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Ion-interactions as driving force in polysaccharide assembly☆

Thomas Bechtold*,[1], Avinash P. Manian[1], Hale B. Öztürk[1], Uttam Paul[1], Barbora Široká[1], Ján Široký[1], Hossam Soliman[1], Loan T.T. Vo[1], Hai Vu-Manh[1]

Research Institute of Textile Chemistry and Textile Physics of the University Innsbruck, Hoechsterstrasse 73, 6850 Dornbirn, Austria

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ABSTRACT

The structure of cellulose is characterised by extensive non-covalent interactions. Recent discussions suggest that hydrophobic interactions between polymer chains also play a significant role in governing cellulose solubility. Surprisingly in almost all cellulose shaping processes, chemical systems or solvents are applied, which base on melts or solutions of charged molecules. Ionic interactions play a significant role in the shaping and modification of cellulose based materials. Dependent on the systems used different principles govern the processes and define the results, e.g. formation of associates with alkali hydroxides, ion-exchange reactions to selectively bind multivalent ions at carboxylic groups, adsorption of dissolved polymers through surface charge neutralisation or metal complex formation, where cellulose takes the role of a polymer ligand system. Presence of charged compounds takes a significant role in cellulose swelling and dissolution, but also directs reassembly of polysaccharide material to solid three-dimensional structures.

1. Introduction

The need to replace petrol-based polymers by renewable more sustainable materials led to growing scientific interest in new strategies to shape and convert polysaccharide materials.

General strategic recommendations for polysaccharide research have been proposed by the European Polysaccharide Network of Excellence (EPNOE) in their roadmap, where three important scientific themes of future activities in polysaccharide research have been identified (Persin et al., 2011):

- Bio-assembly: investigating polymer synthesis and structure formation in complex biological systems.
- Dis-assembly: studying separation and production processes of polysaccharide materials from natural sources.
- Re-assembly: analysing structure formation in polysaccharide products based on ordering principles which govern the arrangement of polymer chains.

All three key-themes, bio-assembly, dis-assembly, re-assembly require an improved understanding of interactions occurring between polysaccharide chains and the respective chemical surrounding, which for example include:

- Interaction of polysaccharides with other polymers in the solid phase and low molecular weight components present in sorbed state (e.g. water),
- Aqueous solutions containing dispersed/dissolved polysaccharides, proteins, low molecular weight compounds, salts
- Organic solvent systems
- Sorption of water or chemicals from the surrounding atmosphere.

Relevant scientific approaches to understand polysaccharide interactions with other polymers or low molecular weight components have been studied in the framework of a European FP7 Initial Training Network STEP (Shaping and Transformation in the Engineering of Polysaccharides) (Hajji, 2001; step-itn, 2011).

One of the major challenges in the conversion of polysaccharides is overcoming the non-covalent interactions that characterise polysaccharide structures and lead to significant restraints on their processability. The non-covalent interactions exert strong influence on polysaccharide conversion by restricting polymer dissolution in solvents, limiting thermal processability of polysaccharides, and dictating the feasibility and extent of polymer functionalisation.

The structure of cellulose is characterised by extensive non-covalent interactions, which restrict polymer solubility in solvents. The consensus of opinion has been that the interactions are primarily intra- and inter-chain hydrogen bonds. However,

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* Corresponding author. Tel.: +43 5572 28533 579; fax: +43 5572 28629.
E-mail address: Thomas.Bechtold@uibk.ac.at (T. Bechtold).

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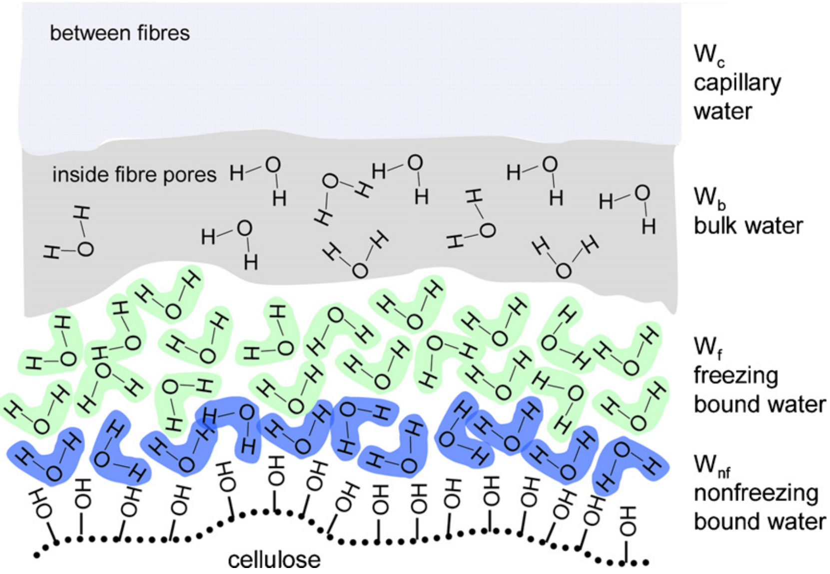

Fig. 1. Sorbed water forms part of the "surface" present in a three-dimensional structure of cellulose fibres: capillary water (bulk water, W_c), bulk water (cluster, W_b), freezing bound water (W_f), nonfreezing water (W_{nf}).

Lindman, Karlström, and Stigsson (2010) have recently argued that hydrophobic interactions between polymer chains may also play a significant role in governing cellulose solubility.

Surprisingly in almost all of the cellulose modification processes, chemical systems are applied, which base on melts or solutions of charged molecules. Ionic interactions play a significant role in the shaping and modification of cellulose based materials.

Dependent on the systems used different principles govern the processes and define the results. In this article, cellulose is used as representative example to demonstrate the different principles of ion-polysaccharide interactions. Important aspects which will be discussed are:

- Accessibility driven alkalisation of cellulose fibres.
- Surface sorption of soluble polysaccharides from aqueous solution.
- Aqueous LiCl/urea systems as swelling agent (Tatárová, Manian, Široká, & Bechtold, 2010).
- Metal-complex formation for shaping and dissolution (Vu-Manh, Öztürk, & Bechtold, 2010; Vu-Manh, Wendler, Öztürk, & Bechtold, 2012).
- High temperature derivatisation and thermal shaping of cellulose (Vo, Tatárová, Široká, Manian, & Bechtold, 2010; Vo, Široká, Manian, & Bechtold, 2010).

2. Results and discussion

2.1. Approaching the cellulose structure

Physico-chemical modification of cellulose based materials can be achieved via two basic strategies:

- Heterogeneous processing e.g. by accessibility driven sorption, swelling operations and mechanical shaping, e.g. mercerisation, fibre crosslinking.
- Homogeneous processing: dissolution followed by coagulation and structure regeneration, e.g. viscose process, fibre formation via viscose process, lyocell process or ionic liquid.

The structure formed during a shaping procedure is determined by two fundamental physico-chemical principles:

- Thermodynamic control will govern the result of a modification step when chemical equilibrium is established, which for example could be assumed for swelling and dissolutions steps as far as no irreversible chemical reactions occur, for sorption processes on three-dimensional polysaccharide structures, for ion exchange reactions. Examples for important parameters to be considered include: hydrogen bonding, hydrophobic interaction, ionic interactions and polarity.
- Kinetic control will govern the outcome of a reaction when different pathways are competing and the product distribution, substitution pattern or modification of a 3-D structure is governed by factors such as: accessibility to reactive sites, crystalline/amorphous structures, exclusion effects (solid structures) and sterical effects (dissolved polysaccharides).

For any modification of solid cellulose a complex situation including different levels of structure has to be considered. A model is required, which describes the structure of the polymer in dissolved state or visualises the 3-D-architecture of the un-dissolved polymer.

At a molecular level the phase transition between solid ordered cellulose (structured polymer chains, crystalline parts), low ordered polymer structures (amorphous regions) and the liquid/gaseous environment represents a complex situation. This includes molecules strongly sorbed at the cellulose surface, which in many cases are water molecules.

Model calculations to simulate interactions between sorbed water and cellulose indicate a strong structuring effect of cellulose to sorbed water layers. The principle of water structuring is primarily based on hydrogen bonding, thus most intensive structuring is supposed to occur at the lateral position of the cellulose polymer, where strong hydrogen bonding to the equatorial hydroxyl groups of anhydroglucose occurs. Less structuring is expected to occur near the more hydrophobic "tops" of the glucopyranose rings. Authors conclude that differences in water structuring will also influence access of reagents and thus contribute to overall chemical reactivity (Matthews et al., 2006).

A schematic representation of the chemical situation in the region of phase transition between cellulose and surrounding environment is shown in Fig. 1. In the zone of phase transition between cellulose and surrounding environment, water is present in different states of sorption, each at differing energy states. Water molecules are bound as non-freezing water (W_{nf}), freezing bound water (W_f) bulk water (cluster, W_b) filling macro pores in the fibrous structure and capillary water (bulk water, W_c) present in spaces between fibres which form a three-dimensional assembly (Maloney, Paulapuro, & Stenius, 1998).

For any chemical modification of the insoluble cellulose matrix the surface coverage with water has to be considered, as access of reagents will require replacement of strongly sorbed water molecules to allow reagents to approach the reactive hydroxyl.

The complex architecture of a 3-D cellulose body introduces another complication into the behaviour of un-dissolved cellulose.

According to the fringed micelle model, structurally ordered parts of the polymer chains form cellulose II crystallites, surrounded by low ordered amorphous parts (Schuster et al., 2003). As a result of the molecular orientation a fibrillar structure is present in which elemental fibrils arrange to microfibrils and macrofibrils. Linkages between fibrils are established by interfibrillar tie molecules, which bridge between gaps. A system of pores of different size exists between the fibrils. On macroscopic level structural differences between fibre core and fibre surface (skin) have been identified, which adds another complication to the already complex three-dimensional structure.

For a modification of cellulose in non-dissolved state the specific structural properties of the insoluble matrix will influence the final result. At the same time, the principles governing reactivity and equilibrium such as hydrogen bonding, hydrophobic interaction and ionic-interactions will determine the effectively observed reaction pathway. Different examples for ionic interactions and their structuring effects will be discussed in the following sections.

2.2. *Accessibility driven alkalisation of cellulose fibres*

The major part of chemical processing steps with cellulose (pulp, textile fibres, textile finishing) is performed in aqueous systems, where cellulose is present in a swollen state. Dependent on the composition of the swelling agent intercrystalline swelling or intracrystalline swelling occur (Klemm, Philipp, & Heinze, 1998; Široký, Blackburn, Bechtold, Taylor, & White, 2010)

The final result of a certain treatment is dependent on both, the concentration of reagent used and the interaction of the swelling agent with the cellulose structure. As a result different parts of a 3-D cellulose matrix will be modified by use of alkali hydroxides (NaOH, KOH, LiOH), quarternary ammonium hydroxides, ionic liquids, salt/solvent systems (e.g. LiCl/N,N-dimethyl-acetamide), liquid ammonia, or metal complex formation (Leipner, Fischer, Brendler, & Voigt, 2000; Liebert, 2010; Öztürk & Bechtold, 2008; Öztürk, Okubayashi, & Bechtold, 2006; Vu-Manh et al., 2010). In the case of alkali hydroxides and quarternary ammonium hydroxides, the concentration of hydroxide ions often is discussed as the major factor which influences the final result of a treatment. However it has been shown that at the same hydroxide concentration, the type of cation present is of decisive importance for the final outcome (Öztürk et al., 2006).

As a result, a wide range of variations can be achieved in the macroscopic properties of alkali treated cellulose textiles such as dimensional stability, water retention value, fibrillation, crease behaviour, dyeability, by use of different alkali concentrations, but also by use of KOH instead of NaOH (Manian et al., 2008; Široký et al., 2009; Široký, Blackburn, Bechtold, Taylor, & White, 2011).

In the alkalisation of cellulose fibres with concentrated NaOH solutions, defined components are formed when equilibrium conditions are established. When ramie fibres are treated in 6.3 NaOH for 15 days, sodium cellulose $C_6H_{10}O_5{\cdot}NaOH{\cdot}2H_2O$ is formed (Nishimura, Okano, & Sarko, 1991). From X-ray diffraction analysis it could be demonstrated that the sodium ions occupy specific positions in the crystal lattice of sodium cellulose. This clearly indicates that the type of cation will directly will influence stability and structure of alkali cellulose formed.

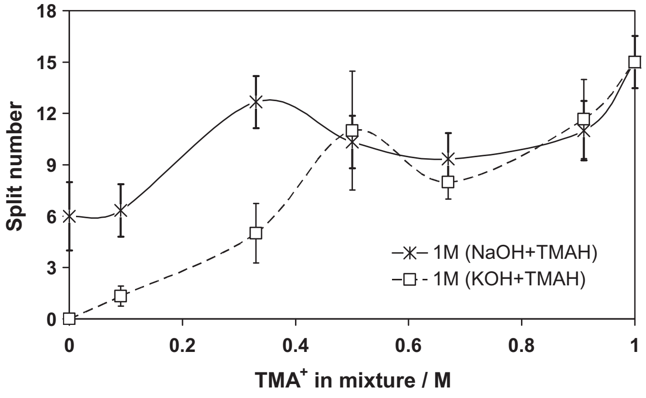

Fig. 2. Effect of cation in 1 M hydroxide solution on splitting of lyocell fibres in NaOH/TMAH or KOH/TMAH mixtures as function of TMA^+ concentration (Öztürk et al., 2006).

In a more general formulation of this approach the cation of the alkali metal hydroxide modulates the overall effect of an alkali processing step, both by different cation size and its accessibility, and by interaction with functional groups present in the cellulose structure.

As a result the observed chemical reactivity as well as the macroscopic properties of swollen cellulose fibres will depend on the cationic counterion (Zhang, Okubayashi, & Bechtold, 2005).

When local pressure is applied to swollen lyocell type cellulose fibres splitting into macrofibrils can occur. This number of macrofibrills, the so-called split number can be used to characterise the access of swelling agents into the fibrous structure (Öztürk et al., 2006). In a study of splitting behaviour of lyocell fibres in different alkali hydroxides or tetra-methyl ammonium hydroxide (TMAH) the influence of the cation could be demonstrated. At the same molar concentration of hydroxide ions completely different split numbers were observed between LiOH, KOH, NaOH and TMAH. A direct prove of the specific influence of a cation could be demonstrated in a study where the effects of a 1 M hydroxide solution with different cations on the split number was studied. The concentration of hydroxide was kept constant, whilst the cations Na^+, or K^+ successively were replaced by the tetra-methyl ammonium ion (TMA^+) (Fig. 2).

Whilst distinct differences in split number are observed for pure 1 M NaOH or 1 M KOH, both curves show similar splitting results, when a concentration above 0.5 M TMA^+ was reached in solution.

The different access of alkali hydroxides into cellulose will affect the alkali distribution in the fibrous structure and thus will influence the apparent reactivity of the alkali.

In a crosslinking experiment using alkali containing lyocell fibres and 2,4-dichloro-6-hydroxy-1,3,5-triazine (NHDT), it could be demonstrated that in similar behaviour with regard to N-content of the crosslinked fibre and modification of tensile strength was observed (Fig. 3) (Okubayashi & Bechtold, 2005).

In these experiments the fibres first were treated with alkali hydroxide and then crosslinked with NHDT in a second step. The alkali hydroxide served as swelling agent and reagent at the same time. It could be shown, that in case of NaOH treated fibres, crosslinking was observed at much lower alkali concentration. Under the experimental conditions applied, less than 10 mmol g^{-1} of fibre were required to obtain a N-content of 2% (Fig. 3). For KOH concentrations up to 70 mmol g^{-1} were required to achieve comparable results with regard to N-content in the fibre and tenacity

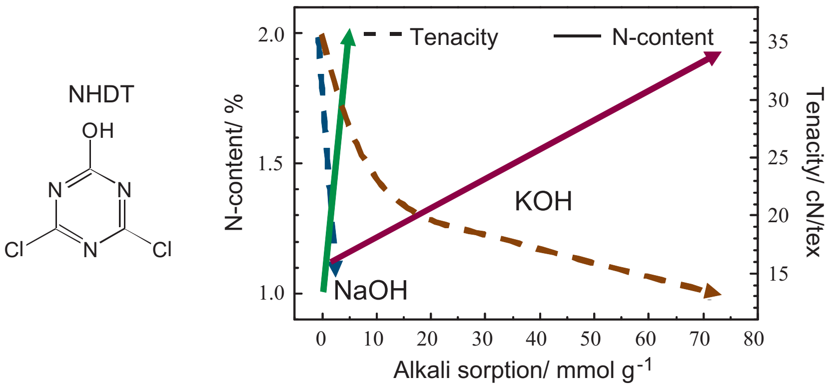

Fig. 3. N-content (—) of the crosslinked fibre and tenacity (– – –) of NHDT treated lyocell fibres as function of type and concentration of alkali hydroxide used (Okubayashi & Bechtold, 2005).

loss. The differences in distribution of KOH and NaOH in the fibre structure cause apparently results in different availability of the alkali for NHDT crosslinking. The cation of the alkali hydroxide solution determines the alkali distribution in the fibre and leads to different local concentrations of MOH, and hence modulates the reactivity of NHDT in the fibre.

A further factor which has to be considered in the discussion of reactivity of a swollen fibre is the molecular dimension of the reagents used, in the given example NHDT. Exclusion effects will lead to molecular size dependent access into the fibre structure and a separation of reagents can occur (Bui et al., 2008; Jaturapiree et al., 2008).

2.3. *Aqueous LiCl/urea systems as swelling agents*

In the literature NaOH/urea solutions, concentrated salt solutions e.g. LiCl, alkali thiocyanates, have been studied extensively with regard to their ability to swell or dissolve cellulose (Liebert, 2010; Lukanoff, Schleicher, & Philipp, 1983; Luo & Zhang, 2010). A solution of LiCl/DMAc (N,N-dimethylacetamide) is widely used as solvent in cellulose analytics (Potthast, Rosenau, Sixta, & Kosma, 2002). From the different systems presented in the literature two general rules can be discerned:

- The effect of a certain salt solution on the cellulose structure is dependent on properties of both ions present in the salt. Replacement of one ion by another changes the swelling/solvent properties of the system completely. Whilst $LiCl{\cdot}2–3H_2O$ or concentrated NaOH solutions both are strong swelling agents, replacement of Li^+ by K^+ to KCl, or OH^- by Cl^- to NaCl reduces the swelling power dramatically.
- The potential of a concentrated salt solution can be enhanced by addition of co-solvents like DMAc and polar substances such as urea and substituted urea (Cai & Zhang, 2005; Herlinger & Hirt, 1987; Tatárová et al., 2010).

The high swelling potential of LiCl/DMAc mixtures or LiCl/urea mixtures can be explained with the specific involvement of all ionic components and the amide to form a complex structure with functional groups of the cellulose chain. In analogy to the proposed structure for the LiCl/DMAc system (Leipner et al., 2000) a model structure for the interaction of a concentrated LiCl/urea solution with the primary OH group at C-6 can be formulated (Fig. 4).

As all ions are involved in the formation of the complex, exchange of an ion by another will change the complex stability or even prevent the formation of a similar structure. As a result the swelling/solution properties of a mixture will change.

2.4. *Surface sorption of soluble polysaccharides*

Sorption processes on the surface of an insoluble 3-D-polysaccharide matrix mainly occur through hydrogen bonding, Van-der-Waals forces, and hydrophobic interactions. Dependent on molecular size of the adsorbed molecule exclusion effects can occur and sorption of high molecular weight compounds may be restricted to the surface of the 3-D-structure or very large cavities and pores.

Ion-binding and ion-complexation reactions also can be involved in sorption processes.

The carboxylic group content in cellulose fibres is in the range of 20 mmol g^{-1}. These carboxylic groups enable cellulose fibres to undergo ion-exchange reactions. In the literature distinct binding tendency of lyocell type fibres for Ca^{2+} ions has been reported, the absolute binding capacity of Ca^{2+} being limited by the respective carboxylic group content (Eq. (1)) (Bechtold & Fitz-Binder, 2009).

$$\mathrm{Cell{-}COOH} + \mathrm{Ca}^{2+} + \mathrm{X}^- \rightleftarrows \mathrm{Cell{-}COO}^-\mathrm{Ca}^{2+}\mathrm{X}^- + \mathrm{H}^+ \qquad (1)$$

Considerable binding capacity for Ca^{2+} ions was indicated by the sorption equilibrium observed in exhaust experiments (Fig. 5). It appears likely that in addition to ionic attraction, complexation effects in the swollen 3-D-structure also contribute to the binding strength of the cellulose matrix for Ca^{2+}.

From analysis of the stoichiometry of Ca^{2+}-containing fibres it could be demonstrated, that a carboxylic group is bound to a single Ca^{2+} ion. Thus, in such a structural element another counter ion is required (Bechtold & Fitz-Binder, 2009). A proposed model structure is given in Fig. 6.

In water these Ca^{2+} containing sites can serve as positively charged binding sites which strengthen absorption of dissolved, carboxylic group containing polysaccharides, such as pectine, alginate, xanthan (Fraeye, Duvetter, Doungla, Van Loey, & Hendrickx,

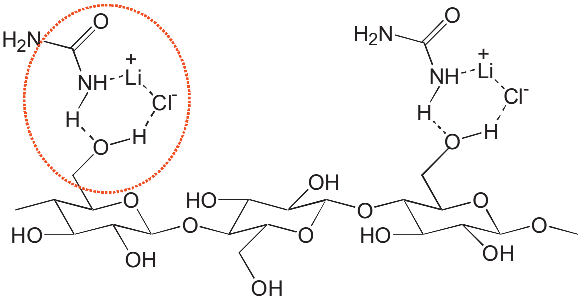

Fig. 4. Proposed model structure for ionic interaction and complex formation in the system cellulose/LiCl/urea.

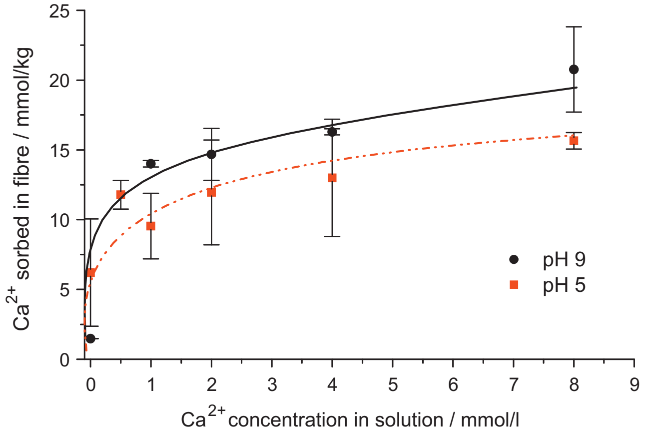

Fig. 5. Binding of Ca^{2+} in lyocell fibres from diluted aqueous Ca^{2+} solutions (pH 9; pH 5) (Bechtold & Fitz-Binder, 2009).

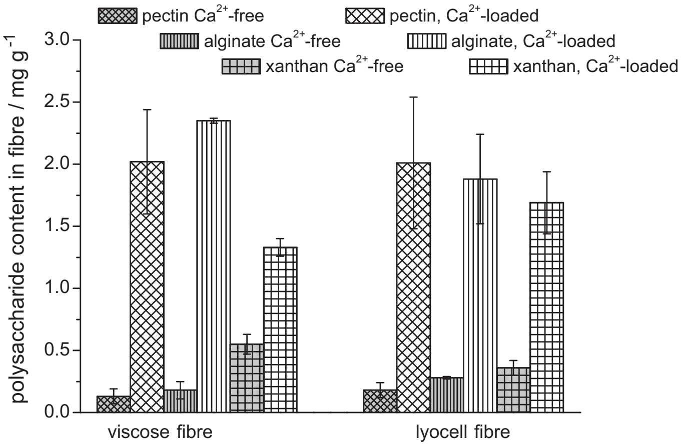

Fig. 7. Sorption of pectin, alginate and xanthan on viscose or lyocell fibres, as function of Ca^{2+} load on the fibre. (Ca^{2+} free fibre and fibres pre-impregnated with 8 mM Ca^{2+}) (Paul et al., 2012).

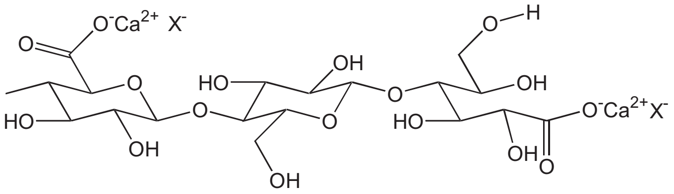

Fig. 6. Proposed model structure for Ca^{2+} bound in cellulose.

2010; Kohn, 1975). Whilst such polymers show only little tendency to adsorb on Ca^{2+} free cellulose fibres, distinct adsorption occurs on Ca^{2+} containing cellulose (Fig. 7) (Paul, Manian, Široká, Duelli, & Bechtold, 2012)

The ionic groups strengthen surface adsorption of charged polysaccharides by ionic interactions. In addition complex formation can contribute to the overall binding strength. In the case of pectin, alginate or xanthan, their molecular size prevents these polysaccharides from entering into the swollen fibre structure, thus only sorption can occur at the outer surface of the fibres. As a result, only a few nm thick layer can be formed, as the sorption is specific to the presence of bound Ca^{2+} ions. A schematic presentation is given in Fig. 8.

Formation of a deposit or visible layer on the fibre surface was not observed in ESEM (environmental scanning electron microscope) analysis of the fibres. This also supports the formation of a molecular layer of polysaccharide adsorbed on the surface of the cellulose fibre.

A similar sorption behaviour could be observed in the case of alginate sorption on iron(III)-containing cellulose fibres. When iron(III)-ions are bound to the negatively charged carboxylic groups present in the cellulose fibres, significantly higher adsorption of alginate on the surface of the cellulose substrate is observed. Compared to the sorption of alginate on fibres which do not contain iron, the ionic interaction with bound iron(III) stimulates formation of sorbed layers of polysaccharide on cellulose. In the case of iron(III) formation of coordination compounds with hydroxyl groups of the polysaccharides will contribute to the binding strength. The complex species formed can be assumed to be similar to complexes formed with gluconic acid and other sugar type acids, which are known to form complexes with high stability constant (Fig. 9) (Berner & Hood, 1983; Nagy, Ohtaki, Yamaguchi, & Nomura, 1989; Pecksock & Sandera, 1955; Whitfield, Stojkovski, & Bibudhendra, 1993).

2.5. *Metal complex formation for shaping and dissolution*

Strongly alkaline iron(III)-tartrate complexes are a well know solvent for viscosimetric characterisation of cellulose. The dissolution of cellulose occurs via iron(III)-complex formation with cellulose. As could be shown in systematic studies a mixed iron(III)-complex is formed, in which cellulose and tartaric acid both serve as ligands (Jayme & Bergmann, 1956, 1957; Vu-Manh et al., 2010). The proposed structure of the dissolved complex is shown in Fig. 10.

The presence of the complex determines the behaviour of the polymer solution. At higher concentration, a gel-like structure is

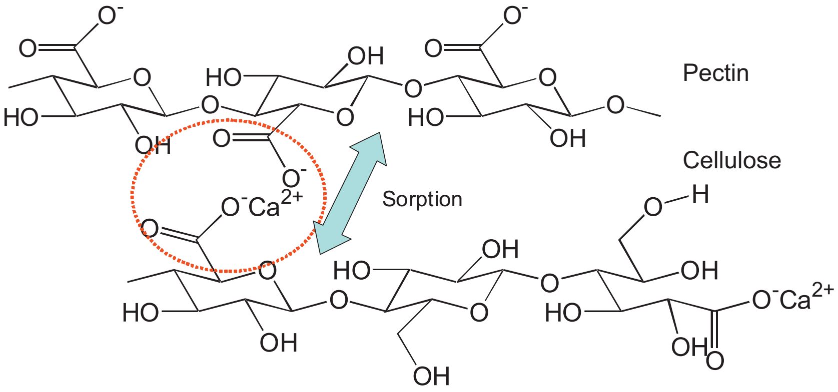

Fig. 8. Proposed model structure for sorption of pectin on Ca^{2+} containing cellulose.

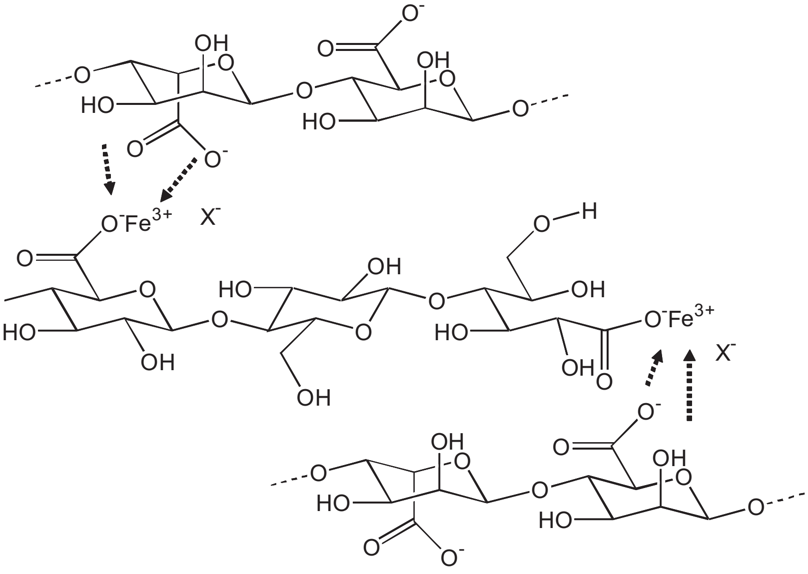

Fig. 9. Proposed model structure for sorption of alginate on Fe^{3+} containing cellulose.

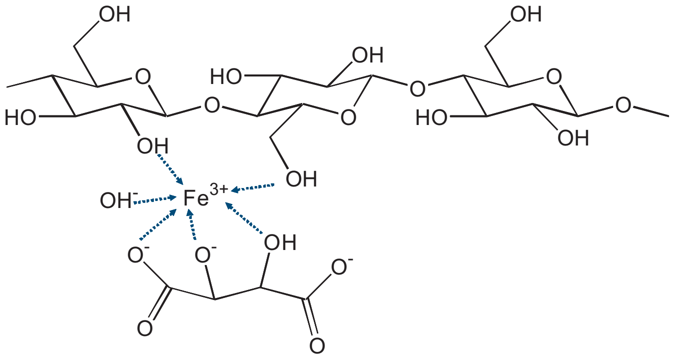

Fig. 10. Proposed model structure for iron(III)-tartaric acid complex.

observed. The elastic behaviour of solutions with concentrations of 8% cellulose prevents the direct use of such solutions for regenerated cellulose fibre spinning (Vu-Manh et al., 2012). When the polysaccharide complex is precipitated and cellulose is regenerated e.g. by dilution with acid the chemical properties of the complex will determine the structure formation during cellulose regeneration. The solubility of the complex will control precipitation and the stability of the complex will determine cellulose regeneration. The structural properties of the regenerated cellulose thus will be dependent on the particular properties of the solvent system from which regeneration occurred.

2.6. High temperature derivatisation of cellulose

Formation of similar complexes involving ionic substances can be assumed to occur during the high temperature treatment of cellulose. When cellulose materials are impregnated with mixtures of polyethylene-glycol, urea and salt, e.g. LiCl, upon heating to

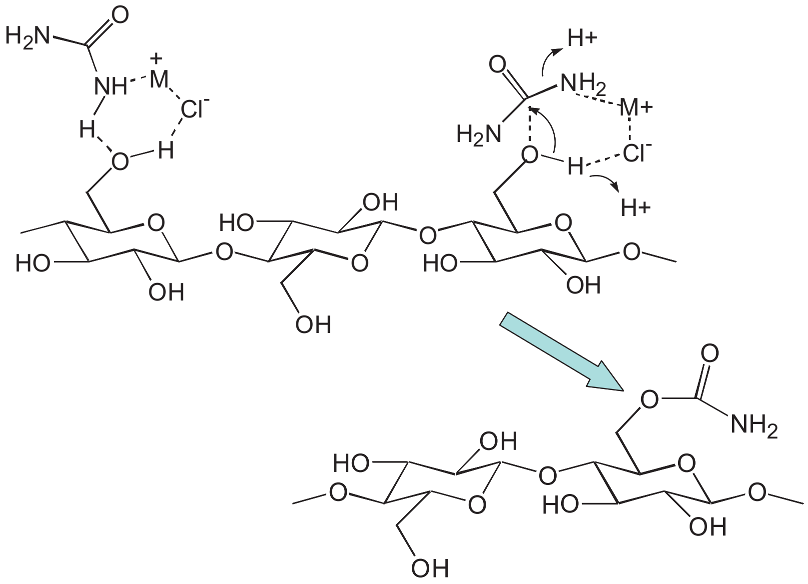

Fig. 11. Proposed model structure for catalytic complex during carbamate formation.

temperatures above 180 °C cellulose carbamate is formed (Vo, Tatárová, et al., 2010; Vo, Široká, et al., 2010).

$$\mathrm{Cell{-}OH + H_2N{-}CO{-}NH_2 \overset{LiCl}{\rightleftarrows} Cell{-}CO{-}NH_2 + NH_3} \tag{2}$$

By heating a mixture of LiCl, PEG 6000 and urea on viscose fabrics, a degree of substitution of DS = 0.2 was reached, which corresponds to a nitrogen content of 1.8%. Whilst the PEG for example PEG 6000 serves as swelling agent and co-solvent, ionic components are required to achieve an acceptable reaction rate, which leads to formation of cellulose carbamate, without significant thermal degradation of the cellulose during the short period of high temperature. Similar to the structures proposed as reaction intermediates for LiCl/DMAc, or for the swelling agent LiCl/urea a molecular arrangement can be formulated which involves the formation of ionic complexes as the reactive intermediate (Fig. 11).

In absence of suited ionic components rate of formation of cellulose carbamate is decreased substantially, thus thermal degradation of the polymer is the predominant reaction.

3. Conclusions

Despite the fact that pure cellulose does not bear charged groups, ionic interactions can play an important role in the reaction pathways which determine reactivity and structure formation of polysaccharide molecules.

Charged groups can result from the presence of neutralised carboxylic groups, introduced by oxidation of the reducing end of the polysaccharide, the primary C-6 hydroxyl group or for example by oxidative cleavage between C-2 and C-3 of the glycosidic ring.

These carboxylic groups can bind di- and tri-valent ions and thus form positively charged sites, which then bind dissolved anionic polysaccharides. Whilst direct adsorption of pectin, alginate and xanthan at cellulose surfaces is quite low, strong adsorption of these charged polymers at Ca^{2+} or Fe(III) containing cellulose surfaces is observed.

A considerable part of the interactions between di- and trivalent ions and the 3-D cellulose structure also bases on complex formation, which is well known to occur in solutions of sugar type acids, like D-gluconic acid or hepta-D-gluconic acid. Similar structuring effect through presence of ionic compounds and formation of complexes can be observed in systems, where concentrated salt solutions e.g. LiCl in presence of urea, are used as swelling agents.

Ionic components can exert significant contribution in the interactions between polysaccharides and thus will modulate observed accessibility, sorption, reactivity and structure formation. Important examples are:

- Structure reorganisation in swelling operations, for example alkalisation of cellulose, treatment in swelling agents.
- Solvent systems for cellulose shaping, e.g. NaOH/urea, molten salt hydrates.
- Structuring of cellulose materials during regeneration e.g. shaping from NMMO, ionic liquids, or FeTNa-complexes.
- Re-assembly of polymers in blends, e.g. gel-formation of soluble polysaccharides, sorption of soluble polysaccharides on cellulose.

A high number of processing concepts used at present actually involve contributions of ionic components. Only a limited number of selected systems have been studied in more detail. For future research there remain an enormous number of possible variations that could be useful for polysaccharide structuring. Thus in the near future we may expect many new approaches using concepts involving ionic interactions for polysaccharide structuring.

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