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Comparing Dichromate Oxidation and Size Exclusion Chromatography of Dissolved Carbohydrates

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Summary: Standardised methods are used to characterise the pulp or cellulosic material for its alkali resistance and alkali solubility. Today, pulp is usually characterised by its solubility in sodium hydroxide. The characterisation test was based on the treatment of pulp with sodium hydroxide solution of a defined concentration, according to a specified procedure. The dissolved organic matter was then determined by dichromate oxidation. The results obtained by size exclusion chromatography showed that both the amount and the molecular weight of the dissolved carbohydrates vary when investigating solubility and α-cellulose content of pulps. The results show further that S_{18} values obtained by dichromate oxidation are overestimated when characterising pulps containing higher amounts of hemicellulose and/ or short chain cellulose, compared with results obtained by the SEC method. On the contrary, S_{10} values are overestimated when determined by dichromate oxidation in higher alpha pulps.

Keywords: cellulose; molecular weight distribution; oxidation; solubility

Introduction

The interaction between cellulose and aqueous alkali hydroxides especially sodium hydroxide has been one of the principal research topics in the chemistry and physics of cellulose. Among the reaction products of cellulose with alkali hydroxide only sodium cellulose is of practical relevance as starting material for subsequent large scale esterification or etherification of cellulose, especially xanthation and carboxymethylation.

The interaction of wood based cellulose and aqueous sodium hydroxide is always connected with the phenomenon of swelling of cellulose and dissolution of a part of cellulose and hemicellulose.

Systematic investigations during the last century revealed some important points of cellulose swelling in aqueous alkali i.e.

- the swelling value passes a maximum in relation to the sodium hydroxide concentration
- intracrystalline swelling caused by the inclusion of alkali and water into crystallites takes place above a sodium hydroxide concentration of 12% to 15% which results from the formation of sodium cellulose (Figure 1).

It is important to know that swelling of cellulose in aqueous sodium hydroxide is dependent on the sodium hydroxide concentration. This can be considered to be the result of defined hydrates of sodium hydroxide ion dipoles, as the hydrates decrease with a stepwise increase of the sodium hydroxide concentration.

Depending on the sodium hydroxide concentration, the maximum of solubility of short chain cellulose and hemicellulose coincides broadly with that of the swelling

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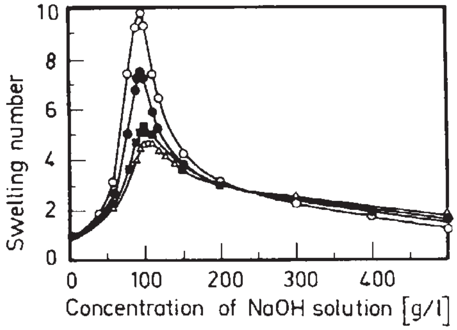

Figure 1.
Influence of sodium hydroxide concentration on the swelling maximum of cellulose.[1]

behaviour, and this can be found at a alkali concentration of about 10% by weight corresponding to about 110 g/l (Figure 2).

The solubility of cellulose in aqueous sodium hydroxide can also be significantly enhanced by lowering the temperature for the treatment.

Both swelling and solubility in aqueous sodium hydroxide depends on sodium hydroxide concentration, and the physical and chemical structure of that particular pulp sample. Therefore, characterisation of the pulp for alkali resistance and alkali solubility is carried out by standardised methods e.g. by DIN methods, Scan methods; Tappi methods etc. A traditionally used method for determining alkali resistance is the determination of α-cellulose content using a sodium hydroxide concentration of 17.5% by weight.

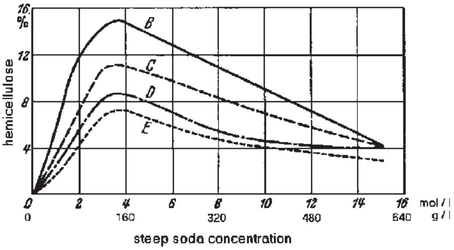

Figure 2.
Influence of sodium hydroxide concentration on the dissolution maximum of short chain cellulose and hemicellulose determined on several commercial pulps.[2]

For alkali resistance or alkali solubility, the symbols R_5, R_{10}, R_{18} or S_5, S_{10}, S_{18} are used, the symbols refer to the resistance or solubility in sodium hydroxide solution of the corresponding concentration.

Today pulp is usually characterised by its solubility in sodium hydroxide. The test is based on the treatment of the pulp with sodium hydroxide solution of a defined concentration, according to a specified procedure, and the dissolved organic matter is determined by a dichromate oxidation. The excess dichromate is re-titrated with iron -II- ammonia sulphate solution.

The aim of the investigation was to characterise the dissolved carbohydrates obtained from the determination of the solubility value and α-cellulose content by size exclusion chromatography. This method should be able to give information on the molecular weight and the mass of the dissolved substances. The results obtained by this method will be compared with results obtained by dichromate oxidation.

Methods

Eucalyptus sulphite pulp was used for the investigations. Alkali solubility was determined according to DIN 54356. Determination of α-cellulose content was carried out according to Zellcheming IV/29A. Size exclusion chromatography was carried out on the matter dissolved determining α-cellulose content and alkali solubility, respectively, on 10 μ columns from Hema (40; 100; 1000), using 0.5 n NaOH for elution. An RI detector from Waters was used. Calibration was carried out by using Pullulan.

Mercerisation of pulps was carried out in steep soda of 220 g NaOH/l at a temperature of 50 °C. Press soda obtained after steeping was filtered before measurements.

Results and Discussion

SEC and dichromate oxidation methods were used in order to investigate the organic matter dissolved during the determining of pulp solubility in aqueous sodium hydroxide containing both 10% and 18% of alkali, respectively and the organic matter dissolved when determining the α-cellulose content of the pulp.

In Figure 3a and Figure 3b characteristic patterns of carbohydrates dissolved in 18% and 10% sodium hydroxide can be seen.

Substances dissolved in 18% aqueous alkali show a monomodal distribution having its peak maximum at around 36 DP units (lg DP: ~1.6). In contrast, the substances dissolved in 10% aqueous alkali show a bimodal distribution having maximums near 36 DP units (lg DP: ~1.6) and 400 DP units (lg DP: 2.6) which means that not only low molecular and short chain cellulose are dissolved but also cellulose having a quite respectable DP.

The difference in dissolved substances can be explained by an increase in swelling of cellulose in sodium hydroxide of a concentration of 10% by weight, but it was unknown up to now that the dissolved carbohydrates show a bimodal distribution function.

The carbohydrates dissolved in the determination of the α-cellulose content show surprisingly also a bimodal distribution function despite using alkali with a concentration of 17.5% by weight (Figure 4).

Comparing Figure 3a and Figure 4, the differences in the composition of the substances dissolved during the determination of α-cellulose content and S_{18} values can be seen.

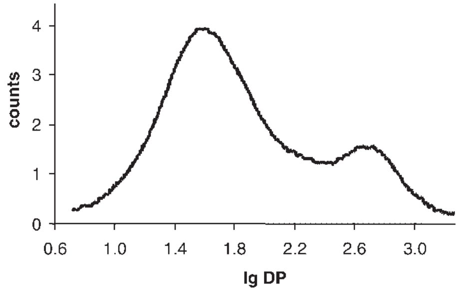

Figure 4.
Distribution of the degree of polymerisation of carbohydrates dissolved during the determination of α-cellulose content.

The key point to note, in the procedure used to determine α-cellulose content is the addition of water to interrupt the reaction, resulting in a dilution of alkali from 17.5% by weight to ~5% by weight. During this process, the concentration of highest swelling power at 10% sodium hydroxide concentration is passed, resulting in a dissolution of cellulosic and hemicellulosic matter showing a comparable chain length with those substances dissolved at an alkali concentration of 10%.

In Figure 5 the molecular weight distribution of matter dissolved during mercerisation can be seen.

Cellulosic and hemicellulosic material which is dissolved during mercerisation shows also a monomodal distribution function, comparable with the shape obtained

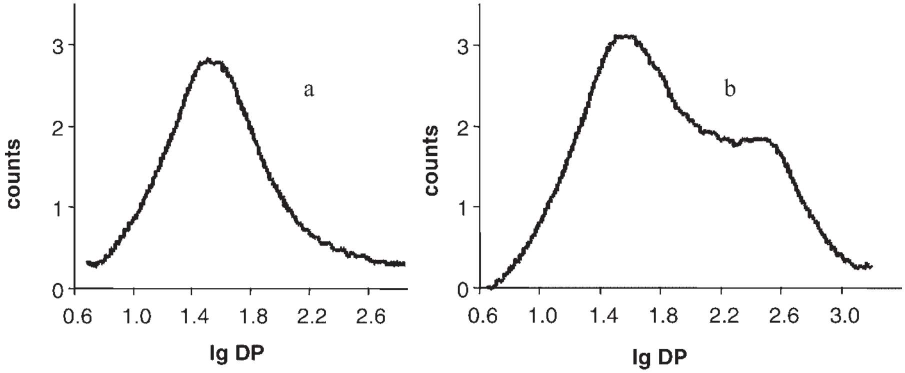

Figure 3.
Distribution of the degree of polymerisation (DP) of carbohydrates dissolved in aqueous 18% (a) and 10% (b) sodium hydroxide, respectively.

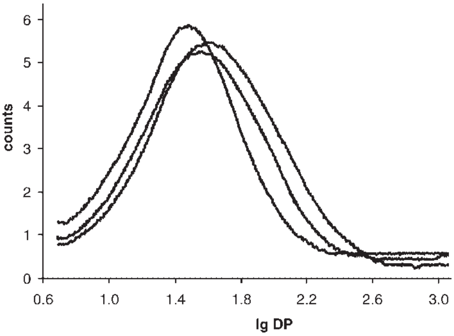

Figure 5.
Distribution of the degree of polymerisation of carbohydrates dissolved during mercerisation using several commercial pulps.

when determining S_{18} values. The content of the dissolved organic matter and its maximum DP depends on the pulps used providing comparable steeping conditions.

From these results it can be seen that during the procedure determining S_{18} values the amount and chain length of short chain cellulose and hemicellulose are comparable to those dissolved during the large scale mercerisation.

The amount of organic matter dissolved in aqueous 18% and 10% by weight sodium hydroxide was determined by dichromate oxidation and compared to the amount obtained when size exclusion chromatography is used. For the calculation of dissolved organic matter determined by dichromate oxidation theoretically 1 milli equivalent of potassium dichromate correspond to 6.75 mg of cellulose or other hexosans and to 6.60 mg of pentosans. As in general the alkali soluble components consume less oxidant than theoretically expected. A somewhat higher factor of 6.85 mg is universally applied in this method for calculating the amount of dissolved matter.[3]

In Table 1 the results obtained from the determination of dissolved organic matter from dichromate oxidation and size exclusion chromatography using aqueous alkali containing 10% and 18% by weight sodium hydroxide are summarised.

The analyses showed that the S_{18} values (Table 1) are overestimated by the dichromate oxidation especially if noted that these pulps have a higher amount of short chain cellulose and hemicellulose. The cause for this can be found in the used equivalent factor.

Table 1.
Results obtained for the determination of dissolved organic matter from dichromate oxidation and size exclusion chromatography using pulps of different solubility.

	S_{10} [%]		S_{18} [%]	
	dichromate oxidation	SEC	dichromate oxidation	SEC
pulp 1	11.6	11.7	5.8	5.1
pulp 2	10.4	10.1	4.7	4.3
pulp 3	9.2	8.6	3.5	3.2
pulp 4	7.5	7.0	3.1	2.9

Considering the S_{10} values (Table 1) the results obtained from dichromate oxidation and the SEC methods differ more with decreasing solubility of the pulps. One reason for that can be the accessibility of highly ordered regions and the composition of dissolved matter.

In order to obtain true data of dissolved carbohydrates in aqueous alkali the equivalent factor has to be adapted.

Conclusion

A comparison of the size exclusion chromatograms of organic matter dissolved in 18 wt% and 10 wt% aqueous alkali showed that the swelling power of the used aqueous alkali influences not only the masses of the dissolved organic matter, but also the chain length of the dissolved material.

Comparing the chromatograms of dissolved matter taken from the determination of α-cellulose content and the determination of S_{18} values it becomes obvious that the procedure used influences also the chain length and amount of cellulose and hemicellulose which are dissolved.

Further it shows that S_{18} values obtained by dichromate oxidation are overestimated when investigating pulps containing a higher amount of hemicellulose and/or short chain cellulose which means higher S_{18} values compared with the SEC method.

In contrary S_{10} values are overestimated determined by dichromate oxidation on pulps of low solubility.

S_{18} values and α-cellulose content cannot directly be compared because of the different material which is dissolved during the procedure used for its determination.

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