Cyanoethylation of Powdered Cross-linked Cellulose

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Conditions of the cyanoethylation of powdered cross-linked cellulose with acrylonitrile in alkaline medium have been studied. The effect of sodium hydroxide concentration and that of the reaction time upon the degree of substitution as well as the effect of salts as ingredients of the reaction mixture upon the utilization of acrylonitrile in the main reaction have been investigated.

It is known [1] that the introduction of cyanoethyl groups into a cellulose macromolecule improves its resistance to the action of certain microorganisms, increases its thermal stability, and also some mechanical properties of the product, *e.g.* dyeing, become better.

The conditions of cyanoethylation have been previously studied by a number of workers. The mechanism of cyanoethylation was also described [2, 3]. In most of the cases the material submitted to cyanoethylation was cotton, the reaction being carried out under alkaline conditions in the presence of water [4—6]. Under these conditions the degree of acrylonitrile participation in side reactions is proportional to the decreasing concentration of the alkali. The major side reaction is the formation of di(β-cyanoethyl)ether for which reaction there is consumed about four to five times as much acrylonitrile as for the main reaction [7]. In order to economize the process of cyanoethylation attempts were made in which cellulose was derivatized with gaseous acrylonitrile [8] or, alternatively, in an inert medium of organic solvents [9].

It has been stated [10] that the alkali used in the process of cyanoethylation of cellulose with acrylonitrile acts exclusively as a catalyst and, since activation of the hydroxyl groups of cellulose is not necessary, the concentration of the alkali may be maintained at a relatively low level.

One of the possibilities to suppress the course of the side reactions was shown to be the addition of salts into the reaction mixture, where these actually decrease the amount of free water. For instance, 10% of sodium chloride present in the reaction mixture substantially improved the conversion of acrylonitrile into the desired product [11]. Similarly, the addition of potassium iodide (137 g per 100 g of 2% sodium hydroxide solution) into the reaction mixture of the cyanoethylation of cotton resulted in a threefold increase of the nitrogen content in the product, compared to the product obtained without the addition of salts [12].

The cyanoethylation of cellulose under alkaline conditions in the presence of water with urea as the ingredient of the reaction mixture was described by *Compton* [13].

The aim of the present work is to increase substantially the yield of the main etherification reaction of cellulose with acrylonitrile by conducting the process in a more concentrated solution of alkali. In order to improve the resistance of ion exchangers to the action of microorganisms the work is mainly concerned with the etherification of powdered cross-linked cellulose commonly used for preparation thereof.

Experimental

Starting material

As the starting material, powdered cellulose cross-linked with epichlorohydrin [14] having DP 800 and containing 8% of moisture was used. Cyanoethylation was carried out with acrylonitrile in an aqueous sodium hydroxide solution (2–40%) into which salts (sodium chloride or urea) were added. For comparison, experiments without the addition of salts were also run.

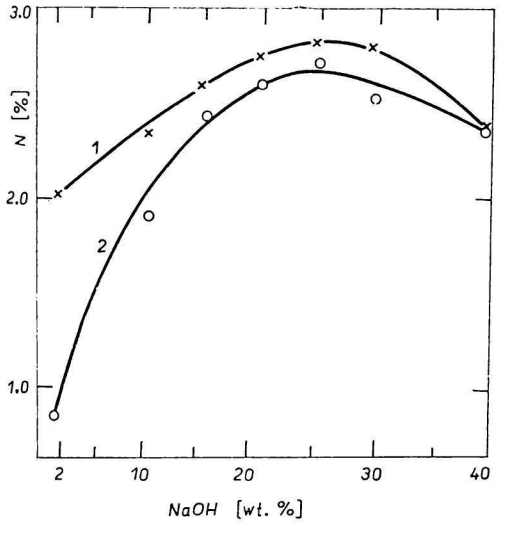

Fig. 1. The effect of the increasing sodium hydroxide concentration upon the nitrogen content in the final powdered cross-linked cyanoethyl cellulose.
Molar ratios cellulose : sodium hydroxide : acrylonitrile.
1. 1 1 : 0.5; *2.* 1 : 2.5 0.5.

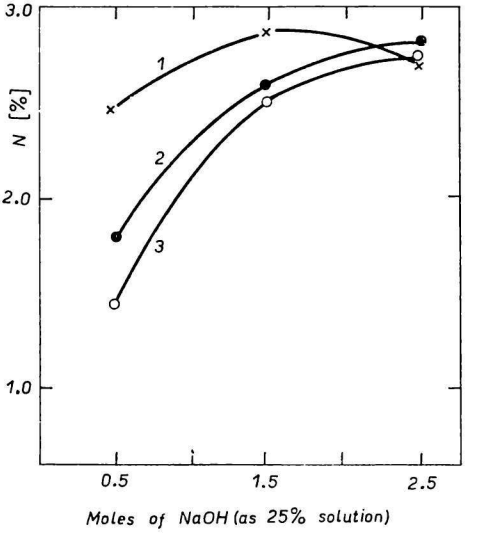

Fig. 2. The effect of the amount of sodium hydroxide upon the nitrogen content in powdered cross-linked cyanoethyl cellulose. Conditions of cyanoethylation: temperature 20°C, time of the reaction 30 minutes.
Molar ratios cellulose : sodium hydroxide 1 0.5, 1 1.5, 1 2.5; cellulose : : acrylonitrile 1 0.5.
1. 25% sodium hydroxide solution without addition of salts; *2.* 25% sodium hydroxide solution with the addition of 5% sodium chloride; *3.* 25% sodium hydroxide solution with the addition of 2% urea.

Working procedure

The needed amount of sodium hydroxide (2—40% aqueous solution) was added dropwise and with stirring into a 100-ml flask containing 1.62 g of air-dried powdered cross-linked cellulose. The swelling of the cellulose was allowed to proceed at 5°C for 60 minutes and, with continued stirring, a calculated amount of acrylonitrile was dropped into the reaction mixture. The flask was closed and the reaction was allowed to proceed with occasional stirring for 30, 60, and 90 minutes at 10, 20, 30, and 40°C. The content of the reaction vessel was neutralized with 10% acetic acid, filtered through a coarse sintered glass funnel, the product was washed successively with water, 50% ethanol and acetone, and dried at 100°C to give a white water insoluble product. The degree of substitution was calculated from the nitrogen content.

The effect of the individual parameters upon the course of cyanoethylation is pictured in Figs. 1—4.

Discussion

As mentioned above, in the process of cyanoethylation of cellulose the alkali is claimed to act only as a catalyst and therefore it is normally used in low concentration. The

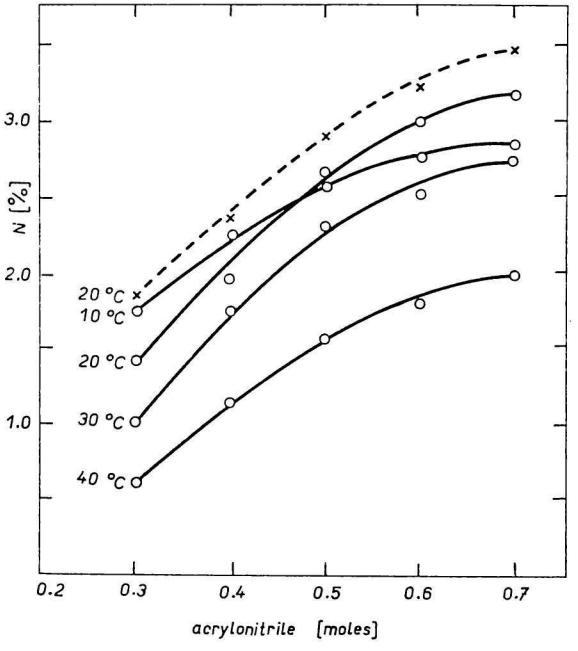

Fig. 3. The effect of the temperature and of the increasing molar ratio of acrylonitrile to cellulose upon the nitrogen content in the final powdered cross-linked cyanoethyl cellulose. Time of the reaction 30 minutes.

Molar ratios cellulose : sodium hydroxide 1 : 1.

———— cyanoethylation in 25% sodium hydroxide containing 2% urea;

— — — — cyanoethylation in 25% sodium hydroxide without additives.

most commonly used concentration of sodium hydroxide has been 2% aqueous solution. Although the claimed function of the alkali may be correct, the use of a low concentration of sodium hydroxide has certain negative effects upon the course of cyanoethylation of cellulose:

a) At low concentration of sodium hydroxide cellulose does not swell appreciably, its phase composition remains practically unchanged, *i.e.* the hydroxyl groups to be derivatized are not made enough accessible, what results in a decreased rate of the heterogeneous etherification reaction.

b) The low concentration of the aqueous sodium hydroxide solution has a positive effect on side reactions to the detriment of the main cyanoethylation reaction:

$$CH_2{=}CHCN + H_2O \rightarrow HO{-}CH_2CH_2{-}CN \quad \text{ethylene cyanohydrin,}$$

$$2CH_2{=}CHCN + H_2O \rightarrow O(CH_2CH_2CN)_2 \quad \text{di}(\beta\text{-cyanoethyl})\text{ether,}$$

$$CH_2{=}CHCN + H_2O \rightarrow CH_2{=}CH{-}CO{-}NH_2 \quad \text{acrylamide.}$$

This is proved by the course of the curves in Fig. 1, where the degree of substitution of cyanoethyl cellulose increases with the increasing sodium hydroxide concentration reaching the DP_{max} at the sodium hydroxide concentration of 25%.

It is also known that an excess of sodium hydroxide impairs the effectiveness of the main etherification reaction, mainly in the range of lower concentrations. The differences in the effectiveness of the main reaction are less pronounced in the range of the sodium hydroxide concentration of 20–25%. When cellulose: sodium hydroxide (25%): acrylonitrile molar ratio of 1 1 : 0.5 was used, 75% conversion of acrylonitrile into the desired product was observed, *i.e.* a considerable improvement compared to what appears to have been achieved previously [7].

The addition of salts into the reaction mixture containing 25% aqueous sodium hydroxide solution has undoubtedly negative effect upon the effectiveness of the main

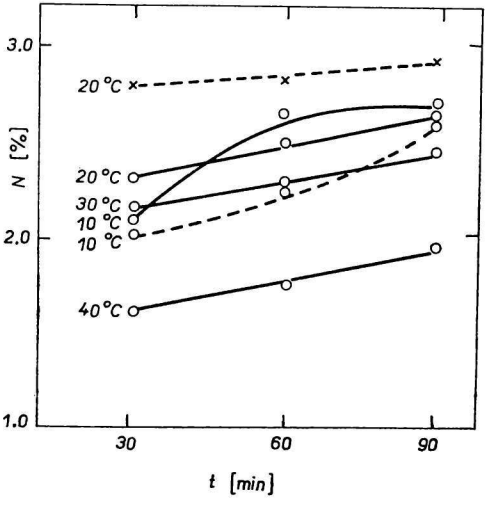

Fig. 4. Effect of the time of the reaction and of temperature upon the nitrogen content in the final powdered cross-linked cyanoethyl cellulose.
Molar ratios cellulose : sodium hydroxide : acrylonitrile 1 : 1 : 0.5.
——— 25% sodium hydroxide containing 2% urea; – – – 25% sodium hydroxide without additives.

etherification reaction at 20°C (Fig. 2). This is quite comprehensible as an addition of salts into 25% sodium hydroxide solution causes a lack of free molecules of water indispensable for the main reaction. This explains why the nitrogen content in the final product increases with the excess of sodium hydroxide used in the given range of concentrations (curves *2* and *3*) whereas the curve *1* reaches its maximum at the amount of sodium hydroxide of 1.5 mole.

Similarly, when the influence of the increasing molar ratio of acrylonitrile to cellulose at different temperatures (Fig. 3) as well as that of the reaction time and the temperature (Fig. 4) upon the degree of substitution was investigated, a negative effect of the addition of salts into the reaction mixture was observed when 25% aqueous sodium hydroxide solution was used.

It follows unambiguously from the feregoing results that the cyanoethylation of cellulose can be very effectively done without addition of salts into the reaction mixture by simply increasing the concentration of sodium hydroxide. This is very economical, particularly when powdered material for making cellulose ion exchangers is being etherified. Thus, cyanoethylation can be carried out in one step with the other etherification (which is to introduce the ion-exchange group) which yields a material resistant to the deteriorating action of microorganisms during its continuous usage.

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