Effects of Alkalinity on Endwise Depolymerization of Hydrocellulose

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Synopsis

The role of hydroxyl ion concentration in the endwise depolymerization of hydrocellulose has been investigated in sodium hydroxide solution (0.05–18.6N) at 120°C, by determining the amount of degradation and the changes of carboxyl content and degree of polymerization in the solid phase. The extent of degradation increases with the base concentration up to about 6N and then sharply decreases thereafter. These data are discussed in terms of altering the accessibility and the relative rates of peeling and stopping reactions in varying concentrations of alkali.

INTRODUCTION

Base-catalyzed reactions of carbohydrates including cellulose have continuously received much attention[1-4] because of their fundamental interest and technical importance, particularly to the pulp and paper industry. Although the mechanism of endwise depolymerization (peeling) and stopping reactions is now reasonably well understood,[3,5,6] alkaline degradation of cellulose in a heterogeneous medium is complicated by its relatively low accessibility in dilute alkali.[7-9] Previous studies with cellulose,[10-12] both the unmercerized and mercerized form, and amylose[13] indicate that the submicroscopic structure of cellulose exerts a dominating influence on the termination process of a degrading chain. In contrast to the peeling reaction of amylose in a homogeneous medium, the number of peeled-off glucose units for each reducing endgroup,[12] either present in hydrocellulose or formed through alkaline hydrolysis of glycosidic bonds, was nearly independent of temperature and alkali concentration below the mercerizing strength (2N).

However, no systematic study has been made on the peeling reaction of cellulose in concentrated alkali which is known to profoundly influence the swelling of the substrate.[14] The purpose of this work is to determine to what extent the effects of hydroxyl ion concentration can be ascribed in terms of altering the accessibility and the relative rates of peeling and stopping reactions.

EXPERIMENTAL

Preparation of Samples

Hydrocellulose was prepared from purified, bleached cotton[15] by heating in 1N sulfuric acid at 90°C for 2 hr with a liquid-to-cellulose ratio of 20:1. The hydrolyzed sample after filtration was washed with water until free of acid and then dried under ambient conditions.

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Reduction of hydrocellulose was carried out in 1% sodium borohydride solution for 24 hr. The reduced sample after acidification was isolated as described above.

Mercerized samples were prepared by treating the hydrocellulose (0.5 g) with concentrated sodium hydroxide solution (20 ml) ranging from 4 to 18.6N for 1 hr under a nitrogen atmosphere at 20°C. After acidification with dilute acetic acid, the above procedure was followed to isolate the mercerized hydrocellulose which was obtained in a nearly quantitative yield.

Alkaline Degradations

The alkaline degradations were carried out in varying concentrations of sodium hydroxide solutions at a liquid-to-cellulose ratio of 100:1. In general, samples of hydrocellulose (0.5 g) and the alkali (50 ml) were sealed in small autoclaves (75 ml) under a nitrogen atmosphere and then heated in an oil bath isothermally at 120°C for 1 hr. The cooled solution after neutralization with dilute acetic acid was filtered, washed with water, and dried at 105°C to constant weight.

A similar procedure was also used to determine the relative stability of these alkali-degraded samples by further treating with alkali (1.15N NaOH) at 120°C for 1 hr. However, these experiments were conducted in smaller samples (0.1 g) and autoclaves (10 ml) at a liquid-to-cellulose ratio of 50:1.

Carboxyl Determinations

Determination of the carboxyl content was made by using the standard methylene blue absorption method, originally developed by Davidson.[16] A Varian 635 UV spectrophotometer was used to measure the methylene blue concentration.

Viscosity and Degree of Polymerization

The viscosities of hydrocellulose and the degraded cellulose were measured by dissolving the sample directly in cadoxen according to the method described by Elmgren and Henley.[17] The intrinsic viscosity was then converted to the degree of polymerization according to the equation suggested by Jedlinska and Nadziakiewicz,[18] $[\eta]_{cadoxen} = 5.6 \times 10^{-3}$ D.P.

RESULTS AND DISCUSSION

Extent of Degradation

Figure 1 illustrates the effect of alkali concentration on the degradation of hydrocellulose for one hr at 120°C. Rather unexpectedly, the extent of degradation is profoundly affected by the concentration of alkali. It increases with the base concentration up to about 6N and then rapidly decreases thereafter. However, the lower amount of degradation in the 0.05–1N sodium hydroxide solutions is partially due to the lower rate of reaction in dilute alkali, which requires a longer reaction time to achieve the maximum degradation, as shown in Table I.
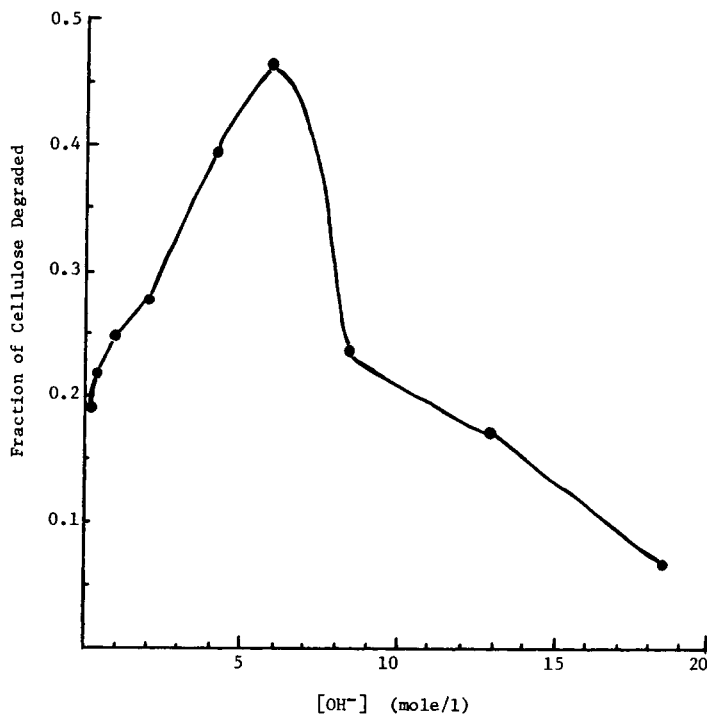
Fig. 1. Effect of alkali concentration on extent of hydrocellulose degradation at 120°C for 1 hr.

The above degradation pattern is parallel to the degrees of the swelling of cellulose in aqueous alkali. It is generally agreed[14] that swelling does not really take place below the $2N$ sodium hydroxide solutions and then increases with increasing concentration, reaching the maximum swelling at about 4–6N NaOH. Thus, the extent of degradation in base concentration below 6N must be predominantly controlled by the relative accessibility of the cellulose to the alkali.

On the other hand, the degradation pattern within the range of 6–18.6N NaOH could be attributed to the changes in the submicroscopic nature of the cellulose and/or the relative rates of peeling and stopping reactions. The first possibility was investigated by determining the extent of degradation of mercerized cellulose prepared with different concentration of alkali. The data in Table I showed that different concentrations of sodium hydroxide used in the mercerization (4–18N) has practically no effects on the alkali stability of the resulting mercerized samples which, consistent with previous studies,[8,11,12] are more stable than the unmercerized cellulose. Thus, it appears that beyond the maximum swelling at 6N NaOH solution the hydroxyl ion has an enhancing effect on the termination rate of the peeling reaction.

The relative stability of these residues obtained at different base concentrations was then investigated by reheating these samples in 1.15N sodium hydroxide solution. The resulting data (Table I) clearly indicate that the residues obtained at base concentration higher than 2N are essentially stable to further alkali treatment. The total yield of hydrocellulose after these two alkali treatments are also listed in Table I, which shows no significant difference within the range of 0.05–2N NaOH. However, it decreases with increasing alkali concentration in the range of 2–6N and then increases rapidly thereafter.

TABLE I
Degradation Data of Hydrocellulose in Varying Conditions of Sodium Hydroxide at 120°C for
1 hr

Hydrocellulose sample	First alkali treatment		Yield of second treatment in 1.15N, %[a]	Total yield, %
	OH−, N	Yield, %		
Unmercerized	0.05	83.9 (78.0)[b]	86.1 (87.9)	72.2 (68.6)
	0.1	79.2 (73.2)	87.1 (90.8)	69.0 (66.5)
	0.3	80.7 (75.9)	89.8 (96.8)	72.5 (73.5)
	0.5	78.1	92.4	72.2
	1.15	75.1	94.7	71.1
	2.15	71.5	96.4	68.9
	4.3	60.2	98.7	59.4
	6.0	53.0	98.3	52.1
	8.5	76.5	97.5	74.6
	13.0	82.5	99.1	81.8
	18.6	93.3	98.4	91.8
Mercerized with				
4.3N	1.15	84.9		
8.5N	1.15	83.6		
18.6N	1.15	83.5		
Reduced with				
borohydride	1.15	99.1		
	4.3	98.5		
	6.0	98.0		
	8.5	99.1		
	18.6	98.8		

[a] Subsequent treatment of the alkali residue with 1.15N NaOH at 120°C for 1 hr.

[b] Numbers in the parentheses are samples heated for 3 hr.

The extent of the above degradation caused by the base-catalyzed cleavage of glycosilic linkages was studied with borohydride-reduced hydrocellulose under similar conditions. The amount of degradation is generally negligible, as shown in Table I. Therefore, it is concluded that the weight loss originated from the alkaline cleavage reactions can be neglected under conditions used in this study.

Characterization of Degraded Cellulose

The alkali-treated cellulose was then analyzed for its carboxyl content, viscosity, and average degree of polymerization $(DP)_n$. The $(DP)_n$ values were estimated indirectly from viscosity values in cadoxen solution. Such estimations are, of course, subject to more error than determinations based on osmometry but were successfully applied in a previous work on alkaline hydrolysis of cellulose[12] and are thought to be adequate for comparative studies on the effects of base concentration.

The data summarized in Table II indicate that the number of carboxyl groups in the degraded samples increases with increases in hydroxyl ion concentration with a rapid rate between 6 and 8.5N sodium hydroxide solution, while the viscosity decreases only slightly with the alkalinity and remains practically unchanged in the 0.5–2.15N alkali range, indicating the loss of some low molecular weight molecules. It should be noted that the most degraded sample obtained

TABLE II
Carboxyl and Viscosity Data for Degraded Hydrocellulose With Alkali at 120° for 1 hr

Concentration, N	Yield, %	Carboxyl content, meq/100 g	Intrinsic viscosity, dl/g
Untreated		0.45	2.00
0.05	83.9	0.99 (1.22)[a]	1.64 (1.60)
0.1	79.2	1.26 (1.53)	1.80 (1.90)
0.3	80.7	1.29 (1.53)	1.78 (1.90)
0.5	78.1	1.43	2.00
1.15	75.1	1.52	2.01
2.15	71.5	1.60	1.95
4.3	60.2	1.80	1.70
6.0	53.0	1.90	[b]
8.5	76.5	2.48	1.68
13.0	82.5	2.59	1.70
18.6	93.3	2.28	1.74

[a] Numbers in parentheses were samples degraded for 3 hr.
[b] The sample was only partially soluble in cadoxen.

with 6N alkali was only partially soluble in cadoxen. This insolubility is probably due to the highly crystalline nature of the residue.

The extent that the peeling reaction proceeds through all units in the cellulose chain was estimated by the decrease in the number of molecules which was obtained from the $(DP)_n$ and yield data. The results (Table III) based on 100 g of original hydrocellulose showed that about 20–30% of the cellulose chains were totally degraded within the range of 0.5–4.3N and less than 10% at other base concentrations. Similarly, the corresponding increase in the number of carboxyl groups (obtained by subtracting the original carboxyl content from the product of carboxyl content and yield) was calculated. Again, there is a rapid rise in the formation of carboxyl group between 4.3 and 8.5N alkali.

TABLE III
Number of Carboxyls Per Cellulose Molecule Remaining in Solid Phase

OH$^-$, N	$(DP)_n$[a]	No. of carboxyls formed and molecules remaining from 100 g of sample		No. of carboxyl per molecule remaining
		Carboxyl, meq[b]	Molecule, meq[c]	
Untreated	357	0	1.73	
0.05	293 (285)[d]	0.38 (0.50)	1.77 (1.69)	0.21 (0.30)
0.1	321 (339)	0.55 (0.67)	1.52 (1.33)	0.36 (0.50)
0.3	317 (339)	0.59 (0.71)	1.57 (1.38)	0.36 (0.51)
0.5	357	0.67	1.35	0.50
1.15	358	0.69	1.29	0.53
2.15	348	0.69	1.27	0.53
4.3	304	0.63	1.22	0.52
8.5	300	1.45	1.57	0.92
13.0	304	1.69	1.67	1.01
18.6	310	2.68	1.85	0.91

[a] According to the equation $[\eta] = (5.6 \times 10^{-3}) (DP)_n$.
[b] Equal to carboxyl content times yield minus original carboxyl content.
[c] Equal to $100 \times$ yield$/(DP)_n \times 162$.
[d] Numbers in parentheses were samples degraded for 3 hr instead of 1 hr.

The above data permit a calculation of the number of carboxyl group per cellulose molecule remaining in the solid phase. The results shown in Table III are divided into two distinct stages. In the first stage with base concentration up to 4.3N, the average value is about 0.5, which is slightly lower than a reported value of 0.6 by Albertsson and Samuelson[19] based on osmotic measurements and alkalimetric method[20] for the carboxyl determination. However, it appears from these data that even under the maximum swelling conditions, a substantial amount of degrading chains still terminates to a nonacidic endgroup. These neutral endgroups are presumed to be normal reducing endgroups which are stable because of inaccessibility.

On the other hand, in the second stage (8.5–18.6N), essentially all the molecules are terminated with a carboxylic acid endgroup. The nature of these stable endgroups formed in concentrated alkali is not very clear and is probably somewhat different from that formed in dilute alkali, which was recently shown[3,21] primarily due to the formation of two carboxylic acid endgroups, 3-deoxyhexonic and 2-C-methylglyceric acids.

CONCLUSIONS

The above data clearly showed that base concentration has a profound influence on the peeling reaction of cellulose, which can be interpreted in terms of altering the accessibility of the substrate and the relative rate of peeling and stopping reactions. The extent of degradation in sodium hydroxide solution up to 6N base concentration is essentially parallel to the degree of swelling of the substrate and then sharply decreases with further increase in alkalinity, because of the high rate of stopping reactions. Polysaccharides like amylose[13] and cellulose can be stabilized considerably at concentrated alkali solutions, and these observations provide a strong support to a recent report by Connors and Sanyer[22] that high yield pulp can be obtained by pulping wood with concentrated alkali.

References

1. E. Sjostrom, *Tappi,* **60,** 151 (1977).

2. J. W. Green, I. A. Pearl, K. W. Hardacker, B. D. Andrews, and F. C. Haigh, *Tappi,* **60,** 120 (1977).

3. M. H. Johansson and O. Samuelson, *J. Appl. Polym. Sci.,* **19,** 3007 (1975).

4. R. A. Young, K. V. Sarkanen, P. G. Johnson, and G. G. Allen, *Carbohydr. Res.,* **21,** 111 (1972).

5. A. Meller, *Holzforschung,* **14,** 129 (1960).

6. A. Meller, *Tappi,* **48,** 231 (1965).

7. D. W. Haas, B. F. Hrutfiord, and K. V. Sarkanen, *J. Appl. Polym. Sci.,* **11,** 587 (1967).

8. G. Machell and G. N. Richards, *Tappi,* **41,** 12 (1958).

9. R. L. Colbran and C. F. Davidson, *J. Text. Inst.,* **52,** T73 (1961).

10. A. Franzon and O. Samuelson, *Svensk Papperstidn.,* **60,** 872 (1957).

11. K. Christofferson and O. Samuelson, *Svensk Papperstidn.,* **65,** 517 (1962).

12. Y. Z. Lai and K. V. Sarkanen, *Cellulose Chem. Technol.,* **1,** 517 (1967).

13. Y. Z. Lai and K. V. Sarkanen, *J. Polym. Sci. C,* **28,** 15 (1969).

14. W. D. Nicoll, N. L. Cox, and R. F. Conaway, in *High Polymers,* Vol. V, Part II, E. Ott and H. M. Spurlin, Eds., Interscience, New York, 1954, p. 825.

15. R. L. Whistler, *Methods in Carbohydrate Chemistry,* Vol. III, Academic, New York, 1963, p. 3.

16. G. F. Davidson, *J. Text. Inst ,* **39,** T65 (1948).

17. H. Elmgren and D. Henley, *Svensk Papperstidn.,* **63,** 139 (1960).

18. H. Jedlinska and H. Nadziakiewicz, *Polimery,* **7,** 89 (1962).

19. V. Albertsson and O. Samuelson, *Svensk Papperstidn.,* **65,** 1001 (1962).

20. O. Samuelson and B. Tornell, *Svensk Papperstidn.,* **64,** 155 (1961).

21. M. H. Johansson and O. Samuelson, *Carbohydr. Res.,* **34,** 33 (1974).

22. W. J. Connors and N. Sanyer, *Tappi,* **58,** 80 (1975).