</sup> and of Mann and Marrinan<sup>8</sup> plotted against the moisture regain values<sup>2,4</sup> used by Howsmon<sup>2,3</sup> and Valentine<sup>5,6</sup> (with a small estimated correction to adjust these sorption values to 60% R.H. and 30°C.). Mann and Marrinan's results, which are measurements of the amorphous fraction as defined and measured in this paper, are in good agreement with the present results. The accessibility values given by Mark and his co-workers are generally somewhat higher than the values for amorphous fraction presented in this paper; this is probably because Mark's values refer to deuteration for 4 hr. in liquid deuterium oxide, and there is little doubt<sup>8,13</sup> that this treatment would deuterate some crystalline cellulose as well as the amorphous cellulose. (Mark, in fact, suggested that his accessible fraction would include the "surfaces" of the crystalline regions.)

The straight line on Figure 2 is the least-squares line of the "best" values; the equation is  $A = 5.795 + 5.416S$ , where  $A$  is the (percentage) amorphous fraction and  $S$  is the moisture regain (grams water per 100 g. dry cellulose).

A considerable amount of caution is necessary in any detailed quantitative interpretation of Figure 2: the scatter of results is large and it should also be remembered that much uncertainty exists in the method of estimating the "best" values for the amorphous fractions. The only detailed conclusion that could be reached (and this only a tentative one) was in a comparison of the group of nine cellulose II samples (1-8 and 11 in Table I) with the group of four cellulose I samples (9, 10, 12, and 13). This comparison was made by considering for each sample the ratio of the moisture regain to the amorphous fraction. It was found that the average of the ratios for the cellulose II samples was slightly larger than the average of the ratios for the cellulose I samples; the ranges of possible values for the amorphous fractions, as indicated in Table I, were considered in the calculations, not merely the "best" values. The statistical significance of this difference between the two averages is rather uncertain, in view of the scatter of results and the limited number of samples, but it does appear that the difference may just be significant at the 5% level.

This difference between cellulose I samples and cellulose II samples, if genuine, must mean either that the cellulose II samples absorb slightly more

water into a unit amount of amorphous material than the cellulose I samples, or that the cellulose II samples absorb up to 1.0 g. water/100 g. dry cellulose into their crystalline regions, the cellulose I crystalline regions being assumed to absorb a negligible amount. This latter explanation, which would mean that the average concentration of water in the accessible parts of the crystalline regions would be a large fraction (a third or even more) of the concentration in the amorphous regions, is thought to be unlikely;<sup>13</sup> it must therefore be concluded that the difference in the ratio of regain to amorphous content between the cellulose I samples and the cellulose II samples is a reflection of a difference in the sorption behavior, and thus the structure, of the amorphous regions. The reason for such a difference in sorption behavior is not clear, but it could be the result of stronger hydrogen bonding in the amorphous regions of the cellulose I samples compared with the amorphous regions of cellulose II samples. Infrared evidence<sup>8,13</sup> shows that this stronger hydrogen bonding certainly exists in bacterial cellulose as compared with regenerated celluloses.

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### Résumé

La réaction d'échange  $\text{OH} \rightarrow \text{OD}$  entre la vapeur d'oxyde de deutérium et la cellulose a été étudiée pour treize types différents de cellulose; l'étendue de l'échange dans la cellulose a été déterminée en mesurant l'augmentation en poids brut de l'échantillon. Avec chaque échantillon de cellulose la réaction au deutérium se faisant en deux étapes, une étape rapide suivie d'une étape lente; la substance échangée pendant l'étape rapide est la fraction amorphe à l'infra-rouge de la cellulose et c'est ainsi que l'on a pu obtenir des valeurs pour les fractions amorphes de treize échantillons. Ces fractions amorphes sont en relation linéaire avec l'augmentation de l'humidité des échantillons. On possède l'évidence que les échantillons de cellulose II absorbent légèrement plus d'eau par unité de matériel amorphe que les échantillons de cellulose I.

### Zusammenfassung

Die Austauschreaktion  $\text{OH} \rightarrow \text{OD}$  zwischen Deuteriumoxyddampf und Cellulose wurde an dreizehn verschiedenen Cellulosearten untersucht. Das Ausmass des Austausches in der Cellulose wurde aus der Zunahme des Trockengewichtes der Probe bestimmt. Bei jeder der Celluloseproben verlief die Austauschreaktion in zwei Schritten einem raschen und einem darauffolgenden langsamen Schritt. Während der rasch verlaufenden Reaktionsperiode geht der Austausch mit dem "infrarotamorphen" Anteil der Cellulose vor sich und es konnten daher Werte für den amorphen Anteil der dreizehn Proben bestimmt werden. Dieser amorphe Anteil steht in linearer Beziehung zur Feuchtigkeitsaufnahme der Proben. Wie vorläufige Ergebnisse zeigen, absorbieren Cellulose-II-Proben etwas mehr Wasser pro Mengeneinheit des amorphen Materials als Cellulose-I-Proben.

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