CELLULOSE CHEMISTRY AND TECHNOLOGY

CATIONIZATION OF NATIVE AND ALKALIZED CELLULOSE: MECHANISM AND KINETICS

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The insertion of functional groups (particularly cationic groups) in starch and cellulose is especially useful with a view to developing new industrial polysaccharide derivatives. The aim of this work was to develop a standard protocol for the mercerization–cationization of cellulose fibres based on the kinetic equations governing the process.The cationization of NaOH-pretreated cellulose with an alkaline solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) was found to be a pseudo second-order reaction. Under the experimental conditions used, the equilibrium condition for nitrogen as a quaternary ammonium ion in cellulose was dependent on the initial amorphous fraction of cellulose, as determined by X-ray spectroscopy. Also, the kinetic constant increased with an increasing amorphous fraction. However, the nitrogen content or degree of substitution in the carbohydrate reached near-equalibrium values after relatively short reaction times.

Keywords: mechanisms, kinetics, cellulose, mercerization, cationization,X-ray spectroscopy

INTRODUCTION

Cellulose, formed by repeated linkage of D-glucose units via anhydroglucose units (AGU), is the most abundant natural resource. This homopolymer has a rigid, highly functionalized linear chain that is chiral, hydrophilic, biodegradable, and easily modified by chemical means or shaped into versatile semi-crystalline fibres.[1]

Some chemical derivatives of cellulose play prominent roles in industrial production processes. Cellulose xanthate, cellulose acetate, carboxymethyl cellulose and cellulose nitrate are largely used inthe manufacturing of plastics, fabrics, packaging, lacquer and explosives. Some recentlydeveloped cellulose derivatives are being explored for uses in textile finishing and sizing agents, absorbable surgical fat, protective colloids, adhesives, pharmaceutical creams and paper products, among others.[1]

Developing new cellulose-based products entails subjecting the polymer to various pretreatments. For example, the treatment of textile cotton with concentrated sodium hydroxide patented by John Mercer in 1844 provides brighter, stronger cellulose fibres amenable to dyeing.[2] This treatment, named "mercerization" after its developer, is still widely used, particularly in textile processes.

Native cellulose (e.g., cotton linter) consists essentially of cellulose I, which is formed by parallel chains in a linear structure. In its reaction with an alkali, cellulose I swells and then shrinks when washed to form a new allomorph: cellulose II.[3] The alkali penetrates fibres and causes parallel chains in cellulose I to rearrange into antiparallel chains of cellulose II.[4] This change is irreversible and accompanied by a decrease in crystallinity and a reduction in the degree of polymerization. The new cellulose form has a more open structure and its fibres possess a higher specific surface area; as aresult, the hydroxyl groups in cellulose macromolecules are easier to access.[5] The ordered structure of the crystalline form and the disordered structure of the amorphous form influence the accessibility and reactivity of cellulose fibres.[6]

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Under specific conditions, a treatment with sodium hydroxide improves the mechanical properties of cellulose fibres to an extent considerably dependent on the treatment time and alkali concentration.[7] Cellulose is modified more markedly by soda than is lignin.[8] As a result, reacting cellulose with an aqueous solution of sodium hydroxide alters its morphological, molecular and supramolecular properties, thereby also changing its crystallinity, pore structure, accessibility, rigidity, unit cell structure and fibre orientation. Some other properties can be improved, including dimensional stability, fibrillation, tensile strength, dyeability, reactivity, brightness and softness in fabrics.[9]

The structure of cellulose is commonly characterized by wide-angle X-ray spectroscopy. This technique has proven effective to distinguish between amorphous and crystalline cellulose andto assess the influence of crystallinity on the rate ofhydrolysis.[6,10]

Another line in the production of new cellulose derivatives involves the insertion of functional groups (e.g., cationic groups) into polysaccharide chains. While cationic starches are widely used by the paper industry to improve retention and draining properties in pulp, the cationization of cellulose is usually performed to improve affinity towards anionic dyes. Cationized cellulosic productsare also useful for the removal of toxic heavy metals from wastewater.[11]

These processes involve making the substrate react with an electrophilic reagent contaning a quaternary ammonium salt. The properties of the resulting cationized derivative are different from and often better than those of the starting substrate. Cationization of cellulose shows little negative impact on the mechanical properties of fibres, although brightness may decrease considerably.[12]To date, no standard protocol for the mercerization–cationization of cellulose fibres has been reported, despite the industrial significance of the process.

The primary aim of this work was thus to develop a standard protocol for the mercerization–cationization of cellulose fibres based on the kinetic equations governing the process. The use of modified natural polysaccharides is currently regarded as a sustainable alternative to synthetic polymers and hence as specially desirable with a view to developing new, improved products.

EXPERIMENTAL

Mercerization

The raw material used here was commercial medium-sized cellulose fibre (Aldrich ref. C6228), which was reacted with an alkaline solution of NaOH from Aldrich, in a batch reactor at room temperature. Nine mercerization experiments were carried out for different raction times and NaOH concentrations (Table 1). Afterwards, fibres were separated by passage through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7µm) and washed with demineralized water. The alkalized cellulose thus obtained was dried in a vacuum stove at 45 ºC.

Cationization

The cationizing agent was an aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 60wt% from Aldrich. An amount of 20 g of dry alkalized cellulose was mixed with the reagent in a CHPTAC/AGU mole ratio of 4, an identical number of moles of CHPTA and 5% NaOH, and enough isopropyl alcohol to make to 1 L.

The reactor was a 2 L three-mouthed spherical glass furnished with a refluxing condenser, a magnetic stirrer, heating controlled by an electronic PID device and a Pt-100 probe for temperature measurements. Temperature was held at 70 ºC, through the process. After the solution containing mercerized cellulose, sodium hydroxide and isopropyl alcohol was heated to setpoint temperature under stirring, the mixture was supplied with the CHPTAC via a funnel and the reaction timer started.

Table 1
Mercerization conditions: codification

Reaction time (min) / Soda concentration (%)	60	120	180
10	A1T1	A1T2	A1T3
20	A2T1	A2T2	A2T3
30	A3T1	A3T2	A3T3

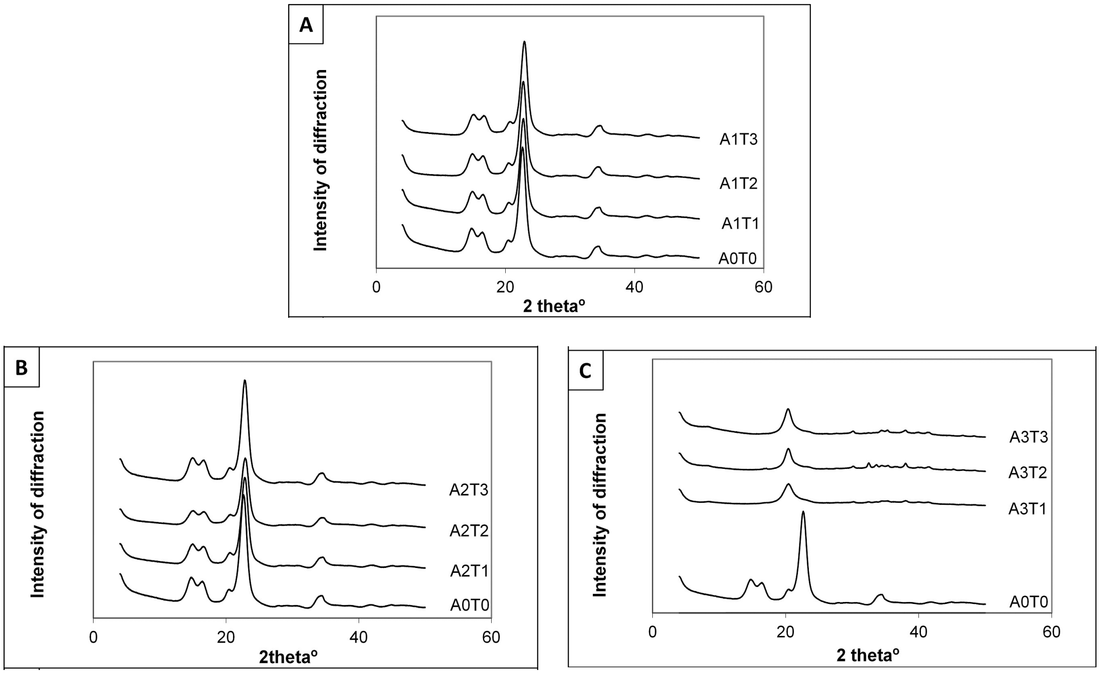

Figure 1: Diffractograms of untreated cellulose (A0T0) and of samples alkalized with different NaOH concentrations and times

Samples from the reaction mixture were withdrawn every 30 minutes by using a 50 mL wide mouth pipette. Immediately, they were diluted ten times with cold water to stop the reaction, passed through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7µm), washed with demineralized water and dried in a vacuum stove at 45 ºC. Dried samples were kept sealed at room temperature.

The process developed in two steps: first, formation of epoxypropyltrimethylammonium chloride (EPTMAC) by reaction with hydroxyl ions; second, nucleophilic substitution of the hydroxyl group bonded to C_6 in the anhydroglucose unit (AGU).

Characterization of samples

Cellulose and alkalized cellulose samples were characterized by using a PANalytical powder X-ray diffractometer in combination with X'Pertsoftware.

Carbon and nitrogen contents were determined by combustion on a LECO CNS-2000I elemental macroanalyser.

RESULTS AND DISCUSSION

X-ray diffraction spectroscopy

Figure 1 shows the XRD patterns for the starting cellulose and alkalized cellulose at the preset 2θ° values used. We chose to represent the patterns in a staged manner in order to envisage the changes in the initial fibres under the effect of the alkaline treatmentmore easily. The structural changes undergone by cellulose in the treatments preceding cationization were used to examine their potential relationship to the cationization results.

The changes caused by a NaOH concentration of 10% were minimal, even at the longest operation times used; however, they increased as the alkali concentration was raised and levelled off at 30%.

Although the enzymatic and non-enzymatic reaction are additionally influenced by other factors, we used the crystallinity index (*XRD CrI*), and the fractions of amorphous cellulose (1 – Am), cellulose I (CI) and cellulose II (CII) in the starting alkalized cellulose to compare and interpret the results of the cationization process.

Oh *et al.*[16] previously examined the structure of cellulose treated with sodium hydroxide and carbon dioxide by X-ray difraction and FTIR spectroscopies. The crystallinity index (*CrI*) was calculated from the height ratio of the intensity at $2\theta = 22.5°$ for cellullose I, or the 101 reflection at $2\theta = 19.8°$ for cellulose II (crystalline height, *hcr*), to the height of the amorphous reflection corresponding to $2\theta = 18.8°$ for cellulose I or $2\theta = 16.1°$ for cellulose II (amorphous height, *ham*), respectively.[6]

The intensity of scattered diffracted light was measured in arbitrary units without normalization of the mass sample. Therefore, samples were compared in terms of peak height ratios rather than absolute intensities.

$$CrI(CI) = 1 - \frac{h_{am}}{h_{cr}} \tag{1}$$

$$\frac{h_{am}}{h_{cr}} = \frac{I_{18.8min}}{I_{19.8max} + I_{22.5max} - I_{18.8min}} \tag{2}$$

$$CrI(CII) = \frac{I_{12.1}}{I_{12.1} + 0.5(I_{14.6} + I_{16.1})} \tag{3}$$

As shown in Table 2, structural changes in cellulose under the influence of the treatments preceding cationization had a marked effect under the experimental conditions used. The conversion into cationized cellulose must be governed largely by those of cellulose I into cellulose II and of the latter into hydrated and amorphous cellulose II.

Elemental analysis

The amounts of elemental nitrogen incorporated as quaternary ammonium ions into cellulose under the effect of the cationization treatment after different reaction times are shown in Table 3. The results were processed with various kinetic models and a pseudo-second-order model was found to provide the best fit.

The pseudo-second-order kinetic model originally proposed by Blanchard *et al.*[17]and Ho *et al.*[18] is typically applied to adsorption phenomena occurring in solution. These kinetic expressions have been applied to a variety of systems.[19]The theoretical background of the pseudo-second-order rate equation has been examined by Azizian.[20]The kinetic constants of pseudo-second-order models are combinations of the initial solute concentration and the adsorption and desorption constants.

Table 2
Crystallinity index of cellulose samples

Allomorph	A0T0	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
Cellulose I	0.52	0.53	0.56	0.45	0.50	0.50	0.53	0.14	0.13	0.05
Cellulose II	0.31	0.32	0.29	0.31	0.33	0.34	0.31	0.50	0.51	0.55
Cellulose amorphous	0.17	0.15	0.15	0.24	0.18	0.17	0.17	0.36	0.36	0.40
XRD crystallinity index	0.83	0.85	0.85	0.76	0.82	0.84	0.83	0.64	0.64	0.60

Table 3
Parameters of pseudo-second order rate equations

Parameters of linearizedequation	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
Intercept: $N_{eq}^{-2} \cdot K^{-1}$, min/%N	19.6	17.2	9.4	31.2	15.5	10.1	7.1	5.3	4.6
Slope: N_{eq}^{-1}, $\%N^{-1}$	9	6.8	5.8	7.7	6.8	5.4	1.5	0.64	0.56
R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.98
Parameters of original kinetic equation	A1T1	A1T2	A1T3	A2T1	A2T2	A2T3	A3T1	A3T2	A3T3
N_{eq}, %N	0.11	0.15	0.17	0.13	0.15	0.19	0.67	1.56	1.79
NSD_{eq}	0.013	0.018	0.020	0.015	0.018	0.022	0.084	0.217	0.257
N_{eq}^2K, %N/min	0.051	0.058	0.106	0.032	0.065	0.099	0.140	0.189	0.217
K, $(\%N \cdot min)^{-1}$	4.13	2.69	3.54	1.93	2.99	2.87	0.32	0.08	0.07
RMSD/10^{-3}	5.1	6.1	6.6E	3.9	4.7	5.1	33	67	78

The proportion of epoxypropyl-trimethylammonium chloride (EPTMAC) bound to cellulose in the cationization reaction was referred to that of elemental nitrogen fixed by cellulose. The driving force was the difference between the proportion of nitrogen fixed by cellulose at time *t* and the maximum (saturation or equilibrium) proportion. The rate equation in terms of the proportion of elemental nitrogen fixed by cellulose was:

$$\frac{dN_t}{dt} = k(N_{eq} - N_t)^2 \tag{4}$$

where $N_t$is proportional to the number of active sites occupied by the active cationic group on cellulose at time *t* and so is N_{eq} to the number of sites available on cellulose fibres at equilibrium (both as percentages of elemental nitrogen).

The integration of this differential equation under the boundary conditions t=0to t=t and N_t=0to N_t=$N_t$yields:

$$N_t = \frac{N_{eq}^2 kt}{1 + N_{eq}kt} \qquad (5)$$

which is the integral form of the equation for a pseudo-second-order reaction. Expressing this equation in terms of the time/fixed nitrogen proportion ratio leads to a linear function of time.

The previous kinetic equation can be written in a linear form as:

$$\frac{t}{N_t} = \frac{t}{N_{eq}} + \frac{1}{kN_{eq}} \qquad (6)$$

The concentrations of nitrogen at different reaction times t as determined by elemental analysis of dry cationized samples were used to plot the linearized form of the equation. If the assumption of a pseudo-second-order model is fulfilled, then the intercept of the curve will represent the highest proportion of elemental nitrogen incorporated by effect of the reaction ofepoxypropyltrimethylammonium chloride (EPTMAC), previously formed in the reaction between 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) with NaOH, with alkali-activated sites of the hydroxyl group on C_6 in the anhydroglucose unit (AGU). Likewise, the slope of the curve will coincide with the reciprocalof the percent equilibrium (saturation) concentration.The figures of merit of the linearized equations as obtained by least-squares regression are shown in Figure 2. As can be seen, the coefficients of correlation ranged from 0.98 to 0.99.

The dotted lines in Figure 3 represent the experimental percent nitrogen contents as measured by elemental analysis as a function of the reaction time for cellulose treated with NaOH, whereas the solid lines represent the integrated kinetic equations in terms of parameters N_{eq} and$K$ as calculated from the linearized equation:t/Nt vs. t (see Table 3).

Table 3 also lists the root mean square deviation (RMSD) as a measure of differences between experimental values and predicted values (i.e., those obtained from the pseudo-second-order kinetic equation). The degree of nitrogen substitution (DNS) of the cellulose was calculated from the nitrogen content (%N) and the molecular weight of the anhydroglucose unit (AGU), 162.15, using the followingexpression:

$$NSD = \frac{162.15 \times \%N}{1400 - 151.64 \times \%N} \qquad (7)$$

where %N denotes the percentage of dry elemental nitrogen, 1400 is 100 times the atomic weight of nitrogen and 151.64 the molecular weight of the epoxypropyltrimethylammonium chloride (EPTMAC) group added.

Comparing theresults of this work with the results of De la Motte *et al.*,[21] under the conditions leading to maximal incorporation of nitrogen in cationic form, DNS was greater in this work: 0.404 (i.e., 40.4%) at the maximum %N level.

We used constant CHPTAC/AGU ratio, NaOH concentration and isopropyl alcohol proportion throughout. DNS for cationic starches typically ranges from 0.0075 to 0.1215 and increases with increasing reaction time and proportion of cationizing reagent. Our results are consistent with those of other studies.[22]

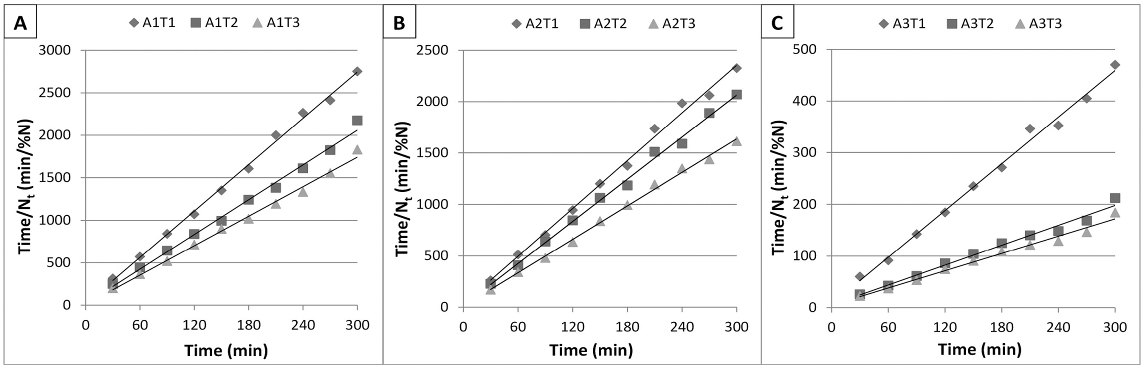

Figure 2: Linearized representation of the pseudo-second-order rate equation: (A) of cellulose alkalized with 10%NaOH; (B) of cellulose alkalized with 20%NaOH; (C) of cellulose alkalized with 30%NaOH

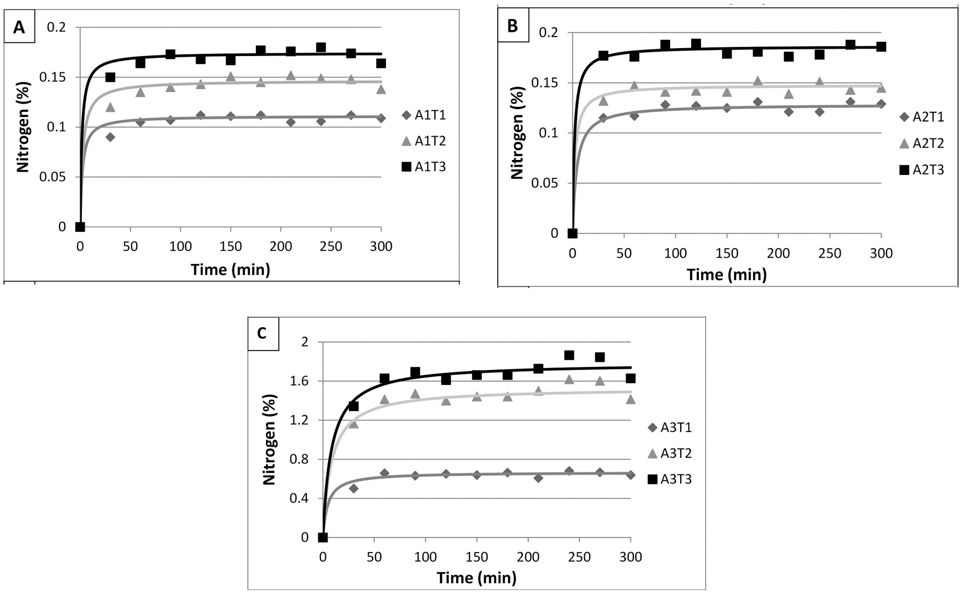

Figure 3: Nitrogen in cellulose vs. reaction time. Isolated points are the experimental data

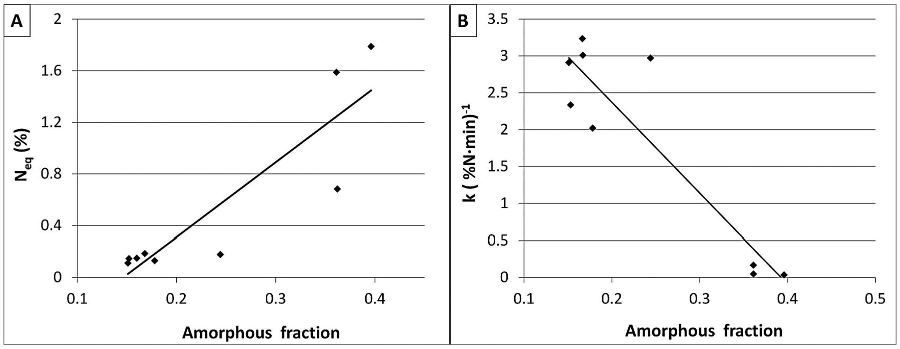

Figure 4: Nitrogen proportion (A) and constant of the pseudo-second-order rate equation (B), versus amorphous fraction of cellulose

Based on available literature, DNS increases with an increase in the CHPTAC concentration; also, using an inadequate amount of NaOH hinders the formation of epoxide and alkoxides from the polysaccharide, whereas excess NaOH causes degradation of the epoxide and decreases the molecular weight of the product.

Figure 4 shows the variation of N_{eq} with the amorphous fraction of cellulose as calculated by XRD analysis of the starting alkalized cellulose. A comparison of the variation of N_{eq} vs. the different cellulose allomorphs revealed that the best results were obtained by linearly fitting this parameter to the amorphous faction (AF):

$$N_{eq} = 5.79AF - 0.85 \qquad (8)$$

with R^2= 0.80. Likewise, the best fit with the pseudo-second-order rate constant k was provided by:

$$k = 12.32AF + 4.84 \qquad (9)$$

with R^2= 0.83. Despite the reduction in k, the overall rate of nitrogen fixation was greater under the influence of the amorphous fraction, increasing the proportion of fixed nitrogen at equilibrium.

CONCLUSION

Under the experimental conditions used in this work, the overall cationization reaction fits a pseudo-second-order kinetic equation. The reaction rate increases with the square of the difference between the equilibrium and the apparent concentrations of nitrogen. This squared difference decreases –and so does the reaction rate, in an asymptotic manner – as the amount of nitrogen fixed to cellulose approaches its equilibrium level.

As previously found for other chemical and enzymatic reactions, the reactivity of cellulose increases with an increasing proportion of the amorphous fraction (AF) to a greater extent than it does with the proportions of cellulose I (CI) and cellulose II (CII), even though the amorphous fraction (AF) is related to CII.

The proportion of nitrogen at equilibrium in cationized cellulose increases linearly with increasing content of amorphous cellulose in the starting material. Initially, the reaction rate is comparatively high. As a result, the proportion of nitrogen reaches a near-equilibrium level within a short time (about 30 min).

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