

## Penetration of Water-Soluble Polymers into Cellulose Fibers

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### Synopsis

Polymetaphosphate and polyethylene glycol in aqueous solution are excluded completely from rayon fibers. Determinations of nonsolvent water ( $\delta$ ) with these reference substances give the same value which can be used as a measure of the true swelling. The polymers can, however, penetrate into porous areas present in cotton. The average polymer concentration inside these areas is lower than in the external solution. High speed centrifugation results in decreased  $\delta$  values, which is explained by a compression of the porous areas. Higher  $\delta$  values are obtained as the molecular weight of the reference substance is increased. With polymetaphosphate the  $\delta$  values decrease when the external concentration is increased, whereas with polyglycol the  $\delta$  value within a wide range is independent of the concentration.

Nonsolvent water ( $\delta$ ) in cotton has been determined by several workers using common electrolytes such as sodium chloride,<sup>1</sup> sodium thiosulfate,<sup>2-5</sup> and potassium cyanocobaltate(III)<sup>6</sup> as reference substances. A comparison between the published results of various authors shows that the  $\delta$  values are largely dependent upon the type of electrolyte. Similarly, the concentration has an appreciable effect, which, however, has been disregarded by most authors.

In earlier papers polyelectrolytes (chiefly polymetaphosphate) were used as reference substances in determinations of nonsolvent water in rayon,<sup>7</sup> cellulose films,<sup>8</sup> and wood pulps.<sup>9</sup> It was shown that in favorable cases the  $\delta$  values can be used as a measure of the total amount of water inside the cellulose phase. The present paper deals with the nonsolvent water in cotton fibers with polymetaphosphate and polyethylene glycol<sup>5</sup> as reference substances. A comparison with the results obtained with other cellulose materials is also given. In order to elucidate the mechanism some experiments with low molecular weight electrolytes are also reported.

### EXPERIMENTAL

#### Cellulose Materials

Raw cotton was purified according to a method recommended by the Division of Cellulose Chemistry of the American Chemical Society.<sup>10</sup> This purification involves an extraction with alcohol and ether and sub-

sequent boiling with 1% sodium hydroxide. Two different samples designated A and B were received from the same factory. With sample B the loss in yield during the alkaline boiling was 3.3%. The carboxyl content before and after this step was 3.0 and 0.5 meq./100 g., respectively. Some experiments were carried out with cut and beaten fibers. The purified cotton was cut in a Wiley mill and passed through a 20-mesh screen. Beating of the cut fibers was carried out in a Lampén beater for 4 hr. The conditions were the same as described in an earlier paper.<sup>9</sup>

A sample of mercerized cotton was prepared by steeping purified cotton in 18% sodium hydroxide for 1 hr. at 20°C. After washing, the sample was dried at room temperature.

Hydrolysis of purified cotton fibers was performed with 0.04*N* sulfuric acid at 100°C. for 16 hr.

In some experiments two samples of oxidized cotton were used. The purified cotton was treated with sodium hypochlorite (1 g. active chlorine/l.). The sample with the lowest carboxyl content was prepared by treatment at pH 10.5 for 10 hr. at 50°C. With the other sample the pH was the same at the start, but was permitted to drop during the treatment (20 hr.).

### Sodium Phosphates

The samples of radioactive sodium polymetaphosphate were prepared as described in an earlier paper.<sup>9</sup> The degree of polymerization is reported as the number average value determined by endgroup titration.<sup>11</sup> Trimetaphosphate was prepared by heating sodium dihydrogen phosphate 2 hr. at 800°C. and then keeping the molten product for 24 hr. at 550°C.

### Polyethylene Glycol

Polyethylene glycol samples were obtained from the British Drug Houses Ltd. and L. Light and Co. Ltd. The molecular weights given are those reported by the suppliers.

### Procedure

The determinations of nonsolvent water ( $\delta$ ) and centrifuge swelling, i.e., the amount of water solution held by the cellulose after centrifugation, were carried out as described in previous papers.<sup>7,9</sup> Both quantities are expressed in grams water per gram dry cellulose (110°C.). The reference substance adhering to the fibers was displaced by washing with water. The phosphates were determined radiometrically. The glycols were determined by oxidation with dichromate. If not otherwise mentioned, the centrifugation has been carried out at a relative centrifugal force (RCF) of 100 *g*. The data given in the tables and figures are average values obtained from two determinations.

In some experiments with purified cotton the sample was dried over P<sub>2</sub>O<sub>5</sub> under vacuum at room temperature for three days. One part of

the dried cotton was then pretreated with 0.001*N* sodium polymetaphosphate solution for 12 hr. at +4°C and another part in water under the same conditions. The  $\delta$  values determined in 0.001*N* solution differed by less than 2% from each other and from the value obtained for the undried sample after preswelling in water for 2 days at room temperature.

## RESULTS AND DISCUSSION

### Experiments with Cotton in Electrolyte Solutions

The results presented in Figures 1 and 2 show that the relative centrifugal force has an influence upon  $\delta$  both with native and mercerized cellulose. In this respect cotton exhibits a behavior different to that of rayon fibers, whose  $\delta$  values are largely unaffected by the rate of centrifugation.<sup>7</sup> The results obtained with cotton are in line with those observed with beaten wood pulp. With both materials the RCF value has a strong influence upon  $\delta$  at low concentrations of polymetaphosphate, whereas at high concentration this influence is slight.

The  $\delta$  values determined for cut fibers differ only slightly from those observed for whole fibers, whereas the centrifuge swelling differs markedly. A comparison between Figure 1 and Figure 2 shows that the amount of nonsolvent water is greater for mercerized cotton than for native cotton.

Polymetaphosphate cannot penetrate into rayon fibers (unless these contain open pores or exhibit an abnormally high swelling), whereas the polyelectrolyte can penetrate into porous areas in beaten wood pulp. In these areas the polymetaphosphate concentration is lower than that in

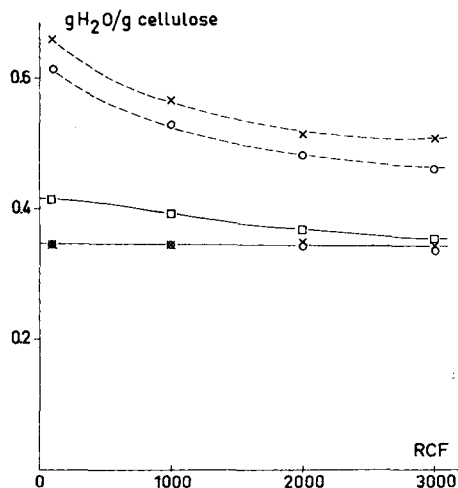


Fig. 1. Influence of the relative centrifugal force (RCF) upon (—) nonsolvent water ( $\delta$ ) with sodium polymetaphosphate ( $DP_n = 85$ ) as reference substance and upon (- -) centrifuge swelling: ( $\square$ ) cotton A, whole fiber in 0.0001*N* solution; ( $\circ$ ) cotton A, whole fiber in 0.01*N* solution; ( $\times$ ) cotton A, cut fiber in 0.01*N* solution.

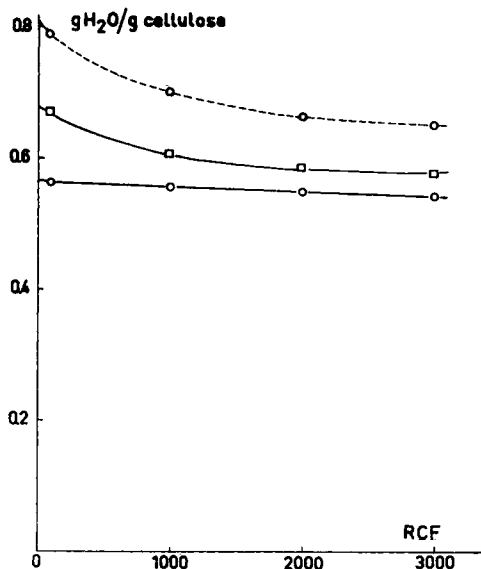


Fig. 2. Influence of the relative centrifugal force (RCF) upon (—) nonsolvent water ( $\delta$ ) with sodium polymetaphosphate ( $DP_n = 85$ ) as reference substance and upon (- -) centrifuge swelling (mercerized cotton A): ( $\square$ ) 0.0001*N* solution; ( $\circ$ ) 0.01*N* solution.

the external solution provided that the external concentration is not too high. During the centrifugation the porous areas are compressed, which explains the decrease in  $\delta$  with an increase in RCF. The similarity between cotton and wood pulp indicates that in cotton there exist certain areas, which, in equilibrium with polymetaphosphate solution, contain polymetaphosphate solution of a lower concentration than that of the external solution. These areas are compressed upon centrifugation.

At high polyelectrolyte concentration the concentration inside these porous area differs only slightly from that of the external solution. A compression of these areas, effected by centrifugation at high speed, will, therefore, only have a slight effect upon the  $\delta$  values.

An alternative (although less plausible) explanation of the effect of the RCF value upon  $\delta$  would be that during the centrifugation pure water is pressed out of some areas in the fiber. The observation (see under procedure) that a direct determination of  $\delta$  with a dry sample gives the same  $\delta$  value as that obtained after preswelling in water indicates that this explanation cannot be correct.

With common types of rayon the concentration of polymetaphosphate has a negligible effect upon the  $\delta$  value except at extremely low concentration, where a decrease in  $\delta$  can be observed. This anomaly is explained by a reversible sorption of a small amount of polymetaphosphate.<sup>12</sup> At higher concentration this adsorption has a negligible effect upon  $\delta$ .

Unlike rayon, the  $\delta$  values obtained with purified cotton decrease significantly for an increased polymetaphosphate concentration (Fig.

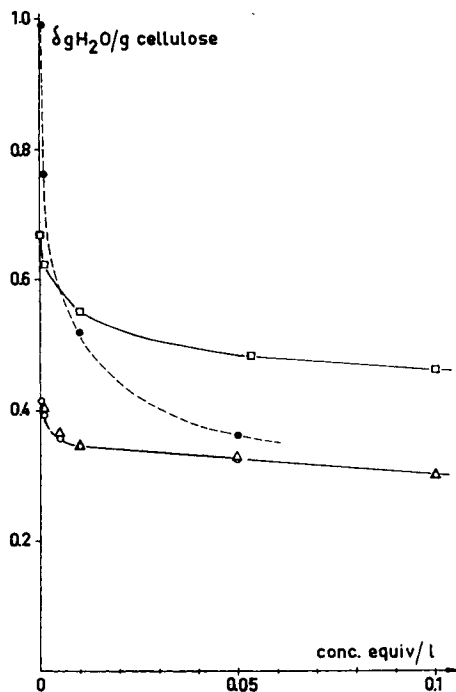


Fig. 3. Influence of the concentration of the sodium polymetaphosphate ( $DP_n = 85$ ) upon  $\delta$ : (●) beaten cotton A; (□) mercerized cotton A; (O) cotton A, whole fiber ( $\Delta$ ) cotton A, cut fiber.

3). It is seen that within the whole range of concentration the  $\delta$  values are higher for mercerized cotton than for native cotton. In agreement with the results earlier observed with wood pulp,<sup>13</sup> beating of cotton results in higher  $\delta$  values and an increased effect of the polyelectrolyte concentration upon  $\delta$ .

Some experiments have been carried out with a polymetaphosphate sample of extremely high molecular weight ( $DP_n = 1000$ ). The results given in Table I show that an increased molecular weight results in higher  $\delta$  values. Similar observations have been made in experiments with

TABLE I  
Nonsolvent Water ( $\delta$ ) with Sodium Polymetaphosphate and Polymetaphosphoric Acid as Reference Substances. Purified Cotton B

$PO_3$ concn., eq./l.	$\delta$ in sodium polymetaphosphate ( $DP_n = 85$ ), g./g.	$\delta$ in sodium polymetaphosphate ( $DP_n = 1000$ ), g./g.	$\delta$ in polymeta- phosphoric acid ( $DP_n = 85$ ), g./g.
0.0003	0.464	0.497	0.356
0.001	0.420	0.478	0.345
0.01	0.378	0.445	0.323
0.1	0.344		

cellulose films.<sup>8</sup> The dependency of concentration of the reference electrolyte observed in all experiments with cotton is typical for swollen solids, whose structure permits a penetration of the electrolyte into the swollen phase but for which the electrolyte concentration inside the solid is lower than that of the external solution.<sup>14</sup>

Like other polyelectrolytes, polymetaphosphate coils in concentrated solutions, whereas the size of the anion increases upon dilution. A possible explanation of the decrease in  $\delta$  with an increased concentration of polymetaphosphate would be that pores present in the cotton fibers have such dimensions that the extended polyelectrolyte is excluded from these pores, whereas the coiled polyelectrolyte present in a more concentrated solution can pass into the pores. If this molecular sieve effect were the dominant factor, a low molecular weight electrolyte would at low electrolyte concentration give a much lower  $\delta$  value, since its dimensions are smaller than those of the coiled polyelectrolyte. The results presented in Table II

TABLE II  
Nonsolvent Water ( $\delta$ ) with Sodium Trimetaphosphate as  
Reference Substance. Purified Cotton B

PO <sub>3</sub> concn., eq./l.	$\delta$ , g./g.
0.0001	0.458
0.001	0.371
0.01	0.271
0.1	0.172

show, however, that at very low concentration sodium trimetaphosphate gives  $\delta$  values which differ only slightly from those obtained with sodium polymetaphosphate. These results show that the effect of concentration upon  $\delta$  in polymetaphosphate solution cannot be explained by the coiling of the polyelectrolyte. At higher concentration the  $\delta$  values determined with trimetaphosphate as reference substance are much lower than those determined with polymetaphosphate. These results suggest that the porous areas present in cotton fibers contain charged carboxyl groups and that the exclusion of ions in dilute solution can qualitatively be explained as a Donnan effect. The concentration of charged groups inside a purified cotton fiber is extremely low and this explains the rapid decrease in  $\delta$  for an increased concentration of trimetaphosphate.

The effect of the carboxyl groups can be offset by working in sufficiently acid medium, where these groups are essentially nondissociated. When working with polymetaphosphoric acid instead of polymetaphosphate<sup>9</sup> the influence of the carboxyl groups can be largely eliminated. Results obtained with polymetaphosphoric acid are included in Table I. It is seen that the  $\delta$  values determined in acid medium are much lower than those observed in neutral medium. This demonstrates that the charged carbonyl groups contribute to the exclusion of polymetaphosphate from

the porous areas in cotton. The concentration dependency of  $\delta$  in sodium polymetaphosphate solution is, therefore, at least partly due to the presence of charged groups in the cellulose.

The carboxyl content in cotton purified by mild alkali boiling is extremely low. It is likely that a great part of the carboxyl groups is located in the porous areas and is present as pectic substances and similar material which have not been completely removed during the alkaline purification. Experiments with raw cotton (extracted with alcohol but not subjected to alkali boiling) lend support to this assumption.

The results given in Table III show that the  $\delta$  values both in polymetaphosphate and in trimetaphosphate are higher for raw cotton than for the

TABLE III  
Nonsolvent Water ( $\delta$ ) with Polymetaphosphate ( $DP_n = 85$ ) and Trimetaphosphate as Reference Substances. Raw Cotton B

PO <sub>3</sub> concn., eq./l.	$\delta$ in sodium	$\delta$ in sodium
	polymetaphosphate, g./g.	trimetaphosphate, g./g.
0.0003	—	0.609
0.0005	0.692 <sup>a</sup>	0.556
0.001	0.694	0.508
0.01	0.663	0.435
0.1	0.512	0.278

<sup>a</sup> At lower concentration the adsorption of polymetaphosphate has a marked influence upon  $\delta$ . The  $\delta$  value determined in 0.0002*N* solution was equal to 0.674.

purified cotton. This comparison shows that the material removed during the mild alkali boiling has a marked influence upon the accessibility of both polyelectrolytes and other electrolytes to the cotton. Both in dilute and more concentrated solutions the  $\delta$  values in trimetaphosphate are lower than in polymetaphosphate and, as can be expected, the difference between the  $\delta$  values increases with an increased concentration.

Experiments with purified cotton subjected to hypochlorite bleaching

TABLE IV  
Nonsolvent Water ( $\delta$ ) with Sodium Polymetaphosphate ( $DP_n = 85$ ) and Sodium Trimetaphosphate as Reference Substances. Experiments with Two Oxidized Samples of Cotton B

PO <sub>3</sub> concn., eq./l.	$\delta$ , g./g.		
	Oxidized cotton, carboxyl number 3.8		Oxidized cotton, carboxyl number 11.7, polymetaphosphate
	Trimeta- phosphate	Polymeta- phosphate	
0.001	0.482	0.551	0.40
0.01	0.403	0.467	0.39
0.1	0.283	0.421	0.38

have been carried out in order to elucidate further the influence of the carboxyl groups upon the  $\delta$  values. Values obtained with a sample subjected to a comparatively mild treatment with hypochlorite are reported in Table IV. A comparison between these values and those obtained with the untreated (purified) cotton (Tables I and II) shows that this treatment results in increased  $\delta$  values. The last column in Table IV gives the  $\delta$  value observed with a sample of purified cotton degraded with hypochlorite under such severe conditions that the fibers collapsed. At extremely low polymetaphosphate concentration the  $\delta$  values for this sample are lower than for the untreated sample. The probable explanation is that part of the porous areas has disappeared during the degradation with hypochlorite. More interesting is the observation that with this sample  $\delta$  is less sensitive towards changes in polymetaphosphate concentration. This observation lends additional support to the conclusion that the carboxyl groups have a great influence upon the penetration of electrolytes into cellulose fibers.

Purified cotton subjected to acid hydrolysis under mild conditions was also investigated. Under these conditions easily accessible material containing carboxyl groups was removed and, as could be expected, the hydrolyzed cotton exhibited lower  $\delta$  values in polymetaphosphate than the purified cotton (Table V).

TABLE V  
Nonsolvent Water ( $\delta$ ) with Sodium Polymetaphosphate ( $DP_n = 85$ ) as Reference  
Substance. Hydrolyzed Cotton A

PO <sub>3</sub> concn., eq./l.	$\delta$ , g./g.
0.0001	0.375
0.001	0.331
0.004	0.322
0.01	0.303

In order to demonstrate the influence of the charged carboxyl groups, experiments have also been carried out with a complex molybdenum cyanide,  $K_4Mo(CN)_8$  prepared according to Troell<sup>15</sup> and the corresponding free acid prepared by ion exchange. The analyses were made spectrophotometrically at 239 m $\mu$ . In 0.001–0.01M solution the observed  $\delta$  values were three to four times greater with the potassium salt than with the free acid. These results confirm that the carboxyl groups have a dominant influence upon the penetration of electrolytes into cotton.

#### Comparison between Cotton and Other Cellulose Materials

A diagram illustrating the influence of the polymetaphosphate concentration upon the nonsolvent water in various cellulose materials is given in Figure 4. It is seen that purified cotton exhibits lower  $\delta$  values than any of the other cellulose materials studied. Mercerized cotton exhibits greater values than native cotton and at low concentration of the



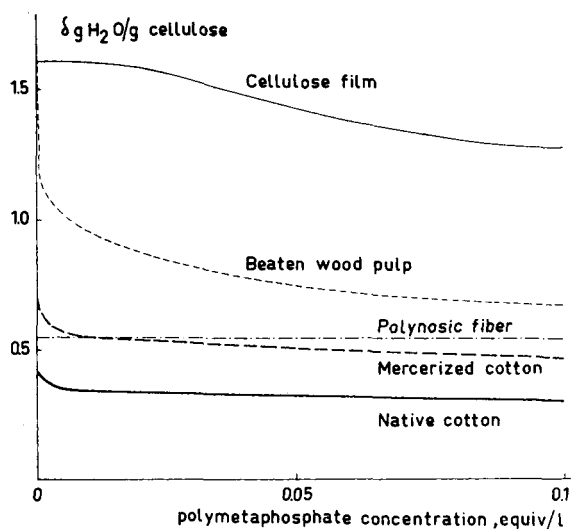


Fig. 4. Influence of the concentration of the sodium polymetaphosphate solution ( $DP_n = 85$ ) upon  $\delta$ .

reference electrolyte mercerized cotton gives higher values than polynosic fibers, which among rayons hitherto studied exhibit the lowest swelling.

With regenerated cellulose (rayon and cellulose films) the  $\delta$  value determined at a low concentration of polymetaphosphate can be used as a measure of the total amount of water held in the cellulose phase. With native cellulose materials the concentration dependency is very great at low polymetaphosphate concentrations. A reliable extrapolation to zero concentration cannot be carried out, which is explained by the presence of porous areas of various dimensions inside the fiber. The loosening of the fiber structure, which occurs when the fibers are beaten is reflected in higher  $\delta$  values which are more sensitive to changes in the electrolyte concentration. These results show that during the beating the uptake of water into areas inaccessible to the polyelectrolyte is increased and areas having such a porous structure that even the polyelectrolyte can penetrate them are formed. Qualitatively, cotton and wood pulp exhibit a similar behavior. The effect of beating is, however, more marked with wood pulps which are rich in hemicellulose.

All cellulose materials studied contain areas from which the polyelectrolyte is excluded completely. In equilibrium with a polymetaphosphate solution the porous areas referred to above contain polymetaphosphate but the concentration is lower than in the external solution. In an earlier paper dealing with the penetration of polymetaphosphate into cellulose films<sup>8</sup> it was shown that the molecular size has an influence upon the penetration of polyelectrolytes. Another important factor which affects the penetration into cellulose films is the charged carboxyl groups present in the porous areas. The results obtained with cotton show that both these

factors have an influence also when the penetration of polyelectrolytes into the porous areas in cotton fibers is concerned. Although the carboxyl content in purified cotton is low, the charged carboxyl groups in porous areas of the fiber have a strong influence upon the distribution of poly-metaphosphate as well as trimetaphosphate between these areas and the external solution. A larger amount of porous material is present in raw cotton and, as can be expected, the  $\delta$  values are higher with raw cotton than with cotton purified by boiling in an alkaline solution.

### Polyethylene Glycol as Reference Substance

In order to elucidate how the dimensions of an uncharged reference substance affect the value of  $\delta$ , experiments were performed with the use of polyethylene glycols of different molecular weights. The results given in Table VI show that within the concentration range studied the glycol con-

TABLE VI  
Nonsolvent Water ( $\delta$ ) with Polyethylene Glycol as Reference Substance

Polyethylene glycol		Nonsolvent water ( $\delta$ ), g. H <sub>2</sub> O/g.	
Concn., %	Molecular weight	Cotton B	Polynosic fiber
0.2	560	0.240	0.413
5	560	0.223	0.417
0.3	3,600	0.341	0.549
1	3,600	0.340	0.546
5	3,600	0.336	0.542

TABLE VII  
Nonsolvent Water ( $\delta$ ) with Polyethylene Glycol (1%) as Reference Substance

Molecular weight of polyethylene glycol	Nonsolvent water ( $\delta$ ), g. H <sub>2</sub> O/g.	
	Cotton B	Polynosic fiber
60	0.069	0.178
180	0.120	0.291
960	0.261	0.471
3,600	0.339	0.546
10,000	0.376	0.544
20,000	0.394	0.546

centration has a negligible effect upon the  $\delta$  values of cotton and polynosic fibers. For this reason, polyethylene glycol may, for certain purposes, be a more favorable reference substance than polymetaphosphate.

The influence of the molecular weight of the glycol is demonstrated in Table VII. It is seen that positive  $\delta$  values are obtained even with the mon-

omeric ethylene glycol and that over the whole range polyinosic fibers give higher values than cotton. With polyinosic fibers an increase in the molecular weight of the glycol results in higher  $\delta$  values. Above a certain molecular weight the  $\delta$  value is, however, independent of the molecular weight. The results indicate that determinations of  $\delta$  in high molecular weight polyethylene glycol can be used as a measure of the true swelling of fibers of this type. This is confirmed by the fact that the determinations of  $\delta$  carried out with polyethylene glycol ( $DP_n = 3600$  or higher) agree very well with the value determined in polymetaphosphate solution ( $\delta = 0.55$ ; cf. Fig. 4). Both types of reference substances are thus prevented from entering the cellulose phase. The observation that with glycols of low molecular weight

TABLE VIII  
Influence of the Relative Centrifugal Force (RCF) upon Nonsolvent Water ( $\delta$ )  
with Polyethylene Glycol (1%) as Reference Substance. Cotton B

Molecular weight of polyethylene glycol	RCF, <i>g</i>	Nonsolvent water ( $\delta$ ) <i>g.</i> H <sub>2</sub> O/ <i>g.</i>	Centrifuge swelling, <i>g.</i> solution/ <i>g.</i>
960	100	0.257	1.48
960	2000	0.249	0.51
20,000	100	0.391	1.55
20,000	2000	0.345	0.52

the  $\delta$  value is independent of the external concentration indicates that in these solutions the average glycol concentration in the cellulose phase is directly proportional to the external concentration [Henry's law].

Cotton shows a different behavior. Over the whole interval the  $\delta$  values increase as the molecular weight of the glycol is increased. This is explained by the presence of pores of various sizes in the native fibers. The results show that these pores have an influence upon the  $\delta$  values even when polymer nonelectrolytes are used as reference substances. The  $\delta$  values determined with polyethylene glycol of varying molecular weights can, therefore, be used to elucidate the pore size distribution in cellulose fibers.

Some experiments carried out at two different speeds of centrifugation are reported in Table VIII. With the polyglycol of low molecular weight the rate of centrifugation has a negligible influence upon the  $\delta$  value. This result indicates that before the centrifugation the larger pores which are compressed during the high speed centrifugation contain a polyglycol solution of nearly the same concentration as the external solution. With the polyglycol of high molecular weight a significant decrease in the  $\delta$  value is observed at high rate of centrifugation indicating that under these conditions a polyglycol solution of lower concentration than that in the external solution is pressed out of some porous areas in the fibers.

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### Résumé

On a extrait totalement de la fibre de rayonne, le polymétaphosphate et le polyéthylène glycol en solution aqueuse. Des déterminations de l'eau ( $\delta$ ) non solvatante avec ces substances de références donnent les mêmes résultats qui peuvent être utilisées comme une mesure du gonflement réel. Les polymères peuvent cependant pénétrer dans les surfaces poreuses présentes dans le coton. La concentration moyenne en polymère à l'intérieur de ces surfaces est plus faible que dans la solution externe. La centrifugation à grande vitesse provoque une diminution des valeurs de  $\delta$ , ce qui est expliqué par une compression des surfaces poreuses. On obtient des valeurs plus élevées de  $\delta$  lorsqu'on utilise comme référence des substances à poids moléculaire plus élevé. Il y a une diminution des valeurs de  $\delta$  dans le cas du polymétaphosphate, lorsque la concentration externe augmente, alors que pour les polyglycols les valeurs de  $\delta$  sont indépendantes de la concentration dans un large domaine.

### Zusammenfassung

Polymetaphosphat und Polyäthylenglykol in wässriger Lösung werden von Rayonfasern nicht aufgenommen. Bestimmung des nicht als Lösungsmittel wirkenden Wassers ( $\delta$ ) mit diesen Bezugssubstanzen liefert Werte, die auch als Mass für die wahre Quellung benutzt werden können. Die Polymeren können jedoch in die in Baumwolle vorhandenen porösen Bereiche eindringen. Die mittlere Polymerkonzentration innerhalb dieser Bereiche ist niedriger als in der äusseren Lösung. Zentrifugieren mit hoher Geschwindigkeit führt zu herabgesetzten  $\delta$ -Werten, was durch eine Kompression der porösen Bereiche erklärt wird. Bei höherem Molekulargewicht der Bezugssubstanz werden höhere  $\delta$ -Werte erhalten. Mit Polymetaphosphat nehmen die  $\delta$ -Werte bei fallender äusserer Konzentration zu, während mit Polyglykol der  $\delta$ -Wert innerhalb eines weiten Bereiches unabhängig von der Konzentration ist.

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