Function of Sheets of Cellulose Chains in Swelling Reactions on Cellulose

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Synopsis

An x-ray investigation of the products formed by the action of caustic soda on different samples of cellulose and those formed on the decomposition of these products by aqueous reagents and alcohols shows that the fundamental reacting unit is a sheet of cellulose chains, and not individual cellulose chains. Although the caustic soda can affect the relative dispositions of the chains within these sheets to some extent, it cannot separate the chains, and the products then depend on the aggregation of the cellulose sheets with or without other molecules between them. Such aggregation leads to variable products whose x-ray diagrams can, however, show distinct reflections and be mistaken for those from more precise crystal structures. It is, therefore, important in swelling reactions to take into account the ability of the swelling agent to modify the cellulose sheets and the mode of decomposition of the complexes formed on swelling. Thus swelling with caustic soda cannot be taken as typical of all aqueous swelling reagents in its reaction towards cellulose, and the possibility with other reagents of finding cellulose I, instead of cellulose II, after a series of swelling reactions must be taken into consideration.

INTRODUCTION

An understanding of the fine structure of cotton, as well as the chemistry of its reactions, is necessary if the effects of swelling treatments and cross-linking treatments are to be used to the full advantage. In a previous paper[1] it was shown that morphological features can play a part in modifying the effect of the reaction of caustic soda on cotton and ramie. In the present paper an x-ray study of the compounds formed between caustic soda and cellulose, as well as the products formed during their decomposition, has shown that fine structural features, which are independent of morphology, also play an important role.

It has been found that in these reactions the fundamental unit that enters into the reaction, is not, as often implied, the isolated cellulose chain, but a sheet of chains held together chiefly by van der Waals forces that maintain a coherence throughout a series of reactions. As a consequence of this, x-ray diagrams can be obtained that superficially appear to be those of definite crystal structures, but, on closer analysis are found to be diagrams from structures that are precisely defined only in two directions. Furthermore, different x-ray diagrams can be obtained from products that have

been formed under apparently similar conditions, thus explaining the great confusion that still exists in the literature on soda celluloses.

This concept of sheets of cellulose chains can also be used to explain the process of mercerization, as well as the apparent impossibility of reconverting cellulose II to cellulose I.

EXPERIMENTAL

Preparation of Soda Celluloses from Native Celluloses

Separate samples of cotton and ramie were made into 1-in. long tufts of mass 10 mg. bound at one end. The tufts were placed in 100 ml. of the required caustic soda solution and left for about $^1/_2$ hr. in a thermostat at the appropriate temperature. One tuft was left in the caustic soda solution, one washed in an aqueous solution of two parts saturated sodium chloride solution and one part $0.1N$ acetic acid; and another was given this washing treatment followed by washing in water until neutral and free from salt; the fourth tuft was washed in water until neutral. In those experiments carried out at temperatures above 20°C. (room temperature), the acidified salt solution was $0.1N$ acetic acid saturated with salt; this was an experimental variant. It is known from the work of Sobue et al.[2] that negligible change, as detected by x-ray analysis, is produced by altering the temperature after swelling. It was therefore decided to bring all specimens to room temperature after swelling at the required temperature before carrying out subsequent treatments.

The wet samples were introduced into special glass tubes designed for x-ray diffraction work (Pantak Ltd.). The tufts were combed out as near to parallel as possible and then pulled into a 1.5-mm. diameter hole in a stainless steel plate (5 mm. thick) by means of a loop of nickel wire. The protruding parts of the tuft were then cut flush with the surfaces of the plate leaving a small block of parallel fibers in the hole. This block was pushed carefully out and introduced into the widened end of a 1.5-mm. Pantak tube and then sucked into the parallel narrow portion of the glass tube by a vacuum pump. If care is taken in this last procedure it is possible to suck off quickly quite an appreciable amount of the adhering liquor without drying the specimen. The Pantak tube was sealed at both ends and mounted on the goniometer of a cylindrical x-ray camera (radius 3 cm.). Nickel-filtered CuKα radiation was used for the x-ray diagrams.

It should be noted that the identification of the exact soda cellulose from the x-ray diagram is generally very difficult, especially with cotton, and in many instances it was not certain whether more than one component was present. The soda celluloses shown in Table I are therefore thought to be the most probable after careful consideration of the x-ray diagrams and reference to the literature.[2-5] Soda cellulose Q was particularly difficult to identify, since the diagrams of cellulose I (i.e., unchanged component) is always present on the x-ray diagrams from these experiments. Difficulty was also experienced in the identification of soda

TABLE I
Preparation of Soda Celluloses

Cellulose	Soda cellulose Q		Soda cellulose I		Soda cellulose I + III		Soda cellulose II		Soda cellulose IIh		Soda cellulose V	
	NaOH concn., N	Temp., °C.	NaOH concn., N	Temp., °C.	NaOH concn., N	Temp., °C.	NaOH concn., N	Temp., °C.	NaOH concn., N	Temp., °C.	NaOH concn., N	Temp., °C.
Ramie	2.0	0	2.5–4.0	0			7.5–10.0	20			6.0–10.0	0
			3.0–5.0	20			10.0	20–80	10.0	100		
			3.5	20–100	5.0	80–100						
			5.0	20–60	7.5	100						
Cotton	2.5	0	3.0–6.0	0			10.0	20			10.0	0
			4.0–7.5	20			10.0	20–80	10.0	100		
			5.0	20–60	5.0	80–100						
					7.5	100						

cellulose II, except with ramie at 100°C. The soda cellulose V, mentioned in Table I, is the one defined by Sobue et al.[2] as formed at low temperatures.

It was an outstanding feature of most of the x-ray diagrams that considerable disorientation and disturbance had occurred in the crystal lattice. This implies that under conditions of free swelling there is a disturbance of the sheets within the fibrils. This fact has often been overlooked in the literature, and as a result the impression is gained that the lattice changes that take place are more regular than is, in fact, the case. The present experiments indicate that regular lattice changes are more probable if tension is used during or after swelling. The observed shrinkage of the fibers under free swelling conditions would also seem to support this conclusion.

X-Ray Results from Soda Celluloses Washed in Aqueous Solutions

In almost every case a water cellulose was produced by washing a soda cellulose. The exceptions resulted from the treatment of soda cellulose IIh, prepared at 80 and 100°C. from both ramie and cotton. With these samples the acidified salt solution gave a sample with a clearer and better defined x-ray diagram of soda cellulose IIh than that given in the presence of caustic soda. This remarkable fact means that either the acidified salt solution does not decompose the soda cellulose despite the presence of acid, or that the soda cellulose IIh contains no caustic soda in the crystal structure. The first explanation seems the more plausible and offers some evidence that saturated salt solutions prevent transient swelling, and thus hinder decomposition of the soda cellulose. Since hydrogen ions do not penetrate the structure sufficiently to decompose it, it might be concluded that the structure also contains no water of hydration.

Another unusual feature was also observed in a few experiments in which the acidified salt solutions were used. The x-ray diagram of ramie treated with $3N$ caustic soda at 20°C. or $5N$ caustic soda at 80°C. and then with acidified salt solution showed additional lines of crystalline sodium chloride. The experiments could be repeated, and care was taken to see that no drying of the sample took place. The phenomenon occurs only under
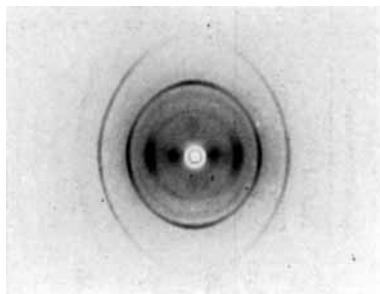

Fig. 1. X-ray diagram of ramie wet with acidified sodium chloride solution after treatment in $3N$ sodium hydroxide solution at 20°C.

specific conditions, and no other concentrations of caustic soda or any other temperature will suffice. This result implies a supersaturation of sodium chloride within the fiber, but it is not clear why only these conditions cause this to occur. Figure 1 illustrates the x-ray diagram of ramie treated with $3N$ caustic soda at $20°C$. and washed in acidified salt solution; it is evident that the (200) plane of the sodium chloride pattern is oriented. Cotton gave this phenomenon only with $10N$ caustic soda at $60°C$. but the salt lines were less definite and apparently unoriented. The latter was probably masked because of the effects of the more complex morphology of cotton.

The main results of interest are concerned with the x-ray diagrams of the products formed on decomposition of the soda celluloses. The fundamental diagram could be identified with that of a water cellulose or a cellulose hydrate, but it became very evident that the first equatorial reflection 101 varied considerably in spacing according to experimental conditions. This fact was also noted by Legrand.[6] Furthermore, although the $10\bar{1}$ and 002 reflections did not vary much in spacing, in many preparations the intensity of the $10\bar{1}$ reflection was distinctly greater than that of the 002 reflection, especially if sodium chloride was present in the washing liquid. If water alone was present, then the $10\bar{1}$ and 002 reflections were more nearly equal in intensity.

Over a hundred "water celluloses" were prepared in the course of these experiments, and it was found that d_{101} varied between 7.44 and 9.24 A., but the spacings of the $10\bar{1}$ and 002 reflections gave mean values of 4.44 and 4.02 A., respectively. The maximum variation for the spacings of these planes was within the limits (4.64–4.30 A. for the $10\bar{1}$ and 4.13–3.91 A. for the 002; the majority of values found were, however, close to the mean values quoted.

Calculation shows that a true cellulose monohydrate would have a spacing of 8.85 A., so that clearly only under special circumstances is a precise monohydrate formed. In most experiments, therefore, there is a statistically variable water content within the sample which is confined to the (101) plane of the structure.

The base of the unit cell calculated for $d_{101} = 9.24$ A., the greatest value of d_{101} found for these experiments, had the dimensions $a = 10.02$ A., $c = 10.20$ A. $\beta = 52.05°$. It is significant that in this cell the distance between the centers of chains in the 101 plane is identical with that found for cellulose II, the product formed on drying the water cellulose. Check calculations show that this is true for all the water celluloses investigated.

If the two main facts are taken into consideration, namely, that there is considerable variation of distance between the (101) planes, but that within the (101) planes the interchain distances are virtually invariant, then it seems clear that the true fundamental unit in these reactions is a sheet of chains and not a single chain. Such a sheet is held together chiefly by van der Waals forces, although the possibility of hydrogen bonds between the primary hydroxyl group of one chain and the secondary hydroxyl of a
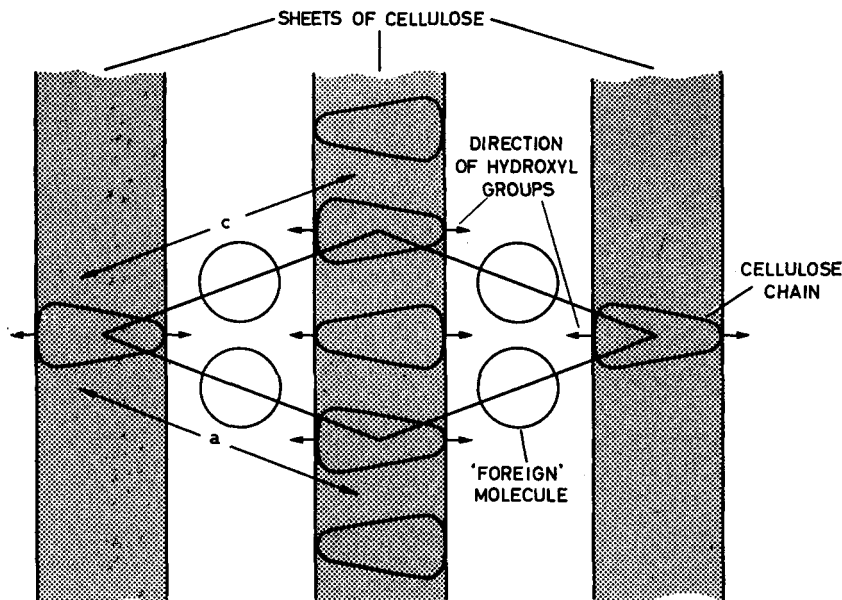
Fig. 2. Diagrammatic representation of a possible aggregation of cellulose sheets. $b =$ fiber and chain axis, at right angles to the plane-view shown.

neighboring chain in the (101) plane must not be overlooked. This was suggested by Frey-Wyssling[7] for the structure of cellulose I. In such sheets the hydroxyl groups project from the surfaces and are free for chemical reaction (see Fig. 2).

The x-ray diagrams for the water celluloses accord with the aggregation of such sheets with an arbitrary water content. It is possible that each sheet may have a definite amount of water per glucose unit attached to it, and yet aggregate with neighboring sheets with a variable free water content between the hydrated sheets. Thus, the unit that is concerned in swelling is the sheet of chains and not a crystal unit. Any compound formation, or sorption complex, is relevant only to such sheets and its exact nature cannot necessarily be derived from calculations based on crystal dimensions.

The variable number of molecules between the (101) planes can affect the intensities found for the $10\bar{1}$ and 002 planes without necessarily affecting the spacings. The difference in intensities for the $10\bar{1}$ and 002 reflections found when sodium chloride was present therefore implies the presence of sodium chloride between the sheets as well as water. As it is improbable that sodium chloride is preferentially adsorbed it is possible that it lies randomly distributed between the cellulose sheets.

What appears to be true for the water celluloses may also be true for the soda celluloses. The sheets probably react with caustic soda in the manner suggested by Chédin and Marsaudon[8] to form a definite complex, but these sheets then aggregate with a variable caustic soda and water content be-

tween them. X-ray diagrams from such complexes can have equatorial reflections and be deficient in layer line reflections because of the precise two-dimensional nature of the sheets themselves. The frequent occurrence of this type of x-ray diagram for soda cellulose explains the variation in spacings of equatorial reflections for apparently similar compounds. Only under precise experimental conditions can defined crystal structures be formed; these conditions are often difficult to obtain and hence cause the confusion of nomenclature of the soda celluloses found in the literature.

This concept of sheets can also be used to explain the difference in those soda celluloses that have a repeat distance of 10.3 A. and those that have a repeat distance of 15.5 A. It has been suggested by Meyer et al.[9] that this change is one from a twofold to a threefold axis along the cellulose chain. In view of the evidence given in this paper this seems highly unlikely. The simpler explanation is that the sheets pack in such a way that each is displaced along the fiber axis relative to the previous one, one-half of a repeat distance in one set of compounds and one-third of a repeat distance in the other set of compounds. There are many arrangements in which sheets with such displacements can be packed, but the simplest is $\pm 1/2$ (or $\pm 1/3$) displacement of alternate sheets. The diffraction effects from such displaced sheets would cause systematic absences along the meridian that would be identical with those postulated for two- and threefold axes, respectively. Absences in other directions would also be predicted, but the poor x-ray diagrams of the soda celluloses do not permit a test of these conditions.

The difference between cellulose I and cellulose II can also be explained in terms of these sheets. It has been suggested by Frey-Wyssling[7] that in cellulose I there are hydrogen bonds between chains in the (101) plane. Such bonds would stabilize the structure and, provided they are not broken, the sheets of chains can be moved apart in the swelling action and restored to the crystal structure of cellulose I on removal of the swelling agent. This appears to be possible in swelling reactions with amines[10] and there is no reason why other swelling agents should not react in a similar way. With caustic soda, however, Chédin and Marsaudon[8] postulate that all the hydroxyl groups of the anhydroglucose unit enter into the caustic soda complex. Under these conditions the hydrogen bond within the (101) plane will be broken, and some rearrangement of chains will take place within the sheet. On removal of the caustic soda, the hydrogen bonds form in a different way from those found in cellulose I because the sheets of chains are fundamentally placed differently with respect to one another due to the rearrangement of the chains, and in consequence a new structure is formed. Indeed, infrared evidence[11] indicates that a new system of hydrogen bonds has been formed. Only by restoration of the disposition of the chains within the sheets is the condition for the re-formation of cellulose I given, and this appears to depend partly on the interchain hydrogen bond, which apparently cannot be easily restored. The nature of the swelling agent thus determined whether rearrangements within the sheets

take place during swelling so that on removal of the swelling agent, the structure is restored to cellulose I or cellulose II. By inference, therefore, the effect of different swelling agents on the fine structure will depend on the fundamental reaction of the swelling agent with the sheets of cellulose chains.

X-Ray Analysis of Soda Celluloses Produced from Mercerized Ramie and Fortisan

Evidence of cellulose sheets as the fundamental reacting units was also found with samples of mercerized ramie and with Fortisan, a highly oriented regenerated cellulose. The ramie was mercerized by treatment with $5N$ caustic soda at 0°C. for 1.5 hr., followed by a thorough wash in water and drying in the air.

Mercerized ramie gave soda cellulose I for caustic soda concentrations 3–$10N$, with some indication of soda cellulose I at $2N$. The x-ray diagrams were disoriented and similar to those given by native celluloses Fortisan gave soda cellulose I for concentrations of caustic soda of 2–$7.5N$, with slight evidence for soda cellulose I at $1N$. A poor cellulose II was given in $10N$ caustic soda. Diffuse x-ray diagrams were obtained for all caustic soda concentrations other than $2N$.

On washing out the caustic soda, the d_{101} spacing of the water cellulose was always less than that expected for the monohydrate (i.e., 8.85 A.) unless caustic soda concentrations above 4N were used in the swelling experiments. Regeneration of the soda celluloses produced in concentrations of caustic soda above $4N$ gave products that had d_{101} spacings close to that required for a monohydrate. Thus, the variable structures found with native celluloses were produced only by treatment of these samples with caustic soda concentrations below $4N$.

Analysis of the results showed that the d_{002} and $d_{10\bar{1}}$ spacings were substantially constant within the limits already given for native celluloses. The difference in intensity between the (10$\bar{1}$) and (002) planes was more marked in the presence of sodium chloride with these samples.

The results, therefore, show that similar factors operate for samples of cellulose II as with native celluloses, but the chance of the definite crystal structure of cellulose monohydrate being formed is higher. It is suggested that this more constant behavior of these samples arises because stable cellulose sheets react throughout and no chain alterations within the sheets complicate the reactions.

X-Ray Results from Soda Celluloses Washed in Alcohols

Further experiments were carried out by washing samples of soda cellulose I prepared from cotton in $5N$ caustic soda at 20°C. in various alcohols. The d_{101} spacings varied considerably (7.42–12.03 A., see Table II) but the $d_{10\bar{1}}$ and d_{002} spacings were substantially constant within similar limits as already given for the aqueous experiments with native celluloses; thus

TABLE II

Values of d_{101} for Soda Cellulose I Treated with Alcohols

Treatment	d_{101}, A.
Washed in methanol	
Wet	8.82
Dried in air	7.73
Dried at 110°C.	7.42
Washed in ethanol	
Wet	12.03
Dried in air	9.86
Dried at 110°C.	8.42
Washed in n-propanol	
Wet	8.73–16.0
Dried in air	10.91
Dried at 110°C.	8.05
Washed in n-butanol	
Wet	10.9
Dried in air	8.42

$d_{101} = 4.44$ A. (maximum variation 4.53–4.39 A.); $d_{002} = 4.02$ A. (maximum variation 4.12–3.96 A.).

Calculation showed that the distance between the chains in the (101) plane was constant within the experimental error so that again only the changes in distance between the (101) planes has to be considered.

It is instructive to discuss the values for d_{101} found under different conditions and these are listed in Table II. With n-propanol the spacing of the (101) plane of the wet complex can vary between 8.73 and 16 A. It is then not surprising to find different complexes formed on drying, and the apparent anomaly of a wet specimen with a 101 spacing of 8.73 A. and a dry specimen with a 101 spacing of 10.91 A. can be explained. The spacing of the (101) plane was also found to vary according to the time of drying. It is evident from the difference between the values for the 101 spacing of the air dried sample and that dried at 100°C. that the air-dried sample contains trapped molecules, but it is uncertain whether these are caustic soda or propanol molecules.

The value of d_{101} given by the sample washed in n-butanol and dried in the air is less than that for a corresponding sample dried from n-propanol, whereas it was expected to be larger on consideration of the sizes of the molecules of n-propanol and n-butanol, provided these are the only entrapped molecules. However, the solubility of caustic soda in these alcohols is different and therefore caustic soda may also be present in the structure to cause this anomaly.

It is interesting to note that the x-ray diagram of the sample washed in n-propanol and dried in the air was particularly sharp, which suggested that a precise crystal structure had been formed.

The axial repeat distances for the samples was found to be 10.3 A. and from the measuring spacings of the (101), (10$\bar{1}$), and (002) planes it was possible to calculate unit cell dimensions. From these dimensions the

TABLE III
Unit Cells of Alcohol-Treated Samples

Sample	Unit cell dimensions[a]					ΔV, A.³	V_a, A.³	$\Delta V/V_a$
	a, A.	b, A.	c, A.	β	V, A.³			
Treated with methanol								
Wet	9.74	10.3	10.01	53°20'	805	129	42.3	3
Dried in air	8.57	10.3	9.32	59°24'	710	34		0.8
Dried at 110°C.	8.22	10.3	9.14	61°38'	681	5		0
Treated with ethanol								
Wet	13.4	10.3	12.5	40°6'	1109	433	59.0	7.3
Dried in air	10.9	10.3	10.75	48°19'	953	277		4.7
Dried at 110°C.	9.28	10.3	9.73	55°38'	768	92		1.5
Treated with n-propanol								
Wet	9.26	10.3	9.59	57	768	92	80.5	1.1
Dried in air	12.11	10.3	11.6	43°56'	1040	364		4.5
Treated with n-butanol								
Wet	12.11	10.3	11.6	43°56'	1040	364	98.5	3.7
Dried in air	9.28	10.3	9.73	55°36'	768	92		0.9

[a] Cellulose II: a = 8.14 A., b = 10.3 A., c = 9.14 A., β = 62°, V = 676 A.³

volumes of the unit cells were calculated, and these are given in Table III. If the volume for the unit cell of cellulose II is subtracted from the volume of these unit cells, then the residual volume V is the volume containing the alcohols if these alone remain in the structure. The volume of the individual alcohol molecules V_a was calculated from the appropriate densities at 20°C. The number of possible molecules in the unit cells then is given by V/V_a. Other factors, however, must be borne in mind. First, other molecules, such as caustic soda and water, may also be present; second, the alcohol molecules will not occupy all the available space; and third, the alcohol molecules can be compressed within the structure. Thus the values are only approximate.

The conclusions from these calculations show that when the sample is wet with methanol, apparently three molecules of methanol are held per unit cell. It is unlikely that an odd number of molecules will be present in defined locations, because there are two chains of cellulose per cell. Therefore, this result indicates that there are two molecules of methanol per unit cell, allowing for the factors just discussed. The possibility of a variable structure is thus indicated, again with cellulose sheets as fundamental reacting units as suggested elsewhere. The sample dried at 110°C. has a unit cell close to that for cellulose II, and the implication is that such drying has removed all the methanol from the structure, and, in fact, no caustic soda was present.

Similar arguments for the ethanol complexes make it possible that a definite compound exists for the sample wet with ethanol (8 mols ethanol), air-dried (4 mols ethanol) and even when dry at 110°C. (2 mols ethanol). It is more probable, however, that the latter is an inclusion compound. Hess and Trogus[3] found that soda cellulose III can be formed by washing soda cellulose I in dry ethanol. Since soda cellulose III can also be prepared by drying soda cellulose I, this would suggest that no ethanol was trapped in this structure. Evidence for variable products according to experimental conditions is thus indicated. The anomalies with n-propanol and n-butanol have already been referred to, and it appears less likely that precise compounds are formed, although it is then difficult to explain the sharp x-ray diagram of the complex with n-propanol.

It would appear that precise complexes with alcohols can be formed only under certain conditions, which are not known. Other complexes with variable molecular content between the cellulose sheets can be formed whose x-ray diagrams can be mistaken for crystalline compounds but seem to be due to statistical packing of precise two-dimensional sheets of cellulose chains with other molecules between them. It is possible that the effect of tension and increase of reaction times could result in the formation of precise compounds, but these suppositions have not been tested.

SUMMARY AND CONCLUSIONS

In the preparation of soda-celluloses and in their decomposition during different washing treatments, individual chains are not the ultimate re-

acting units but sheets of chains that retain a coherence throughout the reactions.

The cellulose sheets are largely held together by van der Waals forces, although additional stability through interchain hydrogen-bonds within the sheets is possible, especially in the native celluloses.

Reaction in caustic soda can affect the interchain dispositions within the sheets but not the coherence of the chains together as sheets.

As a result of the coherence of these sheets throughout a series of reactions, the products can be best analyzed as an aggregate of such sheets with the possibility of other molecules being held between them. Such aggregations of sheets can give recognizable x-ray diagrams, but such diagrams are not necessarily indications of precise crystal structures.

The fact that aggregations of sheets can be formed under the same experimental conditions results in the confusing mass of data found in the literature on soda celluloses.

Inclusion compounds with alcohols can be formed under certain conditions, by the sheets entrapping alcohol molecules between them, but, again, variable products can be found according to experimental conditions.

It is thus concluded that swelling involves mainly the moving apart of sheets of cellulose chains and that the final product formed will depend on the ability of the swelling agent to facilitate readjustments of chains within the sheets and also the mechanism of the decomposition of the swelling complex. Thus, reactions with caustic soda cannot be taken as typical of all swelling reagents.

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Résumé

Une étude aux rayons-X de produits formés par l'action de la soude caustique sur différents échantillons de cellulose et de ceux formés par la décomposition de ces produits par des réactifs aqueux et des alcools montre que l'unité fondamentale qui réagit est une feuille des chaînes cellulosiques, et non la chaîne cellulosique individuelle. Bien que la soude caustique puisse affecter les dispositions relatives des chaînes au sein de ces feuillets jusqu'à un certaine degré, elle ne peut pass éparer les chaînes, et les produits dépendent donc de l'aggrégation des feuillets cellulosiques avec ou sans autre molécules entre eux. Une telle aggrégation amène à des produits variables dont les diagrammes aux rayons-X peuvent toutefois montrer diverses réflexions. Il est dès lors important, au cours des réactions de gonflement de tenir compte de la possibilité

de l'agent gonflant de modifier les feuilles de cellulose et du mode de décomposition de ces complexes formés en cours de gonflement. Donc le gonflement avec la soude caustique ne peut pas être considéré comme un réactif typique de tous les réactifs aqueux de la réaction à l'égard de la cellulose, et la possibilité avec d'autres réactifs de produire la cellulose Ia u lieu de la cellulose II, après une série de réactions de gonflement peut être considérée avec attention.

Zusammenfassung

Eine Röntgenuntersuchung der durch Einwirkung Natroulauge auf verschiedene Celluloseproben gebildeten Produkte, sowie der durch Zersetzung dieser Produkte durch wässrige Reagenzien und Alkohol gebildeten, zeigt, dass die reagierende Grundeinheit eine Schicht von Celluloseketten und nicht die individuellen Celluloseketten selbst ist. Die Natroulauge kann zwar die relative Lage der Ketten in diesen Schichten beeinflussen, aber nicht die Ketten trennen; die Reaktionsprodukte hängen dann von der Ansammlung der Celluloseschichten mit oder ohne dazwischenliegenden anderen Molekülen ab. Eine solche Ansammlung führt zu verschiedenartigen Produkten, deren Röntgendiagramme aber scharfe Reflexe zeigen können und fälschlicherweise für diejenigen einer genaveren Kristallstruktur gehalten werden können. Es ist daher bei Quellungsreaktionen wichtig, die Wirkung des Quellungsmittels zur Modifizierung der Celluloseschichten und der Zersetzung der bei der Quellung gebildeten Komplexe in Betracht zu ziehen. Die Quellung in Natroulauge kann somit in ihrem Verhalten gegen Cellulose nicht als typische für alle wässrigen Quellungsmittel betrachtet werden und die Möglichkeit, mit anderen Reagenzien Cellulose I anstatt Cellulose II nach einer Reihe von Quellungsreaktionen zu erhalten, kann nicht ausgeschlossen werden.