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Aqueous thiocyanate–urea solution as a powerful non-alkaline swelling agent for cellulose fibres

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ABSTRACT

For many applications cellulose fibres are treated with concentrated solutions of swelling agents to increase reactivity and to achieve reorganisation of fibre structure. Representative examples are caustic soda, potassium hydroxide solution or liquid ammonia. These highly concentrated media bear considerable safety hazards during the technical handling thus alternative swelling agents are of interest. The thiocyanate–urea system investigated in this work offers high swelling potential for regenerated cellulose fibres. Experiments with different cations of M^+ in M^+ SCN^- demonstrate the significant influence of the cation on the degree of fibre swelling. In concentrated NaSCN/urea solutions, at 80 °C, lyocell fibres expand the diameter from 12–14 to 100 μm. The treatment in the swelling agent also led to a significant increase in the water retention value which was accompanied by a strength loss of 20–40% of the initial value. FTIR analysis of treated fibres did not indicate substantial changes in structure of the cellulose polymer. Limited weight loss of up to 20% was observed despite the high expansion of the fibre.

1. Introduction

Many physical and chemical techniques have been developed to shape and converse cellulose as raw material for a wide range of products. Compared to the number of proposed processes only a few concepts have found their way to full scale application. An important stage in the treatment of the hydrophilic polymer is the processing in alkaline swelling solutions. Representative examples are activation of pulp, mercerisation of cotton in concentrated NaOH, alkalisation of regenerated cellulose fibres in KOH solutions and the treatment of cellulose fibres in liquid ammonia (Colom & Carrillo, 2002; Goswami, Blackburn, Taylor, & White, 2009; Kasahara, Sasaki, Donkai, & Takagishi, 2004; Yolacan, 2009). Solutions of NaOH and urea are also applied as a solvent system for cellulose.

Dependent on the concentration and conditions of the swelling treatment, more or less intensive reorganisation of the fibre structure occurs (Široky, Blackburn, Bechtold, Taylor, & White, 2010). Besides the restructuring of amorphous parts in the cellulose fibre changes in crystal structure from cellulose I to cellulose II or III occur dependent on the type and concentration of the swelling agent used. The crystalline parts in regenerated cellulose fibres, e.g. viscose, modal and lyocell fibres already are present in the cellulose II form. The crystal structure remained unchanged, however the degree of crystallinity and dimensions of crystallites were modified by a treatment in the swelling agents (Colom & Carrillo, 2002). A distinct modification of the solvent properties of a concentrated NaOH solution could be achieved by the addition of urea which enables such mixtures to behave as a cellulose solvent (Cai & Zhang, 2005, 2006; Kunze & Fink, 2005).

Concentrated solutions of inorganic salts and mixtures with organic compounds, e.g. urea, also have been studied as cellulose solvents during the last decade (Fischer, 2004; Fischer, Leipner, Thümmler, Brendler, & Peters, 2003; Liebert, 2010). Solvents based on concentrated salt solutions or molten salt hydrates have been studied, however a number of drawbacks prevent the wider use of such solvent concepts:

- Availability and costs limit the potential scale-up, which for example has to be considered in the case of Li-based systems (Tatarova, MacNaughtan, Manian, Siroka, & Bechtold, 2012; Tatarova, Manian, Siroka, & Bechtold, 2010).
- Hazards arise from chemicals that are ClO_4^- is a strong oxidant, and N,N-dimethylacetamide is toxic (Liebert, 2010).
- Cellulose chain degradation and derivatisation can occur as result of the reactivity of a solvent system, e.g. $FeCl_3 \cdot 6H_2O$,

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$Ca(SCN)_2 \cdot 3H_2O$, in particular at higher temperatures (Fischer, 2004; Kuga, 1980).

Thiocyanate based systems, e.g. $LiSCN \times 2.5H_2O$ have been studied as cellulose solvent (Leipner, Fischer, Brendler, & Voigt, 2000). Saturated solutions of NaSCN dissolve cellulose at temperatures above 100 °C (Erbring & Geinitz, 1938; Kuga, 1980; Williams, 1921). Aqueous solutions of KSCN and urea have been reported as plasticisers during dyeing-fixation of reactive dyes, which also indicate the potential of thiocyanate mixtures for the processing of cellulose fibres (Khudyakov, Baranov, Moryganov, & Mel'nikov, 1991).

Besides these few studies, only limited information is available about cellulose fibre swelling in thiocyanate–urea mixtures. Thus an investigation of the swelling properties of such mixtures using lyocell fibres as representative example for regenerated cellulose fibres has been undertaken. The major findings describing the swelling power of thiocyanate-based systems are summarised in this article. The swelling power has been determined by microscopy of changes in fibre diameter as a function of solution composition, temperature and time of immersion. The influence of the cation M^+ in M^+ SCN^- has been studied by comparing Na^+, K^+, NH_4^+ thiocyanates in the presence of different amounts of urea. Selected mixtures based on NaSCN/urea were used for fibre processing on a larger scale. The effect of the swelling treatment on fibre properties was investigated by determination of water retention value, tensile strength/elongation behaviour and FTIR analysis.

2. Experimental

2.1. Materials and chemicals

Lyocell staple fibres (CLY, 1.3 dtex, 38 mm length, TENCEL®) without a spin finish were used for these experiments, kindly supplied by Lenzing AG (Lenzing, Austria).

NaSCN (analytical grade, 98% Fluka, Switzerland), urea (analytical grade, 99.6%, Carl Roth, Germany). NH_4SCN (analytical grade, Merck), N,N-dimethyl-formamide (analytical grade, Riedl-de-Haen), 1-ethylurea (97%, Aldrich), (2-hydroxyethyl)-urea (95%, Aldrich), N,N-dimethylurea (98%, Merck-Schuchardt) and KSCN (synthetical grade) were used.

2.2. Swelling experiments – diameter measurement

The preparation of the concentrated solution is explained for the NaSCN–urea system representing example within this study. For the swelling experiments at RT initially a nearly saturated solution of NaSCN (58%, w/w) was prepared at RT. For experiments at 80 °C the higher solubility of NaSCN at 60 °C was utilised and mixtures giving the starting from this concentrate of NaSCN (61–64%, w/w). A defined amount of urea then was added to an exact mass of the concentrated solution and dissolved to obtain the final composition. The exact composition was calculated from the weighted mass of components used for preparation. This procedure allowed preparation of solutions with constant molar ratio of NaSCN to water, while changing their absolute concentrations.

To standardise the conditions and to provide sufficient time for equilibration swelling at RT and −5 °C was performed for 22–24 h and 48 h, respectively, for experiments at 80 °C swelling was limited to 1 h, to minimise the risk of fibre degradation at elevated temperature. From literature experiments with complex forming solutions the time of immersion in the NaSCN/urea solutions should be sufficient for equilibration (Vu-Manh, Öztürk, & Bechtold, 2010).

For swelling experiments a defined mass of fibres was placed in an excess of swelling solution at a liquid to mass ratio level of at least 20 ml per g fibre and then kept at constant temperature (details are given in the respective tables). For diameter measurement, the fibres soaked in swelling agent were placed between object glasses and the diameter was measured at RT using an optical projection microscope with 500× magnification. Results given represent the mean of 20 measurements and corresponding standard deviation.

In experiments to treat a higher amount of fibres, 0.5 g of fibre was placed in 20 times the mass of solution and treated under defined conditions, for example for 22–24 h at RT, or for 1 h at 80 °C in a thermostat-controlled water bath. The samples then were rinsed four times for 5 min with 100 ml tap water and then dried at RT until equilibrium in moisture content was reached. Treated fibres then were analysed for WRV, tensile strength and FTIR.

2.3. Water retention value

For determination of the water retention volume (WRV) 0.25 g of sample was placed in 25 ml of deionised water for 24 h. The wet sample was then centrifuged for 10 min at 4000 × *g* (4660 rpm: Heraeus Multifuge 1 L, D-37520 Osterode, Germany), using a centrifuge filtration tube to remove excess water. After weighing the wet sample, the fibres were dried at 105 °C for 4 h and then were cooled to RT for 24 in a desiccator. WRV was calculated from the mass of the dried sample, m_d and the mass of the wet sample, m_w as seen in Eq. (1). For each sample three repetitions were performed and the mean and standard deviation were calculated.

$$\mathrm{WRV} = \frac{m_w - m_d}{m_d} \quad (1)$$

2.4. Mechanical properties

Vibroskop S 434 (Lenzing Technik Instruments, Lenzing, Austria) was used to determine the linear density of fibres. Tenacity and elongation (%) of the fibre was measured with a fibre tensile strength tester (Vibrodyn S 381, Lenzing Technik Instruments, Lenzing, Austria), according to DIN 53816. Fibres were tested in conditioned state at 20 ± 2 °C and 65 ± 2% RH. A gauge length of 10 mm, a pre-load of 100 mg and a cross-head speed of 10 mm min^{-1} were used. Ten fibre samples were tested to obtain a mean value and standard deviation of fibre tenacity and elongation at breaking point. For some samples the swelling treatment increased adhesion between fibres to a level which prevented the separation of the individual fibres, thus analysis of the tensile strength could not be performed. Tensile strength values are therefore reported only for samples where single fibres could be removed without mechanical damage.

2.5. FTIR spectroscopy

The FTIR spectra of treated and untreated fibres were recorded on a Vector 22, FTIR instrument (Bruker Analytik GmbH, Germany) in transmission mode. Fibres were cut into short pieces and embedded in a KBr pellet. The spectra were obtained by accumulation of 128 scans, with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. The NaSCN/urea system

At temperatures of 120–140 °C molten salt hydrates, e.g. $Ca(SCN)_2 \cdot 3H_2O$ or the eutectic mixture $NaSCN/KSCN/LiSCN \cdot 2H_2O$ dissolve cellulose, however, a considerable decrease in molecular weight occurs (Fischer et al., 2003; Liebert, 2010). As the decrease in molecular weight is most probably due to the reactivity of the system at a higher temperature, the upper temperature limit for this

Table 1
Composition of solution, treatment temperature and fibre diameter in NaSCN/urea/water mixtures.

Sample no.	$\omega_{(NaSCN)}$ (%, w/w)	$\omega_{(urea)}$ (%, w/w)	$\omega_{(water)}$ (%, w/w)	$x_{(NaSCN)}$ (mol/mol)	$x_{(urea)}$ (mol/mol)	$x_{(water)}$ (mol/mol)	T (°C)	t (h)	Vol. solution/fibre mass (ml/g)	Diameter (μm)	Std. dev. (μm)
Untreated	–	–	100	–	–	1	–	–	–	13.9	2.63
1	58.2	0.0	41.8	0.237	0.000	0.763	RT	22–24	20	27.1	2.20
2	48.9	16.0	35.1	0.214	0.094	0.691	RT	22–24	20	37.5	2.74
3	44.8	23.1	32.1	0.203	0.141	0.656	RT	22–24	20	36.3	2.92
4	41.4	28.8	29.7	0.194	0.182	0.625	RT	22–24	20	34.4	1.79
5	38.9	33.2	27.9	0.186	0.214	0.600	RT	22–24	20	30.1	1.77
6	61.7	0.0	38.3	0.264	0.000	0.736	80	1	20	73.6	6.82
7	51.3	16.8	31.8	0.236	0.105	0.659	80	1	20	112.7	7.06
8	47.4	23.2	29.4	0.225	0.148	0.627	80	1	20	89.4	14.31
9	43.7	29.3	27.1	0.213	0.193	0.594	80	1	20	49.9	7.8
10	41.0	33.6	25.4	0.204	0.226	0.570	80	1	20	36.2	3.11
11	58.2	0.0	41.8	0.236	0.000	0.764	5	48	>20	31.9	4.61
12	48.5	16.7	34.9	0.213	0.099	0.689	5	48	>20	37.3	3.06
13	44.8	23.0	32.2	0.203	0.140	0.657	5	48	>20	39.6	4.24
14	41.6	28.5	29.9	0.194	0.179	0.627	5	48	>20	37.4	5.35
15	38.8	33.3	27.9	0.185	0.215	0.600	5	48	>20	32.1	2.79
16	58.2	0.0	41.8	0.236	0.000	0.764	60	0.5	>35	68.3[a]	12.8[a]
17	48.5	16.7	34.9	0.213	0.099	0.689	60	0.5	>35	52.5	5.54
18	44.8	23.0	32.2	0.203	0.140	0.657	60	0.5	>35	32.9	3.28
19	41.6	28.5	29.9	0.194	0.179	0.627	60	0.5	>35	26.0	3.78
20	38.8	33.3	27.9	0.185	0.215	0.600	60	0.5	>35	19.4	2.26
21	58.2	0.0	41.8	0.236	0.000	0.764	80	1	>35	78.0	12.62
22	52.5	0.0	47.5	0.197	0.000	0.803	80	1	>35	30.9	2.79
23	48.5	0.0	51.5	0.173	0.000	0.827	80	1	>35	19.7	2.18
24	44.5	0.0	55.5	0.151	0.000	0.849	80	1	>35	16.1	1.37
25	41.2	0.0	58.8	0.135	0.000	0.865	80	1	>35	14.4	2.35
26	38.8	0.0	61.2	0.124	0.000	0.876	80	1	>35	15.6	2.21

[a] Measurement of diameter difficult through high swelling.

study using the NaSCN/urea system was set at 90 °C. The swelling properties of the NaSCN/urea system were investigated in a temperature range of 5–90 °C and as a function of the composition of the solution.

In Table 1, the fibre diameter is reported as function of solutions composition and treatment conditions. The composition is given both as weight percentage and as a molar fraction. The different formulas have been grouped with regard to similar composition and have been arranged with increasing temperature of treatment. The prepared aqueous NaSCN solutions were near saturation, thus solid urea was added to change the composition to give a lower water content. This procedure allows to reduce the water content of the solution, while the molar ratio of NaSCN to water can be maintained constant, e.g. in the experiments 1–5, 3.2 molecules water were available to hydrate one molecule NaSCN.

For experiments at room temperature (No. 1–5) the molar fraction of urea was varied between 0 and 0.214 mol/mol. For experiments at 80 °C (No. 6–10) higher concentrations could be used, as these solutions were prepared at 60 °C, the molar fraction of urea between 0 and 0.226 were applied. The molar fraction of NaSCN was varied between 0.237 and 0.186 mol/mol for the 5 °C, RT and 60 °C experiments (No. 1–5, 11–20) and between 0.264 and 0.204 mol/mol in the experiments at 80 °C (No. 6–10). The composition of the solutions is shown in a ternary mixture diagram (Fig. 1).

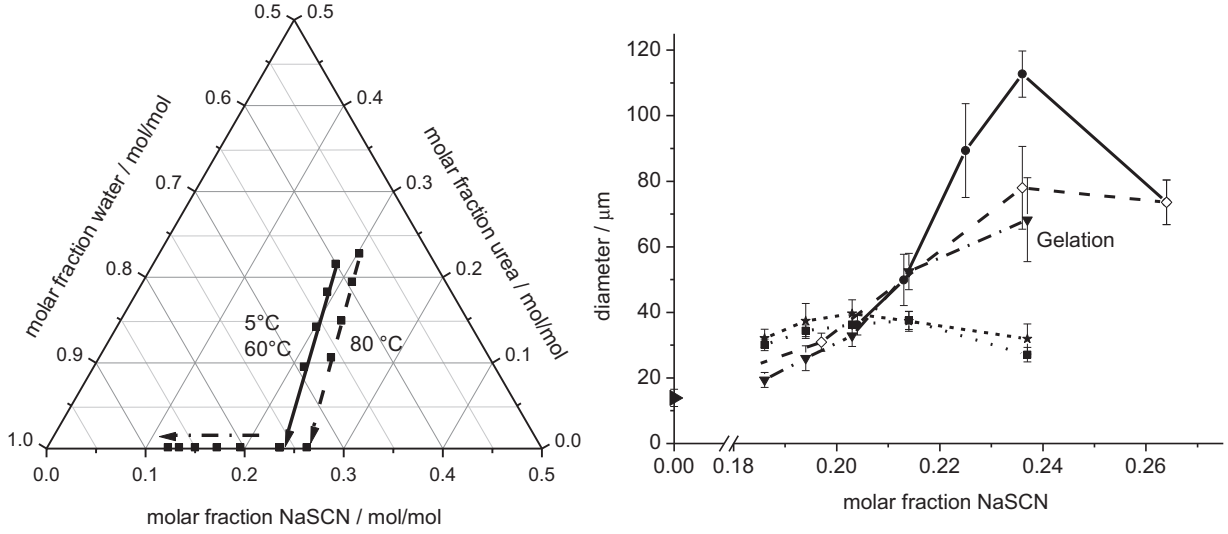


Fig. 1. Ternary diagram representing the experimental conditions (– •pure NaSCN solution; — experiments at 5 and 60 °C; – – experiments at 80 °C) and fibre diameter as a function of the molar fraction NaSCN in NaSCN/urea mixtures and temperature, (► untreated fibre); experiments 1–26 (★ 5 °C, 48 h; ■ RT, 22 h, 1–5; ▼ 60 °C, 0.5 h; ● 80 °C, 1 h; ◊ NaSCN solution 80 °C, 1 h).

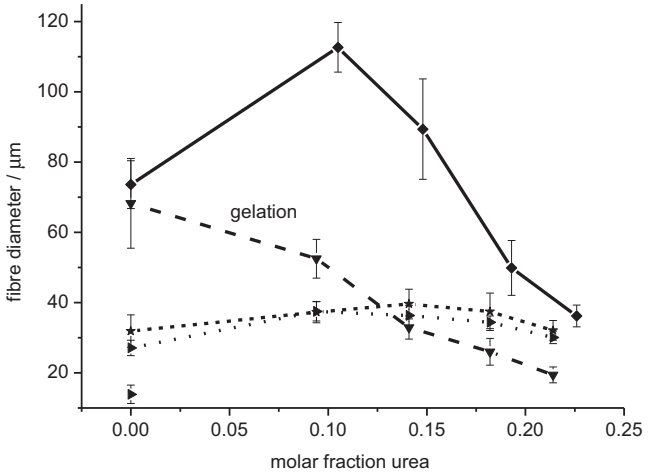


Fig. 2. Fibre diameter as function of molar fraction urea in NaSCN/urea mixtures and temperature (► untreated fibre); experiments 1–20 (⋆ 5 °C, 48 h; ■ RT, 22 h, 1–5; ▼ 60 °C, 0.5 h; ● 80 °C, 1 h).

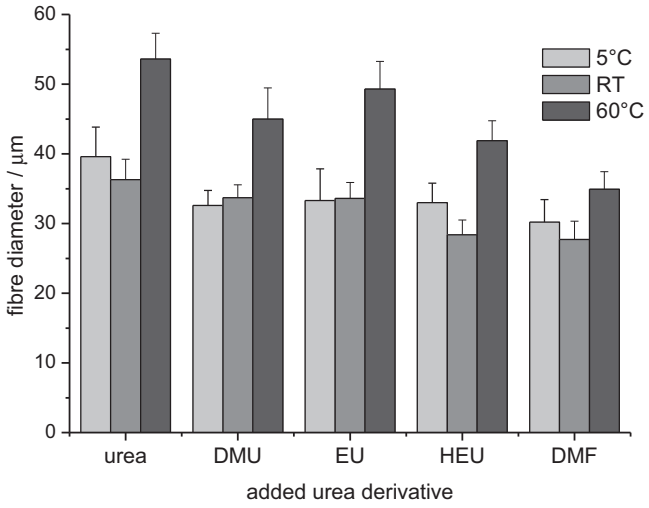


Fig. 3. Swelling properties of NaSCN/urea/subst.urea solutions. NaSCN/urea, NaSCN/urea/EU, NaSCN/urea/DMU, NaSCN/urea/HEU, NaSCN/urea/DMF (experiments 27–41).

As the preparation of the NaSCN solution was performed as first step and urea was then added as solid substance, the molar ratio between water and NaSCN remains constant for each series. For the series at 5 °C, RT and 60 °C (No. 1–5, 11–20) 3.2 mol of water were present for each mol of NaSCN, while at 80 °C (No. 6–10) as an average 2.8 molecules of water were present for one molecule of NaSCN.

For treatment at 5 °C and RT a maximum diameter of 40 μm is observed. Elevated temperatures led to a distinct increase in swelling, at 80 °C maximum fibre diameter is observed near a molar fraction for NaSCN of 0.24 mol/mol (expt. No. 7). Above 60 °C enormous swelling of the treated fibres makes the determination of the fibre diameter difficult causing thus the standard deviation to increase.

The diameter of the untreated fibres in water is near 14 μm and increases during 1 h in a 80 °C solution containing 0.236 mol/mol NaSCN and 0.105 mol/mol urea to a diameter of 113 μm. This indicates a dramatic increase in volume.

For comparison a series of concentrated solutions of NaSCN without addition of urea was studied at 80 °C (Fig. 1, Table 1, no. 21–26). The maximum swelling in the NaSCN solution is observed with a diameter of 78 ± 12 μm at a molar fraction 0.236 mol/mol NaSCN.

An analysis of the fibre diameter as function of the molar fraction urea is given in Fig. 2.

The analysis of the fibre diameter as function of molar fraction urea in solution at a temperature of 80 °C indicates maximum fibre diameter at a urea content of 0.1 mol/mol. From the solutions tested the composition 0.0236 mol/mol NaSCN, 0.105 mol/mol urea and 0.659 mol/mol water was found to swell lyocell fibres most and to exceed the diameter increase of a pure NaSCN solution by more than 40%.

To further evaluate the potential of solutions with a similar composition, a set of solutions near maximum swelling were tested in temperatures between 60 and 90 °C (Supplementary information, solution S1–S12). After 1 h at 90 °C, a maximum fibre diameter of 119.2 μm was observed in a solution of 47.4% NaSCN (0.224 mol/mol), 23.0% urea (0.146 mol/mol) and 29.6% water (0.630 mol/mol). At 80 °C the fibre diameter increased to a lower value of 87.3 μm thus indicating a strong temperature dependency on the swelling (details given in the Supplementary information).

3.2. The M^+SCN^-–urea system

To study the influence of the cation M^+ in M^+SCN^- on fibre swelling, tests with concentrated solutions of K^+ SCN^- or NH_4^+ SCN^- were undertaken by varied temperature. Only small changes in fibre diameter were observed; this indicates a significant contribution of the cation to the overall swelling performance of a thiocyanate-based solution. The fibre diameter in the swollen state ranged between 16 and 18 μm for KSCN/urea solutions and between 15 and 18 μm for NH_4SCN/urea solutions. Detailed conditions and results are given in the Supplementary information (KSCN experiments S13–S25; NH_4SCN experiments S26–S35). The observed increase in fibre diameter was rather low hence studies with these systems were extended further.

The effect of N-alkylation in the urea molecule was studied by the addition of 1-ethylurea (EU), N,N-dimethylurea (DMU), (2-hydroxyethyl)-urea (HEU), or N,N-dimethyl-formamide (DMF) as a polar molecule with constitutional elements similar to urea. In the NaSCN/urea mixture approximately 60% of the un-substituted urea was replaced. Detailed composition and results are summarised in Table 2 (experiments 27–42). The effect of partial replacement of urea by substituted derivatives is shown in Fig. 3. Experiments were performed at 5 °C, RT and 60 °C.

In experiment 42 (Table 2) with use of a 50% (w/w) NaSCN solution in DMF no significant swelling was observed. This demonstrates that a certain amount of water is required to achieve extensive swelling.

3.3. Physical modification of fibres in NaSCN/urea

To study the effects of the high increase in fibre diameter on the physical properties of lyocell fibres a series of larger scale treatments were performed with the application of conditions 1–10 (Table 1). The WRV of an untreated lyocell fibre ranged between 65% and 70% and the increase is dependent on the treatment conditions and can go up to 130–140% (Fras Zemljic et al., 2013). In Fig. 4, the increase in the water retention value (WRV) is shown as a function of NaSCN content in the swelling solution and also as a function of the fibre diameter observed during the treatment.

The dependence of the WRV on the urea content in the solution is available in the Supplementary information (Fig. S1). The correlation between the final WRV and the fibre diameter achieved during

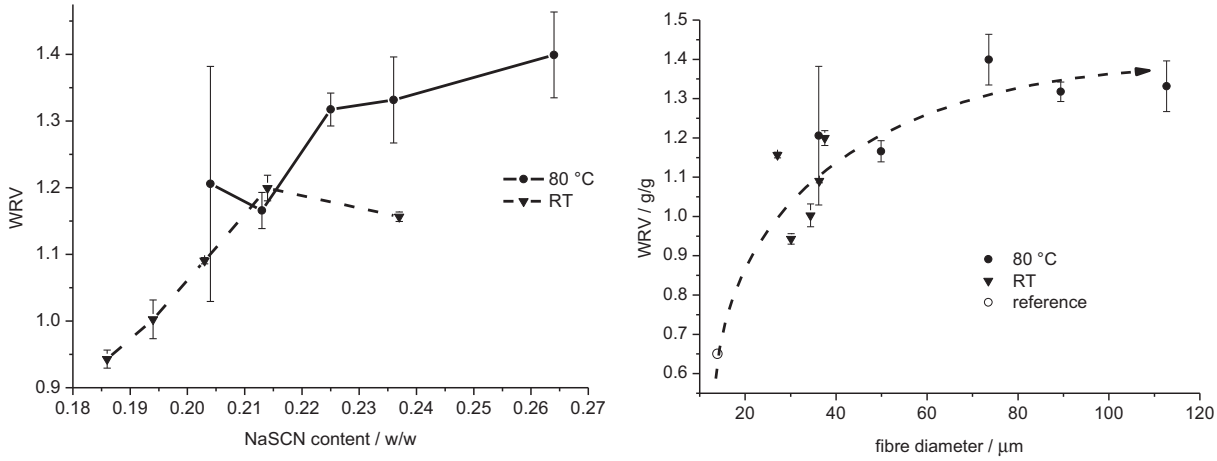


Fig. 4. Water retention value (WRV) as function of NaSCN content and as function of maximum fibre diameter observed in swollen state (conditions according to experiments 1–10).

the treatment indicates the influence of the fibre expansion on the final WRV.

A weight loss of around 5% was observed during 22–24 h at RT and up to 20% of the initial weight of the sample was removed during a treatment at 80 °C. Similar to the weight loss observed during alkali treatment of regenerated cellulose fibres the higher weight loss at 80 °C indicates that part of the fibre mass has been removed. In the optical microscope distinct fibres still were be observed and there was no evidence for possible fibre dissolution.

Results of single fibre tensile strength measurements and elongation to break of dried, treated fibres are shown in Fig. 5. Due to high swelling and softening of the structure the extraction of single fibres was not possible with samples treated in solution 2–4 (RT) and 6–9 (80 °C). Thus the results in Fig. 5 for tensile strength and elongation are shown only for samples 1, 5 and 10 where a distinct decrease in tensile strength was observed. Elongation seems to increase, however, the difference is not significant due to the increased statistical error which results from the difficult handling of the treated fibres.

Derivatisation and decomposition of the cellulose material during the treatment in the concentrated NaSCN/urea solution could lead to undesirable polymer modification. To investigate the treated samples for possible derivatisation or degradation products, representative examples of treated fibres were studied by FTIR analysis (nos. 2 and 7).

Comparison of the FTIR spectra does not indicate significant changes in the cellulose polymer (Fig. 6). For sample 7, the peak at 2050 cm^{-1} indicates the presence of a residual thiocyanate in the fibre (Jones, 1956). The absence of detectable differences supports the assumption that under the conditions applied no reaction between NaSCN or urea and cellulose occurs. The total crystallinity index (TCI) was calculated as quotient of the FTIR absorbance at wavenumber 1364 and 2892 cm^{-1} and the lateral order index (LOI) was calculated as quotient of the absorbance at 1418 and 894 cm^{-1} (Široky et al., 2010). The FTIR spectra indicated no significant changes in TCI, however an increase in LOI was observed both for sample 2 (Fig. 6) and for sample 7, which had been treated at RT and 80 °C, respectively. These results are in agreement with observations published for swelling of lyocell fibres in NaOH solutions of different concentration, where an increase in LOI was observed near the maximum of fibre swelling. Thus with regard to weight loss and fibre reorganisation the swelling behaviour of the NaSCN–urea solutions resembles to the effects observed with aqueous NaOH solutions (Široky et al., 2010).

More extensive studies would be required to further analyse and interpret of this observation. Also the determination of the degree of polymerisation could yield useful information, which however is beyond the scope of the present study.

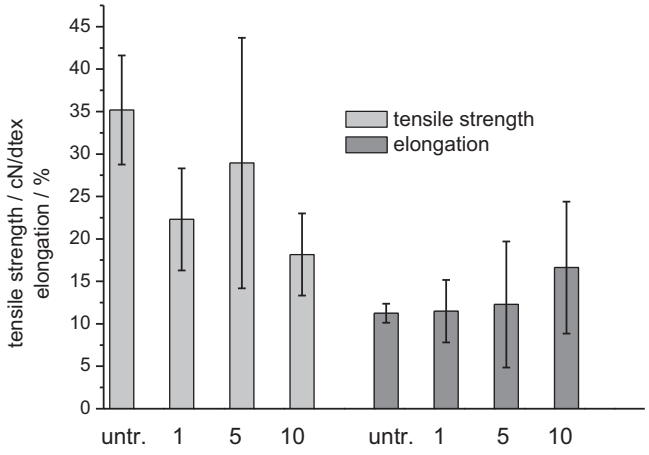


Fig. 5. Tensile strength of NaSCN/urea treated lyocell fibres: untreated reference and experimental conditions 1, 5, 10 (Table 1).

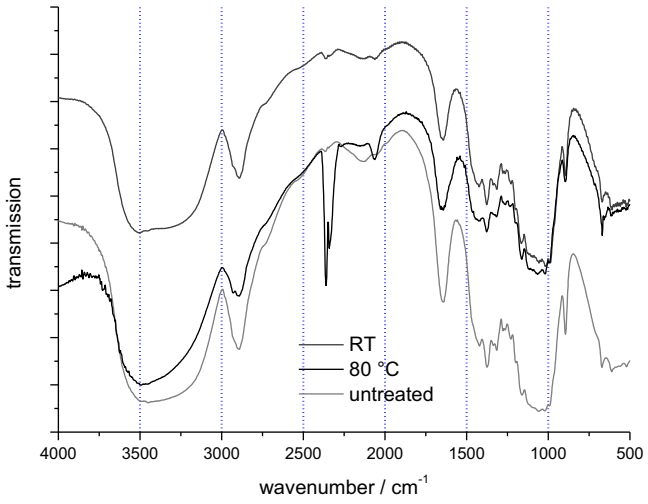


Fig. 6. FTIR spectra of untreated CLY, and sample 2 (48.9%, w/w NaSCN, 16.0%, w/w urea, RT) and sample 7 (51.3%, w/w NaSCN, 16.8%, w/w urea, 80 °C).

Table 2
Fibre diameter of fibres in NaSCN/urea/substituted urea solutions 1-Ethylurea (EU), (2-hydroxyethyl)-urea (HEU), N,N-dimethylurea (DMU), N,N.dimethyl-formamide (DMF).

Datum	Sample no.	$\omega_{(NaSCN)}$ (%, w/w)	$\omega_{(Subst.urea)}$ (%, w/w)	$\omega_{(urea)}$ (%, w/w)	$\omega_{(water)}$ (%, w/w)	$\chi_{(NaSCN)}$ (mol/mol)	$\chi_{(Subst.urea)}$ (mol/mol)	$\chi_{(urea)}$ (mol/mol)	$\chi_{(water)}$ (mol/mol)	T (°C)	t (h)	Diameter (μm)	S.D. (μm)
1-Ethylurea (EU)	27	43.5	10.3	14.9	31.3	0.203	0.044	0.094	0.658	RT	22	33.6	2.30
	28	43.5	10.3	14.9	31.3	0.203	0.044	0.094	0.658	60	1	49.3[a]	3.96
	29	43.5	10.3	14.9	31.3	0.203	0.044	0.094	0.658	5	22	33.3	4.55
	30	44.4	12.2	11.4	32.0	0.207	0.052	0.071	0.669	RT	22	31.4	3.32
	31	44.4	12.2	11.4	32.0	0.207	0.052	0.071	0.669	60	1	39.9	2.29
	32	44.4	12.2	11.4	32.0	0.207	0.052	0.071	0.669	5	22	32.9	5.05
(2-Hydroxyethyl)-urea (HEU)	33	45.1	11.2	11.2	32.5	0.210	0.041	0.070	0.679	RT	22	28.4	2.11
	34	45.1	11.2	11.2	32.5	0.210	0.041	0.070	0.679	60	1	41.9[a]	2.86
	35	45.1	11.2	11.2	32.5	0.210	0.041	0.070	0.679	5	22	33.0	2.79
N,N-dimethylurea (DMU)	36	44.8	11.7	11.4	32.2	0.208	0.050	0.071	0.672	RT	22	33.7	1.87
	37	44.8	11.7	11.4	32.2	0.208	0.050	0.071	0.672	60	1	40–50[a]	–
	38	44.8	11.7	11.4	32.2	0.208	0.050	0.071	0.672	5	22	32.6	2.16
N,N-dimethyl-formamide (DMF)	39	44.8	11.5	11.5	32.2	0.205	0.058	0.071	0.665	RT	22	27.7	2.62
	40	44.8	11.5	11.5	32.2	0.208	0.049	0.072	0.672	60	1	34.9	2.55
	41	44.8	11.5	11.5	32.2	0.208	0.049	0.072	0.672	5	22	30.2	3.24
	42	49.9	50.1	0	0	0.520	0.480	0	0	RT	22	12.4	2.56

[a] High swelling.

4. Conclusion

Concentrated aqueous solutions of NaSCN induce intensive swelling of lyocell type regenerated cellulose fibres. The diameter expansion can be further increased by the addition of urea to the concentrated NaSCN solution. Under the conditions applied the diameter of a lyocell fibre expands from 13.9 μm (water) to 112.7 ± 7.06 μm after 1 h at 80 °C in an aqueous solution containing NaSCN (0.236 mol/mol, 51.3%, w/w) and urea (0.105 mol/mol, 16.8%, w/w). Aqueous NaSCN solution of comparable concentration swells fibres less, which demonstrates the effect of the addition of urea.

In the literature, studies describing the behaviour of concentrated aqueous $Ca(SCN)_2$ solutions for swelling/dissolution of cellulose have been presented (Hattori, Koga, Shimaya, & Saito 1998; Hattori, Shimaya, & Saito, 1998a, 1998b). These data can help to explain the behaviour of the NaSCN/urea/water system. From conductivity and viscosity measurements it could be concluded that the dissociation of $Ca(SCN)_2$ reduces with concentration. In the concentration range between 25% and 50% (w/w) $Ca(SCN)^+$ and SCN^- and undissociated $Ca(SCN)_2$ are the main species present, while above 50% (w/w) the undissociated $Ca(SCN)_2$ represents the main species. Furthermore authors state that the calcium coordination of the SCN^- most probably occurs via the nitrogen of the SCN^-, thus the formulation NCS^- is used to indicate this behaviour.

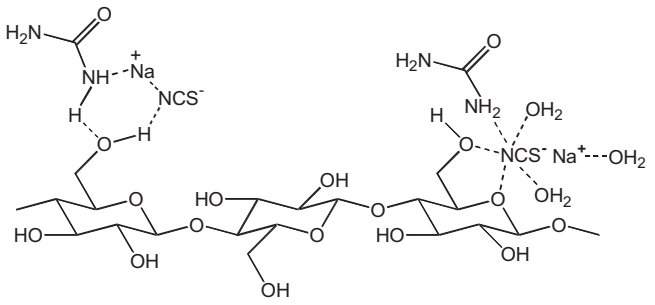
The concentrated NaSCN solutions studied in this work contain rather low amounts of hydrate water and thus are comparable to $Ca(NCS)_2$ solutions above 50% (w/w). Thus NaSCN mainly will be present in undissociated form and similarly the coordination of SCN^- to the Na^+ is expected to occur via the nitrogen atom.

For the interaction of cellulose with highly concentrated $Ca(SCN)_2$ solutions above 50% (w/w) authors propose the formation of an adduct with the composition Cell. $Ca(SCN)_2{\cdot}(H_2O)_2$ and the presence of a five-membered ring with involvement of two oxygen atoms (O(5) and O(6)) of a glucopyranose unit.

A similar adduct can be formulated for NaSCN, which then coordinates to two oxygen atoms (O(5) and O(6)) of a glucopyranose unit, one NCS^- and three water molecules, or two water molecules and one urea, to achieve hexagonal coordination. The involvement of the cation as coordination centre explains the strong dependency of fibre swelling on the type of cation used.

As a result the cation present in the solution is of significant influence and the fibre swelling follows the order $Na^+ \gg K^+$, NH_4^+. Thus concentrated KSCN and NH_4SCN/urea solutions are much less effective swelling agents. If you exchange part of the urea with substituted urea molecules such as 1-ethylurea (EU), N,N-dimethylurea (DMU), (2-hydroxyethyl)-urea (HEU), N,N-dimethyl-formamide (DMF) there still remained considerable swelling, however, the mixtures were less effective.

In the formulas used between 2.8 and 3.2 molecules of water were present per one molecule of NaSCN. A pure NaSCN/DMF based solution did not exhibit any swelling which indicates the involvement of H_2O molecules in the overall cellulose–ion complex formation. The urea molecules can participate in the solution as co-solvent and also can be part of the coordination compound with cellulose. In the literature the fundamentals of the interaction between LiOH/urea and NaOH/urea solution and cellulose has been studied in detail (Cai & Zhang, 2005). In these solutions urea takes the function of a hydrogen bonding donor and acceptor. Salt hydrates, urea hydrates and free water penetrate the cellulose structure and destroy inter- and intramolecular bonds in the cellulose polymer network. Similar to this work the swelling/dissolution power of KOH/urea was found much lower compared to NaOH/urea, which demonstrates the participation of the cation in complex formation.



Scheme 1. Presentation of representative interactions in the NaSCN/urea/cellulose system (left from analogy to LiCl/urea solutions, right in analogy to $Ca(NCS)_2$ solutions (Hattori, Koga, et al., 1998).

Two proposed formulations for the interaction of the NaSCN/urea system with cellulose are given in Scheme 1, which either relates to previous proposals for the LiCl system or include results obtained with the $Ca(SCN)_2$ system (Bechtold et al., 2013; Hattori, Koga, et al., 1998).

While NaSCN/urea solutions only lead to swelling and fibre expansion, NaOH/urea solutions can dissolve cellulose, which can be explained with the better access of hydroxide ions into the crystalline regions of the cellulose. Thus only minor changes were observed in the FTIR-crystallinity of NaSCN/urea treated fibres and weight loss during swelling treatment was low. As a result of the reorganisation of the amorphous fibre structure, the water retention value of treated fibres increases substantially.

Due to its low toxicity and low hazards, NaSCN/urea/water systems are of high interest as swelling agents for cellulose processing. After further optimisation NaSCN/urea/water solutions also may be of interest as a cellulose solvent for the shaping and conversion of cellulose.

The discussion of the effects of a certain solution on the expansion of cellulose fibres based on the assumption that the solution inside the swollen fibre is similar to the remaining solution in the bulk. Selective access and uptake of components in the swollen fibre will alter the composition in the remaining liquid solution. This will be of relevance for the remaining bulk solution, in particular when the system is studied further with regard to its application as a possible cellulose solvent. Investigations to identify the maximum fibre swelling should thus be expanded to experiments with use of a higher – apparently infinite – volume of solution for given amount of fibres and include the analysis of the liquid remaining outside the swollen fibres.

Along with the increase in diameter shrinkage in fibre length is also expected to occur as this increase would not be possible without the reduction of fibre length.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.04.084.

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