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Influence of ZnO on the properties of dilute and semi-dilute cellulose-NaOH-water solutions

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Abstract

The influence of ZnO as cellulose-8%NaOH-water solution stabilizer against gelation is studied. Cellulose intrinsic viscosity in 8%NaOH-water as a function of solution temperature is investigated in the presence and absence of ZnO. The addition of ZnO did not bring any significant improvement in terms of solvent thermodynamic quality. Gelation of cellulose-8%NaOH solutions with and without ZnO are studied for various cellulose and ZnO concentrations (4-6% and 0-1.5%, respectively) in a wide range of temperatures (-5°C to 50°C). Non-dissolved ZnO particles were observed above 0.8-0.9% ZnO in 8%NaOH-water. Gelation times were exponentially increasing with increasing ZnO concentration and with decreasing cellulose concentration and solution temperature. Gelation times of cellulose-NaOH-water-ZnO systems were found to follow a semi-empirical model correlating these three parameters. We suggest that ZnO is acting as water molecular “binder” stabilizing cellulose-NaOH-water solutions.

Key-words: cellulose, sodium hydroxide, rheology, viscosity, gelation, ZnO

1. Introduction

The processing of cellulose has been investigated for more than one century. Since cellulose cannot melt, it should be processed via dissolution or derivatisation, except for direct application in its natural fiber form (some textiles, composites or paper). There are several cellulose solvents (McCormick et al 1985; Frey et al 1996; Fischer et al 2003; Ramos et al 2005), but only two are used to produce regenerated cellulose, tetraaminecopper dihydroxide (cupra rayon process) with a very low production (Burchard et al 1994) and N-methylmorpholine-N-oxide/water (Lyocell process) (Bang et al 1999; Fink et al 2001; Zhang et al 2001b). The most common widely used way to produce cellulose fibers is through derivatisation (viscose process with associated complex de-pollution treatments) (Wilkes 2001). Another promising method, still at laboratory stage, is to use ionic liquids as solvents to produce fibers and films (Swatloski et al 2002; Turner et al 2004; Kosan et al 2008; Sescousse et al 2010).

Dissolving cellulose in aqueous solution of sodium hydroxide is another possible route that has been widely investigated since the 1980's. It is known since the work of Sobue that cellulose is soluble in a narrow range of temperature and NaOH concentration (Sobue et al 1939). This method is potentially cheap, non-polluting, using very common chemicals and easy to handle. The dissolution of cellulose in NaOH-water for cellulose processing was first considered by Japanese scientists (Kamide et al 1984; Kamide et al 1992; Matsui et al 1995; Isogai and Atalla 1998) and then continued later in several places (Kuo and Hong 2005; Cuissinat and Navard 2006; Ciechańska et al 2009). The major drawbacks are that the concentration of cellulose which could be dissolved is relatively low (less than 10%) (Egal et al 2007), and that gelation occurs with time and temperature increases (Roy et al 2003). Researchers have tried several paths to overcome these difficulties, for example, to use enzymatic activation of the cellulose pulp (Stupinska et al 2007). Another way of enhancing

dissolution and stabilizing solutions is to add other components to the cellulose-NaOH-water system. Urea and thiourea have been investigated, showing a clear improvement of the dissolution process and allowing preparing regenerated products like fiber (Cai et al 2004), films (Zhang et al 2001a; Zhang et al 2002) or membranes (Zhou et al 2002; Mao et al 2006). However, the maximal concentration of cellulose possible to dissolve in NaOH-water-urea remain as low as without urea (Egal et al 2008), and solutions with urea are gelling as well (Cai and Zhang 2006). Zinc oxide, also reported as additive improving cellulose dissolution several decades ago, was used in few studies (Vehvilainen et al 2008; Eds of "Dyer and Calico Printer" 1903; Davidson 1937; Mikolajczyk et al 2002). Recently it was reported that the maximal cellulose dissolution is reached at 0.5% ZnO in the mixture of 7%NaOH-12%urea (Yang et al 2011). The reason of the improved solubility was supposed to be the stronger hydrogen bonds between cellulose and $\text{Zn}(\text{OH})_4^{2-}$ as compared with cellulose-NaOH and cellulose-urea.

The goal of this work is to make a comprehensive investigation of the influence of ZnO on cellulose-NaOH-water solution properties, and especially on its gelation delaying effect. Using viscometry and rheology, we correlate solution properties with the amount of added ZnO, cellulose concentration and solution temperature, both in dilute and semi-dilute regions. We propose a hypothesis explaining the mechanism of ZnO action on cellulose. The dependence of gelation time on temperature, cellulose and ZnO concentration was studied. Finally, we suggest a semi-empirical equation predicting gelation time as a function of these parameters.

2. Experimental section

2.1 Materials

We used Avicel[®] PH-101 microcrystalline cellulose (“cellulose” in the following) from FMC Biopolymer Corporation to prepare cellulose-8%NaOH-water solutions. It is a purified, partially depolymerized α -cellulose, with a mean degree of polymerization of 170, as given by the manufacturer. We have chosen this type of cellulose with low DP to ensure a good solubility, pulp fiber being not fully dissolved in NaOH-water systems, including NaOH-water-ZnO (Cuissinat and Navard 2006). The use of Avicel excludes also any influence of other-than-cellulose components that are present in cellulose fibers originating from plant cell walls.

Sodium hydroxide in pellets was supplied by Merck, with purity higher than 97%. Zinc oxide powder (particles with the size several microns) of 99.9% purity was from Sigma-Aldrich. All solutions were prepared with distilled water.

2.2 Preparation of solutions

Cellulose solutions were prepared following the procedure described elsewhere (Egal et al 2007; Egal et al 2008). An aqueous solution of NaOH (18%~20% of NaOH) was cooled to -6°C. ZnO was added into this solution when applicable. Cellulose was dried in a vacuum at 50 °C for 1 hour to remove water residues, and then swollen by distilled water at 5°C for 1 hour. We mixed NaOH solution (with or without ZnO) and swollen cellulose/water with an overhead mixer at 800 rpm for 2 hours in a -6°C to obtain the cellulose solutions of various cellulose and ZnO concentrations in 8%NaOH-water. Solutions were stored in refrigerator at 5°C and studied within one day to avoid aging.

It should be noted that solution pH strongly influence ZnO solubility (Liu and Piron 1998). It was shown that ZnO is practically insoluble in water (solubility below 10^{-6} g/L), and becomes more soluble in strong acidic or basic media (Liu and Piron 1998). In this work the preparation of solutions is started by making 18-20%NaOH-water (pH \approx 14.7) and adding a certain amount of ZnO. At this pH, ZnO can be dissolved up to 27 g/L (Liu and Piron 1998). The pH of the final cellulose solutions is 14.3 in which ZnO solubility decreases to about 4 g/L. Thus the saturation of ZnO is reached in the final solutions containing cellulose and part of ZnO is in suspended state. To check the presence of ZnO particles in solutions, they were observed with optical microscopy (Figure 1). The dispersion of undissolved ZnO was homogenous, with two-size populations, i.e. ZnO particles of about 1 μ m and a few aggregates of about 10-20 μ m. The sedimentation time of suspended ZnO particles was roughly estimated for two solutions of different cellulose concentrations with Stokes' law (eq. 1):

$$V_s = \frac{2}{9} \frac{\rho_p - \rho_f}{\eta} gR^2 \quad (1)$$

where V_s is the settling velocity of particles, $\rho_f \approx 1.1$ g/cm³ is the density of solution at room temperature which slightly varies depending on cellulose concentration, $\rho_p = 5.606$ g/cm³ is the density of ZnO particles (Hu and Gordon 1992), $\eta = 0.15$ Pa.s and 0.5 Pa.s are the viscosities of freshly prepared 4% cellulose-8%NaOH-water solution and 6%cellulose-8%NaOH-water at 5°C, respectively, and R is the radius of particles. The sedimentation times in a beaker of 20 cm in height are from about 8 hours to 28 hours for larger aggregates, and from about one month to four month for smaller particles, for 4% and 6% cellulose solutions, respectively. For gelation experiments this time-dependent sedimentation can be neglected as

far as solution viscosity strongly increases during the measurement. However, in case of storing solutions in refrigerator where gelation is extremely slow, sedimentation of ZnO particles were observed for 1.2% and 1.5% ZnO after several days. Thus we limited ZnO concentration to 1.5% to exclude consideration of particle sedimentation.

Different concentrations of components in cellulose solutions will be noted as X%cellulose-Y%NaOH-Z%ZnO-water, in which X% is the weight concentration of cellulose, calculated as:

$$X \% = 100 \times M_{\text{cell}} / (M_{\text{cell}} + M_{\text{water}} + M_{\text{NaOH}} + M_{\text{ZnO}})$$

where M_i is the weight of each component. Y and Z% are the weight concentrations of NaOH and ZnO, respectively, in solvent only, calculated as:

$$Y \% = 100 \times M_{\text{NaOH}} / (M_{\text{water}} + M_{\text{NaOH}} + M_{\text{ZnO}})$$

$$Z \% = 100 \times M_{\text{ZnO}} / (M_{\text{water}} + M_{\text{NaOH}} + M_{\text{ZnO}})$$

The concentration of NaOH in the final solution was fixed to 8%, and the concentration of ZnO was varied from 0 to 1.5%. For the calculation of intrinsic viscosity, we use cellulose concentration in g/cm^3 . In the first approximation $\text{g}/\text{cm}^3 = \text{g}/\text{g}$ as far as solvent density is less than $1.1 \text{ g}/\text{cm}^3$.

For intrinsic viscosity measurements, 2% solutions were prepared as described above, and then diluted with the corresponding solvent to have a starting solution of 0.5 %. Solutions were not filtered in order not to lose micron-size non-dissolved ZnO particles and thus change ZnO concentration. The presence of 0.7% ZnO in 8%NaOH-water with some non-dissolved particles does not change solvent viscosity within the experimental error (for example,

kinematic viscosity at 25°C of 8%NaOH-water was 1.32 mm²/s and of 8%NaOH-0.7%ZnO-water was 1.33 mm²/s)

2.3 Methods

2.3.1 Intrinsic viscosity measurement

Intrinsic viscosities of cellulose in 8%NaOH-water and in 8%NaOH-0.7%ZnO-water were measured with a Lauda PVS-1 (Lauda, Germany) Ubbelohde type viscometer with capillary tube 53110/I (Schott AG, Germany). The viscometer was placed in a thermally controlled water bath at least 15 minutes before measurement. The system is equipped with an automatic dosing device (Dosimat 765, Metrohm, Switzerland) to control sample concentration by sequential dilution. A magnetic stirrer was used for concentration homogenization at each dilution. For each concentration, one pre-measurement and three measurements were performed. The mean flow time was recorded and the reduced viscosity was calculated by software automatically. Temperature was varied from 5° to 30°C with 5° increment. The intrinsic viscosity values are with 5% experimental error.

2.3.2 Rheological measurement

Dynamic rheological measurements were performed with a stress-controlled Bohlin Gemini™ 150 rheometer (Malvern Instruments, UK) with a Peltier plate for temperature control. Measuring system was a cone and plate geometry with 4° angle and 40 mm diameter. Temperature was varied from -10°C to 40°C. Silicone oil (DC 200, Sigma-Aldrich) was spread at the edge of gap to prevent water evaporation or absorption. Silicone oil is not miscible with cellulose solutions and had a much lower viscosity; thus it did not perturb the measurements. A solvent trap was used to cover the measuring cell to prevent the variation of

water content. The solvent trap was wrapped by PARAFILM[®] (Pechiney Plastic Packaging, US) during low temperature tests, isolating it from water condensation from the air. Stress and frequency were selected and set for all measurements at $f = 0.1$ Hz and $\sigma = 0.01$ Pa to guarantee being in a linear visco-elastic regime.

3. Results and discussion

3.1 Dilute solutions: influence of ZnO on cellulose intrinsic viscosity in 8%NaOH-water

The temperature dependence of cellulose intrinsic viscosity, $[\eta]$, in 8%NaOH-water with 0.7%ZnO and without ZnO is given in Figure 2. A steady decrease of the intrinsic viscosity with increasing temperature was observed for both cases, with and without ZnO, and is consistent with the results already reported for cellulose of another molecular weight dissolved in 8% NaOH-water without any additive (Egal 2006) and in 9% NaOH-water (Roy et al 2003). The drop of $[\eta]$ signifies that the thermodynamic quality of solvent decreases with temperature. The mechanism of this phenomenon is thought to be as follows: during the dissolution process, the NaOH hydrates break intra-chain hydrogen bonds between cellulose macromolecules and link to cellulose chains. It was shown that at least four NaOH per one anhydroglucose unit are needed to dissolve cellulose (Egal et al 2007). We assume that there is an unstable equilibrium between NaOH hydrates bound to cellulose chains. When temperature is raised, cellulose-cellulose interactions become more favored compared to cellulose-NaOH interactions leading to the shrinkage of cellulose coils in dilute solution and decrease of intrinsic viscosity. In semi-dilute solution, this leads to the inter-chain connection of cellulose coils, and eventually gelation happens.

The presence of ZnO did not bring any noticeable change to the intrinsic viscosity of cellulose. As it will be shown in the following, when 0.7% ZnO is mixed with 8% NaOH-water, only part of ZnO is dissolved. The unaffected value of $[\eta]$ indicates that neither dissolved nor suspended ZnO influences the conformation and behavior of cellulose chains at molecular level in dilute region. Similar results were reported when thiourea was added into cellulose-NaOH-water solution, giving the same intrinsic viscosity up to a thiourea content of 0.75M (Zhang et al 2002).

3.2 Semi-dilute solutions: gelation

3.2.1. Overall results

Gelation of cellulose-NaOH-water solution is thermally-induced and irreversible. Oscillatory rheological measurement is a simple and efficient method to investigate the time and temperature dependence of gelation process. By tracking elastic modulus G' and viscous modulus G'' as a function of time at a given temperature, we ascribe the gel point, in the first approximation, when the value of G' meets G'' , and obtain the gelation time t_{gel} . In some cases, curves of G' and G'' stayed parallel and did not cross after considerable measurement time. We can then only state that if gelation ever occurs, it takes longer than three days which is a maximal reasonable duration of a rheological experiment.

The results on gelation time of cellulose-8% NaOH-water solutions at temperatures from -5° to 50°C at various cellulose and ZnO concentrations are summarized in Table 1. An example of gelation time as a function of solution temperature for two cellulose concentrations is given in Figure 3. The results obtained clearly show that gelation is significantly delayed in the presence of ZnO: for example, a 6% cellulose solution at 20°C is gelling in 15 minutes in 8% NaOH-water and in 36 hours in the presence of 1.5% ZnO. The results presented in Table 1 also show that gelation time depends on solution temperature and

cellulose and ZnO concentrations. In the following we shall analyze the influence of each parameter, one after another, on gelation time.

3.2.2. Influence of temperature on gelation

A special attention was paid on studying gelation time of cellulose solutions at low temperatures, around -5° - $+5^{\circ}\text{C}$. The reason was to check if a sudden decrease of gelation time with temperature decrease below -0°C , reported for cellulose-7%NaOH-12%urea system is reproduced for our solutions (Cai and Zhang 2006). The exceptionally long experiments, from 3 to 5 days, were performed for 4%cellulose solutions (see Table 1). In no case we observed any decrease of gelation time with temperature decrease. According to our previous observations, gelation cannot be studied below -5°C as far as water in 8%NaOH-water may start crystallizing at this temperature: the end of water melting peak was recorded at -6° - -4°C when solutions were heated from -60°C to room temperature (Egal et al 2007).

The thermally-induced gelation of cellulose-NaOH solutions can be explained as follows. As shown for dilute solutions, solvent thermodynamic quality decreases with temperature increase. This leads to cellulose chains association via inter- and intra-chain interactions. In dilute solutions below polymer overlap concentration, the coils contract. Above the overlap concentration, gelation occurs via intra-chain interactions. The higher the temperature is, the quicker is gelation. As already suggested in literatures (Roy et al 2003; Gavillon and Budtova 2008), at given cellulose concentration gelation time is exponentially temperature-dependent (eq. 2):

$$t_{gel} = Dexp(-aT) \quad (2)$$

where D and a are adjustable constants. Examples of the exponential approximations of gelation time versus temperature are shown in Figure 3. In the range of cellulose and ZnO concentrations studied, the exponent a varies from 0.28 to 0.46. Similar results were obtained for the same microcrystalline cellulose dissolved in 7.6%NaOH-water ($a = 0.35$) (Gavillon and Budtova 2008) and in 9%NaOH-water ($a = 0.4$) (Roy et al 2003).

3.2.3. Influence of cellulose concentration of gelation

Increasing polymer concentration facilitates gelation, since chains are closer to each other, allowing an easier formation of a network. The influence of cellulose concentration on gelation time is given in Figure 4. The inverse of t_{gel} as a function of cellulose concentration C_{cell} presented in a double logarithmic plot shows that there is a power law relation between these two parameters.

A power law dependence of gelation time on carrageenan concentration was suggested by Ross-Murphy (Ross-Murphy 1991):

$$t_{gel} \approx \frac{K}{[(C/C_0)^{n'} - 1]^p} \quad (3)$$

where C_0 is the critical concentration above which gelation could happen, n' is the number of polymer chains involved in a junction zone (assumed to be 2), K is a rate constant and p is a percolation exponent estimated to be around 2. An analogy between carrageenan gels and cellulose gels seems to be worth looking at. For cellulose solutions, the overlap concentration C^* , which could be considered as critical concentration for gelation, is around 1%, depending on temperature (see Figure 2). C^* of the same microcrystalline Avicel cellulose in 9%NaOH-

water was reported to be 0.83% below 20°C and 1.25% at 40°C (Roy et al 2003). Considering these values, equation 3 can be simplified as follows:

$$t_{gel} \approx \frac{k}{C_{cell}^n} \quad (4)$$

where k is a rate constant and n is a kinetic exponent. There is a good fit between the above model and the experimental data, as shows Figure 4. The exponent n is related to the gelation kinetics as well as to the organization of the junction zones in gel. From Figure 4, the values of n are more or less constant (within the experimental errors) and equal to 9 ± 2 , with or without ZnO. Although the gelation kinetics and the detailed description of the junction zones are not possible at this stage of investigations, we can conclude that they are not strongly influenced by the addition of ZnO.

An increase of cellulose concentration increases the strength of the gel, as expected. The dependence of G' as a function of cellulose concentration is demonstrated in Figure 5. A strong power law correlation between G' at gel point and C_{cell} , $G' \sim C_{cell}^u$ is observed with the scaling exponents u varying from 2 to 3.6. A similar dependence was reported for Avicel and other types of cellulose with the scaling constant varying from 3 to 4 (Zhang et al 2002). Such strong power law concentration dependence is not typical for gelling polysaccharides: for example, the Young modulus of gelled agarose or k-carrageenan is square-concentration dependent (Nijenhuis 1997). Gelation of cellulose-NaOH-water solutions is a complex process coupled with a micro-phase separation. Network defects such as loose ends and loops are not participating to gel mechanical strength. The number of cellulose-cellulose bonds in each junction point may also vary with cellulose concentration.

3.2.4. Influence of ZnO concentration on gelation

Table 1 shows that the increase of ZnO concentration delays gelation. We measured the gelation time of 6%cellulose-8%NaOH-water at various ZnO content, 0%, 0.7% and 1.5% from 10°C to 45°C. The results are presented in Figure 6a. A master plot can be obtained by shifting two data sets, for 0.7% and 1.5% ZnO, towards the one without ZnO (Figure 6b). The same shape of the initial curves indicates that that despite ZnO efficiency in delaying gelation, the increase in ZnO concentration does not change gelation kinetics.

Gelation time was studied as a function of ZnO concentration, C_{ZnO} , at fixed temperature and cellulose concentration. Figure 7 shows results for $T = 40^\circ\text{C}$ and $C_{cell} = 4\%$. Gelation time exponentially increases with ZnO concentration and can be described by the following equation in the studied ZnO concentration range:

$$t_{gel} = t_0 + B \times C_{ZnO}^m \quad (5)$$

where t_0 is the gelation time at $C_{ZnO} = 0$, B is a constant and m is an exponent indicating the influence of ZnO. For 4%Avicel-8%NaOH-water solutions at 40°C we have $t_0 \approx 0$ (almost immediate gelation without ZnO) and the least square approximation gives $B = 10^{9.13}$ and $m = 3.53$.

3.2.5. Role of ZnO as gelation delayer

Summarizing the results obtained on the influence of ZnO on cellulose-NaOH-water solution properties, the following three major facts can be listed:

- 1) ZnO is quite efficient in delaying gelation of cellulose solutions;
- 2) ZnO does not have much influence on either gelation kinetic order or the junction zones in cellulose gels.

3) ZnO does not change the properties of cellulose at the molecular level and does not improve the thermodynamic property of solvent towards cellulose.

Correlating the facts mentioned above with the results obtained on the role of urea as a stabilizer for cellulose-NaOH-water solutions (Egal et al 2008), we can speculate about the role of ZnO in the stabilization of cellulose-NaOH-water solutions. It was demonstrated that to dissolve cellulose, at least four NaOH molecules per one anhydroglucose unit are needed (Egal et al 2007); NaOH hydrates are breaking cellulose intra-chain hydrogen bonds and linking to cellulose chains. The same is valid for cellulose-NaOH-water solutions containing urea (Egal et al 2008). Cellulose-NaOH-water solutions are not stable; cellulose chains tend to aggregate, leading to gelation. When ZnO is suspended in NaOH-water solutions, a “network” of tiny particles is formed. The surface of particles is hydrolyzed and a layer of hydroxide is formed ($\equiv\text{Zn-OH}$) attracting water molecules. When dissolved, Zn(OH)_3^- and Zn(OH)_4^{2-} ions are formed (Reichle et al 1975; Degen and Kosec 2000) that also trap water. Thus ZnO may play the role of a water “binder”, decreasing strongly the amount of free water around the cellulose chains that may drive chain aggregation. ZnO stabilizes the solution by keeping water far from the cellulose chains, as urea does (Egal et al 2008). This could explain why ZnO only delays the gelation but does not change cellulose dissolution, solvent quality and gelation kinetics in NaOH-water solutions.

3.2.6. Semi-empirical model to estimate gelation times

As shown in Sections 3.2.2-3.2.4, the gelation time of cellulose solution in NaOH-ZnO-water is influenced by temperature and cellulose and ZnO concentrations. Combining equations 2, 4 and 5, an equation correlating gelation time with these three variables can be built:

$$t_{gel} = \left(\frac{A}{C_{Avicel}^n} + B \cdot C_{ZnO}^m \right) e^{-a \cdot T} \quad (6)$$

where the exponents n and m in the power-law concentration dependences are the arithmetic mean values of the corresponding exponents obtained for all data according to equations 4 and 5 ($n = 9$ and $m = 3.5$, see sections 3.2.3 and 3.2.4), constant a is the mean value of a -constants (eq. 2) obtained for all data ($a = 0.35$, see section 3.2.2) and A and B are fit parameters found with the least square approximation. The comparison between the calculated values of t_{gel} according to eq. 6 and experimental data is shown in Figure 8. The semi-empirical model suggested fits reasonably well the experimental values, allowing making an approximate estimation of gelation time of cellulose (Avicel) solutions as a function of temperature and cellulose and ZnO concentrations.

4. Conclusions

The influence of ZnO on the properties of cellulose-8%NaOH-water solutions in dilute and semi-dilute state was investigated in details at various temperatures and cellulose and ZnO concentrations. We confirmed that ZnO plays a role of solution stabilizer against gelation. This function is power-law ZnO concentration dependent despite that ZnO is both in dissolved and in suspended state above a certain concentration. The fact that *suspended* ZnO is a good stabilizer explains why it does not influence cellulose properties on the molecular level both in dilute solutions (intrinsic viscosity and solvent thermodynamic quality) and in semi-dilute state (gelation kinetics and composition of junction zones). We suggest that the physical mechanism of gelation delaying effect of ZnO is due to its role as free water “binder” via formation of hydrates (in dissolved state) and hydroxides (on particles surface). We also

obtain a semi-empirical model predicting gelation time as a function of Avicel concentration, ZnO concentration and temperature.

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Figure Captions

Fig.1

Optical microscope images of (a) 4% Avicel-8% NaOH-0.7% ZnO-water and (b) 4% Avicel-8% NaOH-1.5% ZnO-water, observed shortly after the preparation at room temperature

Fig.2

Intrinsic viscosity of cellulose-8% NaOH-water solutions without or with 0.7% ZnO, from 5°C to 30°C; with error bars of 5%

Fig.3

Gelation times of 4% and 6% cellulose-8% NaOH-water solutions, without and with ZnO added, at different temperatures. Lines are exponential approximations according to eq.2. The error bars are of 20%

Fig.4

Double logarithmic plot of $1/t_{gel}$ versus cellulose concentration, with and without ZnO added, at 5 different temperatures. Lines are power law approximations according to eq.4

Fig.5

Double logarithmic plot of elastic modulus G' at gel point versus cellulose concentration, with or without ZnO added at five different temperatures. Lines are power law approximations $G' \sim C_{cell}^u$

Fig.6

Gelation time versus temperature for 6%cellulose-8%NaOH-water solutions with 0%, 0.7% and 1.5% ZnO: a) initial data, b) shifted towards 0%ZnO by 6.5 °C for 0.7% ZnO and by 14 °C for 1.5% ZnO. The lines are given to guide the eye

Fig.7

Double logarithmic plot of gelation time versus ZnO concentration for 4%Avicel-8%NaOH-water solutions at T= 40°C. The solid line is power law approximation according to eq.5 with $t_0 \approx 0$ for this temperature

Fig.8

Estimated (solid lines) and experimental (points) gelation times as a function of temperature for solutions of different cellulose and ZnO concentrations. Filled points: solutions without ZnO 4%cellulose-8%NaOH (1) and 6%cellulose-8%NaOH (2); open points: with ZnO 4%cellulose-8%NaOH-1.5%ZnO (3), 6%cellulose-8%NaOH-0.7%ZnO (4) and 6%cellulose-8%NaOH-1.5%ZnO (5)

Figures

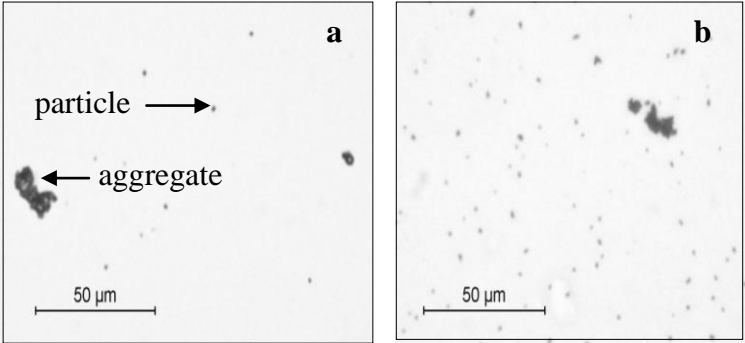


Fig.1 Optical microscope images of (a) 4%Avicel-8%NaOH-0.7%ZnO-water and (b) 4%Avicel-8%NaOH-1.5%ZnO-water, observed shortly after the preparation at room temperature

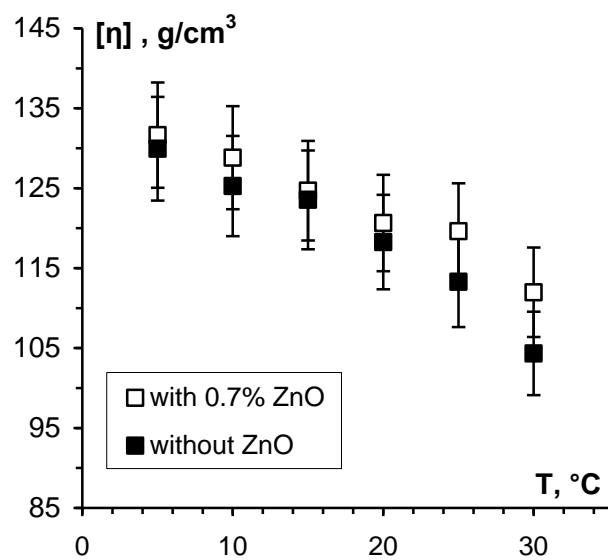


Fig.2 Intrinsic viscosity of cellulose-8%NaOH-water solutions without or with 0.7% ZnO, from 5°C to 30°C; with error bars of 5%

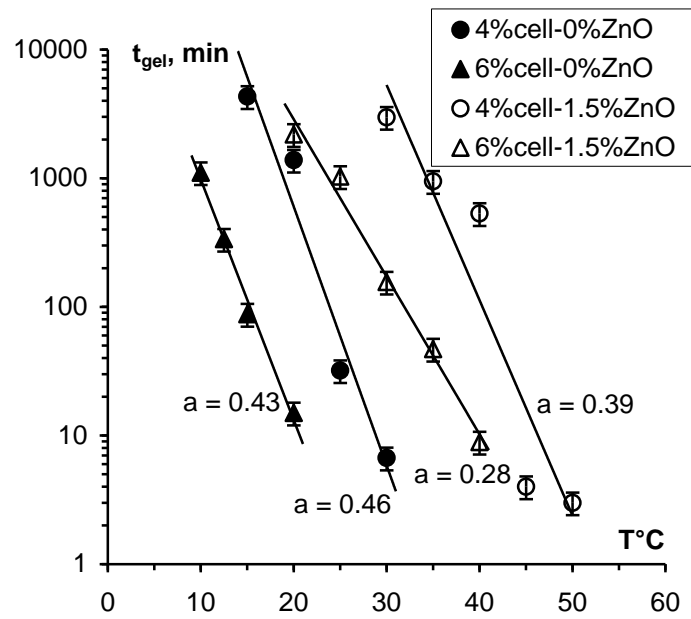


Fig.3 Gelation times of 4% and 6% cellulose-8%NaOH-water solutions, without and with ZnO added, at different temperatures. Lines are exponential approximations according to eq.2. The error bars are of 20%

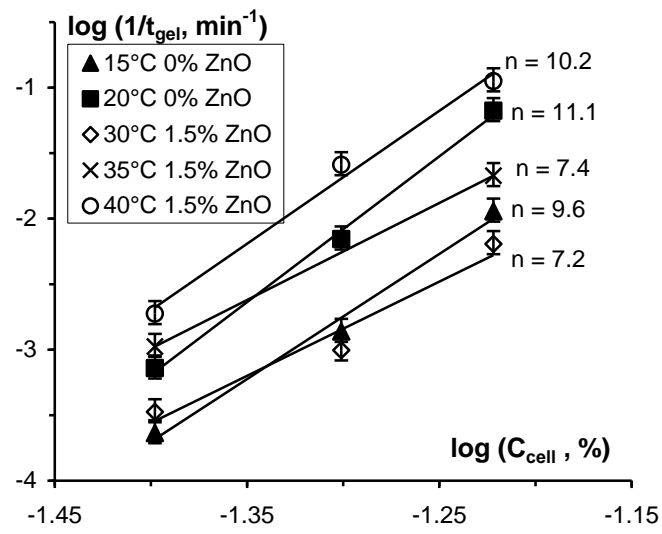


Fig.4 Double logarithmic plot of $1/t_{gel}$ versus cellulose concentration, with and without ZnO added, at 5 different temperatures. Lines are power law approximations according to eq.4

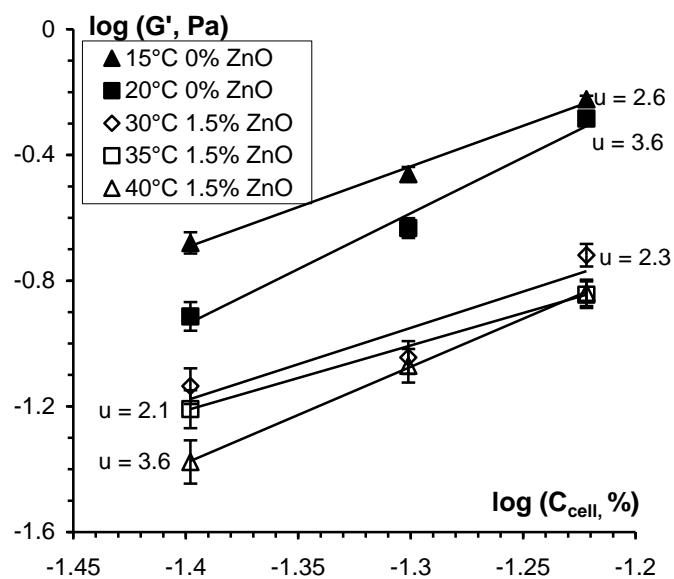


Fig.5 Double logarithmic plot of elastic modulus G' at gel point versus cellulose concentration, with or without ZnO added at five different temperatures. Lines are power law approximations $G' \sim C_{cell}^u$

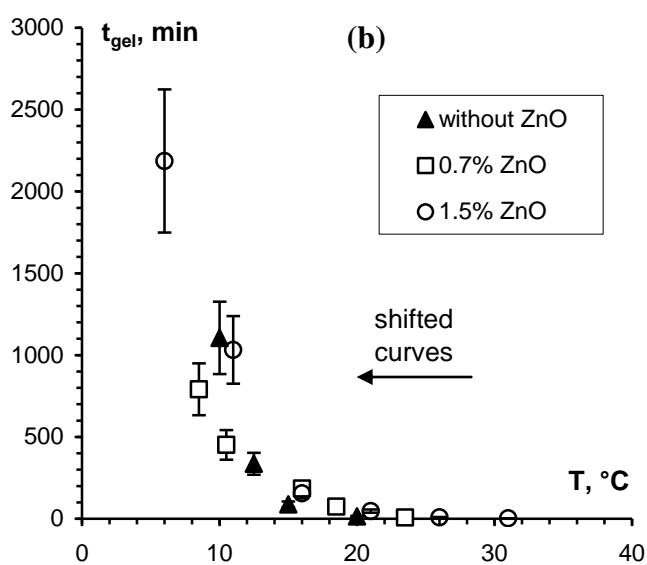
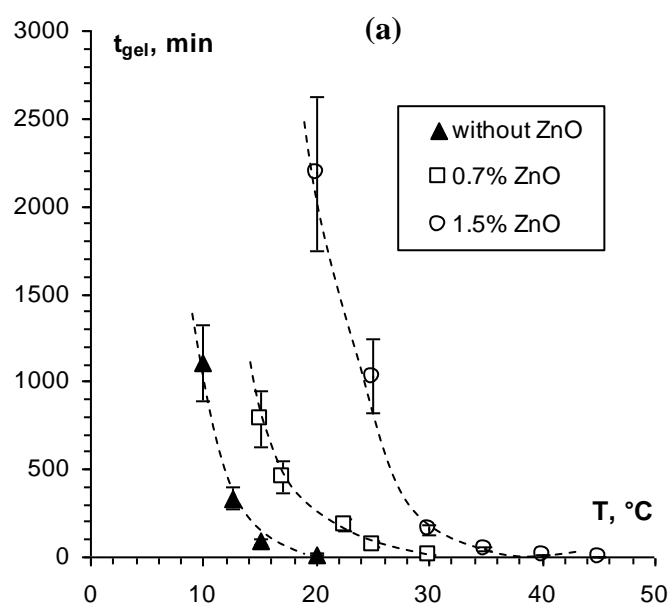


Fig.6 Gelation time versus temperature for 6%cellulose-8%NaOH-water solutions with 0%, 0.7% and 1.5% ZnO: a) initial data, b) shifted towards 0%ZnO by 6.5 °C for 0.7% ZnO and by 14 °C for 1.5% ZnO. The lines are given to guide the eye

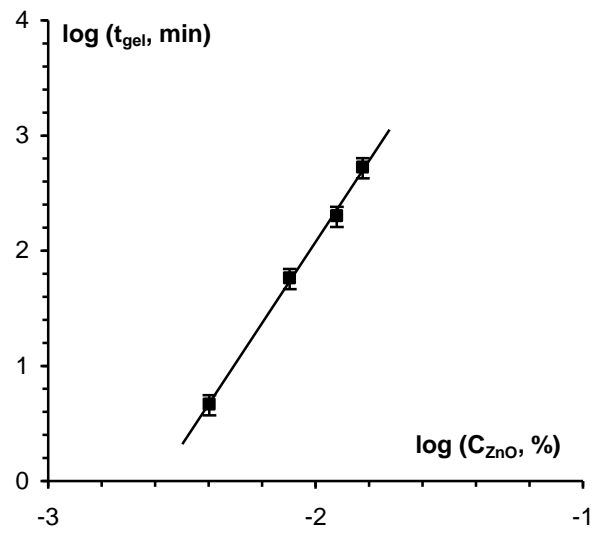


Fig.7 Double logarithmic plot of gelation time versus ZnO concentration for 4%Avicel-8%NaOH-water solutions at $T= 40^{\circ}\text{C}$. The solid line is power law approximation according to eq.5 with $t_0 \approx 0$ for this temperature

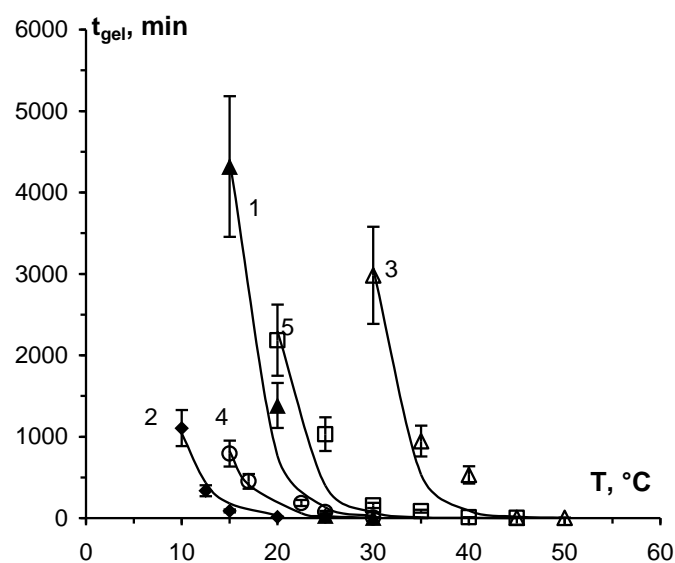


Fig.8 Estimated (solid lines) and experimental (points) gelation times as a function of temperature for solutions of different cellulose and ZnO concentrations. Filled points: solutions without ZnO 4%cellulose-8%NaOH (1) and 6%cellulose-8%NaOH (2); open points: with ZnO 4%cellulose-8%NaOH-1.5%ZnO (3), 6%cellulose-8%NaOH-0.7%ZnO (4) and 6%cellulose-8%NaOH-1.5%ZnO (5)

Table

Table 1 Gelation times of cellulose-8%NaOH-water solutions at different temperatures and concentrations of ZnO

T°C	Gelation times, min				
	4%cellulose-8%NaOH		6%cellulose-8%NaOH		
	0%ZnO	0.7%ZnO	0%ZnO	0.7%ZnO	1.5%ZnO
-5	>5 days	>3 days			
0	>2 days	>2 days			
5	>2 days		> 2days		
10			1106	>2 days	
12.5			336		
15	4320		87.75	791	>2 days
17				452	
20	1384		15		2190
22.5				185	
25	32			74	1032
30	6.7	2980		7.7	156
35		946			47
40		532			8.9
45		4			
50		3			