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Water Solubility of Ethyl Cellulose

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A series of ethyl celluloses have been prepared from spruce sulphite pulp. The mercerization was carried out with soda lye of 24 to 40 % concentration; subsequent etherification with ethyl chloride. The degree of substitution varies from 0.9 to 1.35. The solubility in water shows a pronounced maximum at the degree of substitution 1.2.

The solubility properties of ethyl cellulose change with increasing ethoxyl content. At first it is soluble only in alkaline solutions, then in water and lastly only in organic solvents. As is well known this is the same sequence as for methyl cellulose but, owing to the stronger hydrophobic character of the ethyl group, the range of water-solubility is rather small.

Scattered information about the degree of ethylation which gives solubility in water is obtainable from literature. Berl and Schupp[1] etherified alkali cellulose from linters with diethyl sulphate and obtained water soluble products within the DS range 0.7—1.5 (DS = degree of substitution). The products must have been rather degraded as in one case the viscosity of a 3 % solution was only 57 cp. Bock[2] made the reaction in homogeneous medium. Cellulose was dissolved in quarternary ammonium bases and etherified with diethyl sulphate. A product with DS 0.6 was soluble in water whereas DS 1.2 gave insolubility.

Other figures are given by Traill[3] (DS 1.2), Lorand[4] (DS 0.8—1.3), Mahoney and Purves[5] (DS 0.6 and 1.2, resp.), Sönnerskog[6] (DS 1.2—1.4), but in all these cases very little information is given about raw material, etherification and method for measuring the solubility.

Some information is also found in patent literature [7-9]. It is claimed that ethyl celluloses with DS between 1.0 and 1.5 are soluble in cold water.

The widely differing figures and the lack of information in most cases about experimental conditions seem to justify a description of a series of experiments which were made as part of a broader research programme.

It is expected that the solubility of an ethyl cellulose will depend not only upon the DS but also upon the method of manufacture (homogeneity of etherification) and the molecular weight. It is also necessary to specify how the solubility was measured.

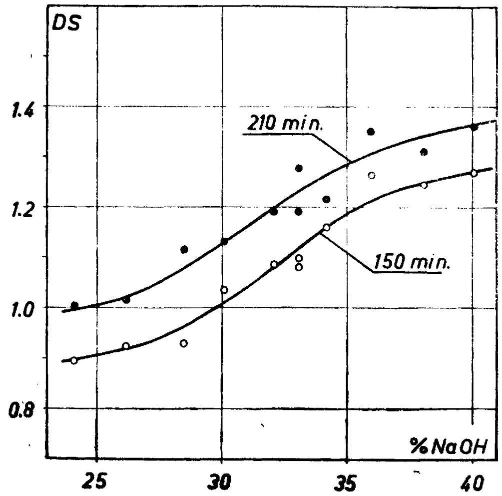

Fig. 1. Degree of substitution (DS) of ethyl cellulose as function of strength of mercerizing lye. Time of reaction 150 min. and 210 min. respectively.

Standard viscose sulphite pulp from spruce was mercerized and etherified in autoclaves with ethyl chloride. The resulting DS depends upon the time and temperature of the reaction and the strength of the mercerizing lye. The temperature cannot be varied very much, because below 90° C the reaction is very slow and above 110°—120° C the ether formed is rapidly degraded. In order to get a reasonably uniform substitution, the time of reaction should not be too short and the reaction is preferably broken off shortly before all the alkali has been used up. If it is allowed to proceed further, a hydrolytic breakdown of the chain molecules will start. In practice the main variable will therefore be the strength of the lye.

Raw material: Sulphite cellulose from spruce with alpha content 89.7 % [10] and viscosity 26 cp (1 % solution in cuprammonium [11]).

Cellulose sheets were mercerised 45 minutes at a temperature of 21°—24° C, squeezed to a press factor 2.5—2.6 (2.2 for the two lowest lye concentrations), and then shredded and aged for 35—60 minutes at room temperature. The autoclave (1 lit. capacity, stainless steel) was charged with alkali cellulose corresponding to 40 g air-dry cellulose and with 200 ml ethyl chloride. Another part of the alkali cellulose was regenerated with dilute acetic acid and the cuprammonium viscosity determined. The autoclave was rotated in an oil bath, the temperature of which was increased to 100° C over a period of 1.5 hours and then kept at 102°—104° C for 150 or 210 min. The raw product was suspended in boiling water, neutralized with acetic acid, sucked off on a Büchner funnel, and dried.

The ethoxyl analysis was made by the method of Vieböck and Schwappach [12] with modifications of Samsel and Mc Hard [13]. The ethoxyl percentage given is based on bone-dry and salt-free cellulose ether.

Viscosities of 2 % aqueous solutions of the cellulose ethers were measured with a Höppler viscometer, precision model HV 303. Transmission measurements on the same solutions were made by a method previously used in the study of ethyl-hydroxyethyl cellulose [14]. Lumetron photoelectric colorimeter, model 402—E, filter M 550, light path in cuvette 2 cm, displacement of cuvette 12 cm.

The cuprammonium viscosities were determined by the Swedish standard method CCA 16, the values recalculated to CCA 13 (TAPPI) [11].

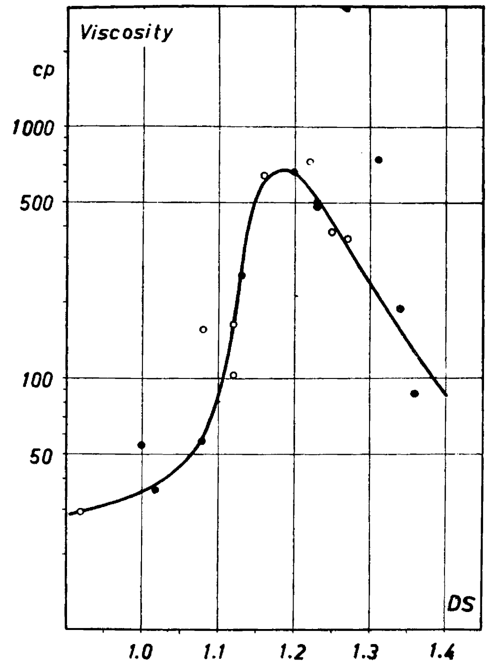

Fig. 2. Viscosity of 2 % solutions of ethyl cellulose which have been frozen, as function of degree of substitution. Temp. 20° C. For explanation of points, see Fig. 1.

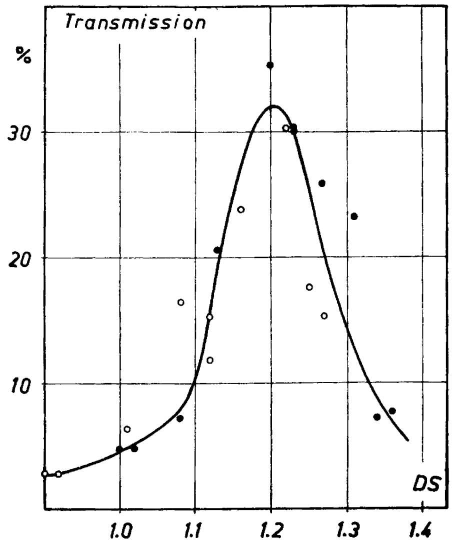

Fig. 3. Transmission of same solutions as in Fig. 2.

The degree of substitution as function of the lye concentration is shown in Fig. 1. Quadruple analyses were made in some cases, duplicate analyses in the other; standard deviation 0.02. The overall variation in DS is not very large and a closer study of the diagram shows that a considerable part of the spreading of the points may be due to the analytical errors. For that reason smoothed DS values were used as abscissae in the diagrams to follow.

The viscosity and turbidity of 2 % solutions of cellulose ether in water were measured and used as estimate of the solubility, a loosely defined concept for substances of this kind. A unique property of water-soluble cellulose ethers is that the viscosity of their solutions often increases irreversibly by cooling and subsequent warming back to the original temperature[14]. It is therefore necessary not only to state the temperature of measurement but also the minimum temperature to which the solution has ever been brought. With the exception of Sönnerskog [6] no information of this kind has been given in the literature references quoted.

The ethyl celluloses turned out to be typical cases of products showing irreversible viscosity increase after cooling. At 20° C they all gave a suspension of swollen fibers rather than a solution. Viscosity and turbidity measurements could not be carried out. Decrease of the temperature to 15° C did not improve matters but, after freezing, viscous solutions were obtained (Figs. 2 and 3). There is a sharp viscosity and transmission maximum around DS 1.2

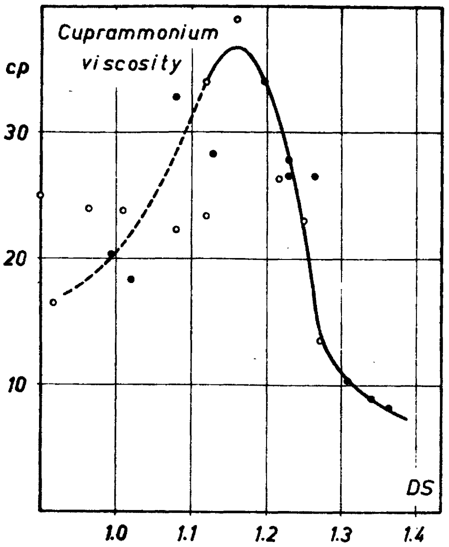

Fig. 4. Cuprammonium viscosity (1 % solution, TAPPI method) of ethyl cellulose as function of degree of substitution. For explanation of points, see Fig. 1.

at which point the steric influence of the substituted groups in keeping the cellulose chains apart and the hydrophobic character of the ethyl groups balance each other.

Determinations of the molecular weight were not carried out, but some information is gained from cuprammonium viscosity measurements on cellulose regenerated from the alkali cellulose immediately before the start of the etherification, and on the cellulose ethers. The first series of values decreased a little from 21 to 17 cp with increasing soda lye concentration; the second series is shown diagrammatically in Fig. 4. Even though the values spread very much at low DS the existence of a maximum seems well established. It is also remarkable that most viscosities are higher than those found for the regenerated cellulose. The same thing has also been repeatedly observed in the case of ethyl-hydroxyethyl cellulose[15]. No direct measure of the degradation which occurs during the etherification is available but the values in Fig. 4 indicate that it must be moderate.

The high values and the existence of a maximum can both be explained by the assumption that the chains get stiffer with increasing degree of substitution and that the hydration decreases because of the hydrophobic character of the ethoxyl groups. Highly etherified ethyl cellulose is not soluble in cuprammonium[1]. The result is a viscosity maximum at the same DS that gave a solubility maximum in water.

No doubt the solubility range will become broader with decreasing average chain length and this may explain some of the low DS values reported in literature. A more efficient way of increasing the water solubility is co-etherification with ethylene oxide[16,14].

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