Kinetics of Cellulose Regeneration from Cellulose−NaOH−Water Gels and Comparison with Cellulose−*N*-Methylmorpholine-*N*-Oxide−Water Solutions

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The regeneration kinetics of cellulose from cellulose−NaOH−water gels immersed in a nonsolvent bath is studied in detail. Cellulose concentration, bath type, and temperature were varied, and diffusion coefficients were determined. The results were compared with data measured and taken from the literature on the regeneration kinetics of cellulose from cellulose−*N*-methylmorpholine-*N*-oxide (NMMO) monohydrate solutions. Different theories developed for the transport behavior of solutes in hydrogels or in porous media were tested on the systems studied. While the diffusion of NaOH from cellulose−NaOH−water gels into water has to be described with "porous media" approaches, the interpretation of NMMO diffusion is complicated because of the change of NMMO's state during regeneration (from solid crystalline to liquid) and the high concentration of NMMO in the sample. The activation energies were calculated from diffusion coefficient dependence on temperature for both systems and compared with the ones obtained from the rheological measurements. The activation energy of cellulose−NaOH−water systems does not depend on cellulose concentration or the way of measurement. This result shows that whatever the system is, pure NaOH−water solution, cellulose−NaOH−water solution, or cellulose−NaOH−water gel, it is NaOH hydrate with or without cellulose in solution, which is moving in the system. The swelling of cellulose in different nonsolvent liquids such as water or different alcohols during regeneration was investigated and interpreted using the Hildebrand parameter.

1. Introduction

Processing of cellulose is more that 100 years old, but it still attracts the attention of research and industry because of the search for less polluting, simpler, and less energy-consuming methods than the existing ones. Therefore, cellulose dissolution in aqueous solutions of NaOH is a topic of intensive research. Since the publication of the cellulose−NaOH−water phase diagram by Sobue et al.,[1] it has been known that it is possible to dissolve cellulose in a narrow range of low temperatures and concentrations of NaOH (from 7% to 10% NaOH in water at −6 °C). From that time there has been ongoing research on the structure and properties of cellulose−NaOH−water solutions (see, for example, refs 2−5). Several papers report that cellulose dissolution in NaOH−water may be improved if substances such as urea or thiourea are added,[6−10] with the NaOH concentration range remaining the same as that shown in ref 1.

Fibers and membranes from cellulose−NaOH−water or cellulose−NaOH−additive solutions can be made by so-called regeneration or coagulation techniques[8,11−18] that are used to make shaped cellulose objects from viscose or cellulose−*N*-methylmorpholine-*N*-oxide (NMMO) solutions.[19] Regeneration of cellulose from either cellulose−NaOH or cellulose−NMMO solutions should occur in a more or less similar way because in both cases cellulose is not initially derivitized but directly dissolved and then regenerated due to phase separation. In the case under consideration, the solvent (NaOH−water or NaOH−additive−water) is replaced by cellulose nonsolvent, the latter usually being water, aqueous acid or salt solutions,[15,16] or some organic liquid combinations such as ethanol and acetone.[16] The main principle is that the regenerating liquid must be miscible with the aqueous NaOH solution and be a nonsolvent for cellulose. As well as for cellulose−NMMO solutions, the type of regenerating liquid is shown to strongly influence the structure, morphology, and properties of cellulose fibers and membranes made from cellulose−NaOH solutions (see, for example, ref 19 for cellulose materials regenerated from cellulose−NMMO and refs 13−17 for cellulose−NaOH membranes). However, there is no publication giving any insight on the kinetic aspects of the regeneration process for objects made from cellulose−NaOH solutions. The kinetics of cellulose regeneration should be controlled by the diffusion of NaOH from the cellulose−NaOH solution into the regeneration bath and of the nonsolvent from the bath into the cellulose solution. Is regeneration kinetics of cellulose from cellulose−NaOH−water solutions comparable to that of cellulose−NMMO solutions? What is the influence of cellulose concentration, nonsolvent power, bath type and temperature on regeneration of cellulose from cellulose−NaOH solutions? These questions are important for understanding and controlling the process of cellulose shaping from NaOH−water solutions.

The goal of this work is to describe the regeneration kinetics of cellulose−NaOH−water gels. The fact that cellulose−NaOH−water solutions gel with time and temperature[5] was used to prepare samples with a well-defined shape and volume that were placed in a regenerating bath. To have a defined shape is required for the adequate calculation of diffusion coefficients using Fick theory and for the analysis of results obtained with

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Table 1. Weight Concentrations of Solucell, NMMO, and Water in Solucell−NMMO Solutions, as Given by Lenzing AG

Solucell (wt %)	NMMO (wt %)	H_2O (wt %)
0.3	80.4	19.3
1.09	80.21	18.7
2.28	80.54	17.18
3.0	82.0	15.0

different diffusion approaches developed for membranes and hydrogels. The influence of cellulose concentration, bath type, and temperature on regeneration kinetics of cellulose−NaOH−water gels was investigated and compared with the regeneration of cellulose−NMMO solutions in the same conditions.

2. Experimental Section

2.1. Materials. *2.1.1. Cellulose.* Two types of native cellulose were used: Avicel PH-101, DP = 180, purchased from FMC (Avicel in the following), and Solucell 400, mean DP 950, kindly provided by Lenzing AG (Solucell in the following). Avicel was used for the regeneration studies of cellulose−7.6% NaOH−water gels, and Solucell was used for cellulose−(NMMO monohydrate) solutions.

2.1.2. Solvents. NaOH and NMMO were of 97% purity, purchased from VWR and Aldrich, respectively. Distilled water was used to prepare the solutions and the regenerating bath. Different alcohols were used for the regenerating bath as nonsolvents of cellulose: ethanol (Bioblock, 99.9% purity), isopropanol, butanol, pentanol, and hexanol (all from Aldrich, 98−99% purity).

The concentrations are given in wt %.

2.1.3. Sample Preparation. Avicel−NaOH−water solutions were prepared as follows: Avicel was mixed with 7.6% NaOH−water solution, at −6 °C, for 2 h, with a stirring rate of 1000 rpm; Avicel concentration was varied from 3% to 7%. Solutions were poured into a mold of 22 mm × 18 mm × *h* mm dimensions, *h* being the sample thickness which varied from 1.2 to 2 mm, and kept at room temperature for 15 h. In these conditions cellulose−7.6% NaOH−water solutions gel irreversibly.[5] As a result, rectangular gel slabs were ready for diffusion experiments. Gel dimensions were chosen as a compromise between ease of sample handling and infinite plane approximation (see section 3.1).

Solucell−NMMO solutions were prepared in Lenzing AG. The proportions of Solucell/NMMO/water components in solutions are listed in Table 1.

Solucell−NMMO solutions are in a crystalline state at room temperature; they were melted at 80 °C, and the hot solution was poured into the same mold as used for the Avicel−NaOH−water solutions. The solutions cooled down to room temperature, and as a result, solid rectangular samples of the same shape as Avicel−NaOH−water gels were obtained.

Avicel−NaOH−water gels or Solucell−NMMO solutions were placed into a regenerating bath, and the diffusion coefficient of NaOH or NMMO was measured using various methods (see section 2.2). When regeneration was completed, the morphology of the swollen cellulose was investigated by environmental scanning electron microscopy (ESEM). The pictures of regenerated cellulose swollen in water are shown in Figure 1. Both samples (regenerated from Avicel−NaOH−water gels or Solucell−NMMO solutions) show a porous structure; the one regenerated from Avicel−NaOH−water gels (Figure 1a) is denser and has smaller pores than that regenerated from the Solucell−NMMO solution (Figure 1b).

2.2. Methods. Regeneration of cellulose was performed in a bath of cellulose nonsolvent, water, or alcohol, with a controlled volume and temperature. The diffusion coefficient of cellulose solvent (either NaOH or NMMO) from a sample toward the regeneration bath was studied as follows. A sample of Avicel−NaOH−water gel or Solucell−NMMO solution of a given weight and volume was placed in the regenerating bath at a fixed temperature. The proportion of the sample/bath weights was kept constant and equal to 10. A magnetic stirrer was used to gently mix liquids in a regenerating bath during NaOH or NMMO release for homogenization. The amount of NaOH or NMMO released into the bath was measured as a function of time using methods described in the following paragraphs (refractometry for NMMO and potentiometry and titration for NaOH). Each experiment was repeated 3−5, times and the mean value of the diffusion coefficient (see details on diffusion coefficient determination in the Results and Discussion section) was calculated.

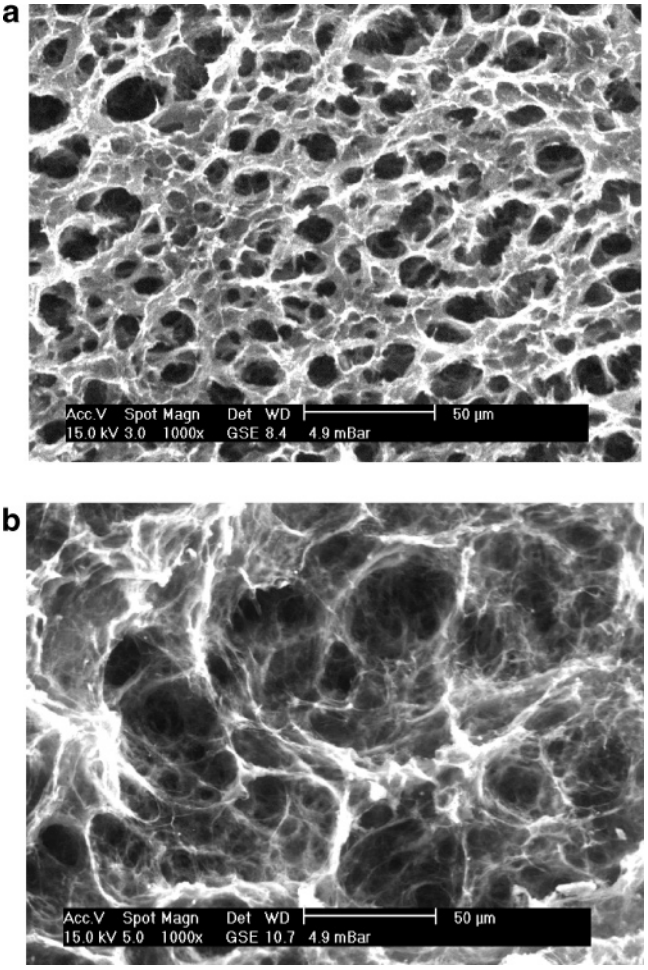

Figure 1. ESEM images of regenerated cellulose from (a) 5% Avicel−NaOH−water gels and (b) 3% Solucell−NMMO solutions, both regenerated in a water bath at 25 °C.

2.2.1. Refractometry. The concentration of NMMO in the regenerating bath was measured using an Abbe refractometer. First, the calibration dependence was obtained by measuring the refractive index of NMMO−water or NMMO−alcohol solutions as a function of known NMMO concentration. During regenerating experiments, small amounts of regenerating bath liquids were taken in time, and their refractive index was measured. NMMO concentration in the bath was determined with the help of the calibration dependence. These data were used to describe the kinetics of NMMO release from the sample.

2.2.2. Titration and Potentiometry. The evolution of NaOH concentration in the regenerating bath as a function of time was measured using titration with acetic acid in the presence of an indicator. The amount of NaOH released from the sample in time was calculated knowing the initial sample and bath weights.

To double-check the values of the NaOH diffusion coefficients obtained with titration, the NaOH concentration during cellulose regeneration in the bath at room temperature was measured using an ion-selective (Na^+) electrode (Mettler Toledo) coupled with a pH meter

from Denver Instruments. The electrode was inserted in the bath. First, a calibration curve of conductivity (mV) versus known NaOH concentration was built. This calibration was then used to follow the kinetics of NaOH release. The diffusion coefficient obtained with this method coincided with those obtained with titration within experimental error.

The experimental errors on concentration measurements were less than 10%.

2.2.3. Rheological Measurements. The viscosity of 7.6% NaOH−water, NMMO monohydrate, and 1% and 3% Solucell−NMMO solutions was measured as a function of the shear rate at different temperatures with a cone-plate geometry using a Bohlin Gemini rheometer equipped with a Peltier temperature control system. The temperature intervals were as follows: from 10 to 25 °C for the 7.6% NaOH−water solution and from 70 to 90 °C for NMMO monohydrate and Solucell−NMMO solutions, with a temperature increment of 5 °C. All solutions studied showed a Newtonian behavior in the 1−100 s^{-1} shear rate range. A viscosity value (Pa s) corresponding to each temperature was taken for plotting viscosity versus temperature dependence for the further calculation of the activation energy.

2.2.4. Scanning Electron Microscopy. The morphology of wet cellulose−NaOH−water gels was characterized by a Philips XL environmental scanning electron microscope. ESEM works under controlled environmental conditions and requires no conductive coating of the specimen. The Peltier cooling stage PW6750 was used to control the temperature. Images were acquired at a temperature of 2 °C, and the chamber pressure was maintained at 5 mbar.

3. Results and Discussion

3.1. Analysis of Experimental Data: Choice of the Approach. The experimental data, i.e., the increase of NaOH or NMMO amount in the regenerating bath as a function of time and in different conditions (various cellulose concentrations, regenerating bath liquids, or bath temperatures), was analyzed using the Fick approach. It is widely applied in drug release field and to study the formation of membranes due to phase separation and was already used to describe the kinetics of cellulose regeneration from cellulose−NMMO−water solutions.[18] The applicability of the Fick approach was checked by plotting the cumulative amount of substance $M(t)$ (here, NaOH or NMMO) released in time t as a function of $\sqrt{t}$. The experimental data were approximated with a straight line, within 10% experimental error, up to ~80% of $M(t)$, which indicates a diffusion-controlled process. All samples, except cellulose−NaOH−water gels placed in alcohol baths, practically did not change their volume during regeneration (within 10% error) allowing the application of the Fick approach.

The amount of a substance released in time from a semi-infinite plane can be described as follows[20]

$$\frac{M(t)}{M} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D\pi^2 t(2n+1)^2}{l^2}\right) \quad (1)$$

where M is the amount of substance released at $t = \infty$ (in our case M coincides with the amount of substance in the initial sample), D is the diffusion coefficient, and l is half of the sample thickness because diffusion takes place from both its sides.

If the diffusion coefficient is constant, then several simplifications are used to determine D from the slope of $M(t)/M = f(\sqrt{t/l^2})$ curves:

(a) Early-time approximation ($0 \le (M(t))/(M) \le 0.4$):

$$\frac{M(t)}{M} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2} \quad (2)$$

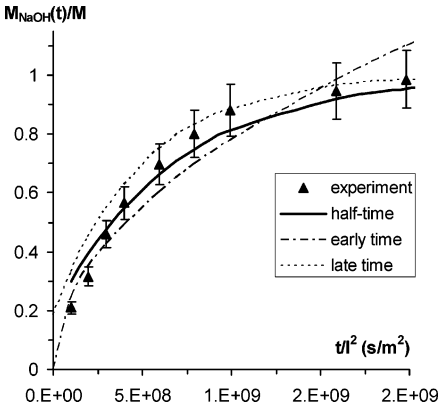

Figure 2. Illustration of the choice of approximation. Experimental data: regeneration of 6% Avicel−NaOH−water gel in a water bath at 25 °C.

(b) Late-time approximation ($0.4 \le (M(t))/(M) \le 1$):

$$\frac{M(t)}{M} = 1 - \frac{8}{\pi^2} \exp\left(\frac{-\pi^2 Dt}{l^2}\right) \quad (3)$$

(c) Half-time ($(M(t))/(M) = {}^1/_2$) approximation: Here the diffusion coefficient is calculated at the point where $(M(t))/(M) = {}^1/_2$; it is equal to $D = (0.049)/((t/l^2)_{1/2})$ where $(t/l^2)_{1/2}$ is the abscissa when $(M(t))/(M) = {}^1/_2$. The experimental data can then be fitted with eq 1 with $n = 0$.

To select the approximation for the calculation of the diffusion coefficient, the experimental data $(M_{NaOH}(t))/(M) = f(\sqrt{(t)/(l^2)})$ were fitted with early-, half-, and late-time approaches (Figure 2). The best fit gives the half-time approximation; it will be used to determine all of the diffusion coefficients in the following.

The regeneration of cellulose from Avicel−NaOH−water gels into a water bath was performed in different conditions: at different bath temperatures (25, 50, and 80 °C, $C_{cell} = 5\%$) and with different cellulose concentrations C_{cell} (3%, 5%, 6%, and 7%, all in a water bath at 25 °C). $(M_{NaOH}(t))/(M) = f(\sqrt{(t)/(l^2)})$ was plotted for each case, and D_{NaOH} was calculated using the half-time approximation.

The same procedure was performed for solid Solucell−NMMO samples in the part that concerns the influence of bath temperature (25, 50, and 80 °C); the Solucell concentration in this case was 3%. (Using NMR[21] it was shown that the NMMO diffusion coefficient varies as a function of the position inside the cellulose sample. However, this was not detectable with our technique; thus the diffusion coefficient measured is a mean value.)

As for the influence of cellulose concentration on NMMO diffusion, the values of D_{NMMO} were partly taken from ref 18 for $C_{cell} = 3-12\%$ and partly measured using refractometry for low cellulose concentrations, $C_{cell} = 0.5-3.0\%$. It was possible to combine all data because the cellulose molecular weight does not affect the diffusion of NMMO during cellulose regeneration[18] and our samples and the ones in ref 18 were prepared in the same way by Lenzing AG. Indeed, we measured D_{NMMO} at $C_{cell} = 3\%$, and it coincided with the value from ref 18 for this cellulose concentration within the experimental error.

Because the concentration of the released substance (NaOH or NMMO) in the bath was always low, lower than 0.8% for NaOH and 8% for NMMO, the dependence of the diffusion coefficient on NaOH or NMMO concentration in the bath was neglected. For cellulose−NMMO solutions it was shown[18] that

the D_{NMMO} decrease starts to be noticeable when the NMMO content in the bath is higher than 10%, which was never our case.

The influence of the bath type on the kinetics of cellulose regeneration was also studied. Because Avicel−7.6% NaOH−water gels were strongly contracting in alcohol baths, it was not possible to use the Fick approach, and D_{NaOH} values were not calculated. The correlation between sample contraction and the solubility parameter will be discussed. On the contrary, Solucell−NMMO samples were practically not contracting; thus D_{NMMO} values were obtained using refractometry. These results will be correlated with the viscosity of each alcohol used.

3.2. Influence of Cellulose Concentration on the Diffusion of NaOH from Avicel−NaOH−Water Gels and NMMO from Solucell−NMMO Solutions. The values of the diffusion coefficients of NaOH and NMMO during regeneration of cellulose in a water bath at 25 °C are presented in Table 2. D_{NaOH} and D_{NMMO} at zero cellulose concentration, $D_{NaOH}(C_{cell} = 0)$ and $D_{NMMO}(C_{cell} = 0)$, respectively, are added for comparison and will be used in the following when considering different theoretical models. The value of $D_{NaOH}(C_{cell} = 0) = 1.5 \times 10^{-9}$ m/s^2 was taken from ref 22. The value of D_{NMMO} ($C_{cell} = 0$) was calculated using the Stokes−Einstein formula that relates the diffusion coefficient and hydrodynamic size R of the solute (here, NMMO)

$$D(C_{cell} = 0) = \frac{k_B T}{6\pi\eta R} \tag{4}$$

where k_B is the Boltzmann constant, T is temperature, and η is the viscosity of the bath liquid (here, water, or alcohol in section 3.4) at temperature T. The size $R_{NMMO} = 3.1 \times 10^{-10}$ m was kindly calculated by T. Rosenau, Universität für Bodenkultur Wien, Austria, using density functional theory. It should be noted that the Stokes−Einstein approach is developed to describe the motion of a solid sphere in a dilute suspension. To fulfill this condition (i.e., to use eq 4 for the calculation of the diffusion coefficient at $C_{cell} = 0$), the concentration of the solute, NaOH or NMMO, should be low. While this is more or less the case for NaOH (7.6% in water), it is not at all the case for NMMO (80% in water), but there is no theory allowing the calculation of the diffusion coefficient at high solute concentrations. Thus the value of $D_{NMMO}(C_{cell} = 0)$ calculated in the approximation of a dilute suspension (i.e., one NMMO molecule moving in a pure water) will be, by definition, higher than what could be obtained in reality for the diffusion of NMMO during the dissolution of a solid NMMO monohydrate. Unfortunately, it was not possible to directly measure this specific D_{NMMO} value because of extremely high sample hygroscopicity. As it will be shown in the following paragraphs, the value of D_{NMMO} at $C_{cell} = 0$ calculated with eq 4 is indeed higher than what can be deduced from the experiment.

The values of the NaOH and NMMO diffusion coefficients at 5−7% cellulose concentration are very close (Table 2 and Figure 3), which means that regeneration of cellulose from the samples (cellulose−NaOH−water gel or solid cellulose−NMMO solution) of the same geometry in the same conditions will take about the same time. However, the trend for the decrease of the diffusion coefficient with the increase of the cellulose concentration is not the same for NaOH and NMMO (Figure 3). The analysis of diffusion data with theoretical models and of the difference between D_{NaOH} and D_{NMMO} evolution as a function of cellulose concentration is discussed below.

The initial state of the Avicel−NaOH−water samples is a gel, and the final state is regenerated (or precipitated) swollen cellulose. During regeneration, the state of cellulose changes: A phase separation takes place. Different types of models explaining the transport behavior of solutes in hydrogels or in porous media can be thus tested. These models mainly include free volume theory, hydrodynamic, and obstruction approaches and their combinations as well. A review of these models and their applicability toward experimental data obtained for different types of hydrogels (homogeneous or not, charged or not) and solutes (polymers, micelles, and low molecular weight compounds) is given in ref 23. The free volume model was strongly criticized when being applied to hydrogels with a high water content[23] despite it being widely used in the field of controlled drug release. Initially, the free volume model was developed for homogeneous membranes in which the pores are fixed neither in size nor in location.[24] The hydrodynamic models seem to provide a reasonable description of solute diffusion in homogeneous hydrogels, while the models containing obstruction effects are more consistent with the diffusion behavior in heterogeneous gels.

Nothing is known about the structure of cellulose−NaOH−water gels. What we know is that gelation of cellulose−NaOH−water solution occurs in time and with an increase in temperature due to the decrease of solvent quality and the increase of cellulose−cellulose macromolecular interactions.[5] On one hand, cellulose−NaOH−water gels should be considered as heterogeneous, as most of polysaccharide hydrogels. The main difference between approaches used for heterogeneous and homogeneous gels is that the first one takes into account the size of the polymer chain and the other does not. On the other hand, during the regeneration process cellulose coagulates due to phase separation, leading to a cellulose-swollen-in-water "membrane" (Figure 1a). The latter can be seen as a porous medium, and thus the free volume or hydrodynamic approach could be applied to describe NaOH diffusion.

Before the application of different approaches to our experimental data, several system parameters had to be determined. First of all, the cellulose volume fraction f_{cell} must be calculated. It is related with the cellulose weight concentration C_{cell} as follows

$$f_{cell} = \frac{C_{cell}/d_{cell}}{C_{solution}/d_{solution} + C_{cell}/d_{cell}} \tag{5}$$

where $d_{cell} = 1.52 \times 10^{-3}$ kg/m^{-3} (from FMC data sheet) and $d_{solution} = 1.0813 \times 10^{-3}$ kg/m^3 [25] are the densities of Avicell and 7.6% NaOH−water solution, respectively. The approaches used to describe diffusion in heterogeneous gels require solute and polymer chain radii: $R_{NaOH} = 1.4 \times 10^{-10}$ m was calculated from eq 4 knowing $D_{NaOH}(C_{cell} = 0)$ from ref 22, and the cellulose mean chain radius $R_{cell} = 5.1 \times 10^{-10}$ m was calculated from the crystalline structure of cellulose.[26]

The diffusion models that were used to approximate the dependence of the NaOH diffusion coefficient as a function of cellulose concentration are listed in Table 3 and shown in Figure 4, together with experimental data. The results are presented in semilogarithmic coordinates: reduced NaOH diffusion coefficient as a function of cellulose volume fraction f_{cell} in the gel.

Figure 4 shows that approaches developed for heterogeneous and homogeneous gels split into two parts, respectively. Five approaches that take into account the influence of polymer chain radius on solute diffusion are far from experimental data. (The sequence of these five curves from top to bottom is the same as the sequence of approaches/equations listed in Table 3.) On the contrary, free volume and hydrodynamic models seem to

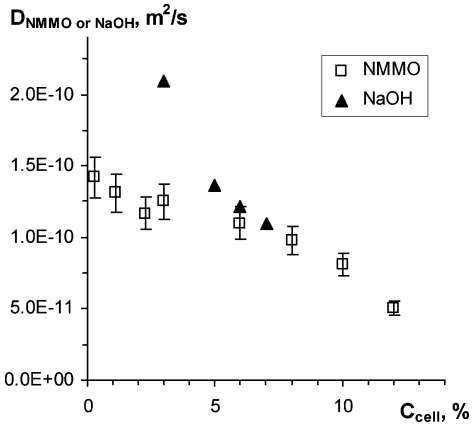

Figure 3. NaOH and NMMO diffusion coefficients measured during regeneration of Avicel−7.6% NaOH−water gels and Solucell−NMMO solutions, as a function of cellulose weight concentration. Regeneration bath: water at 25 °C.

better describe the diffusion of NaOH in cellulose−NaOH−water gel during cellulose regeneration in water. Another way to treat experimental data with a free volume approach is shown in Figure 5. The theory predicts a linear dependence of the logarithm of the reduced diffusion coefficient as a function of water volume fraction f_{water} in the sample as follows: $\ln(D_{NaOH}/D(C_{cell}=0)) \sim (1/f_{water} - 1)$.[24] Figure 5 shows that experimental data are well approximated by a straight line. This means that "membrane" and not "hydrogel" approaches should be used to describe the diffusion of NaOH during the regeneration of cellulose−NaOH−water gels.

The influence of cellulose concentration on the diffusion coefficient of NMMO during regeneration of Solucell−NMMO solutions in water was revised in the same way as described for the diffusion of NaOH. The dependences calculated for NMMO according to the approaches developed for heterogeneous gels fall far from experimental data and thus will not be shown. The reduced diffusion coefficients of NMMO are presented in Figure 6 together with those of NaOH; the curves corresponding to hydrodynamic and free volume approaches are shown for each solvent. For the calculation of the cellulose volume fraction in the sample according to eq 5, the density of NMMO monohydrate solution was taken as $d_{solution} = 1.2 \times 10^{-3}$ kg/m^3.[33]

It is clear that the trend of decreasing D_{NaOH} and D_{NMMO} with the increase of the cellulose volume fraction is different (Figure 6). D_{NaOH} smoothly decreases from $D_{NaOH}(C_{cell} = 0)$ with the increase of f_{cell}. On the contrary, D_{NMMO} shows saturation at low cellulose concentrations. The saturation of D_{NMMO} at low cellulose concentrations was predicted in ref 18, and our experimental data confirm it. The reason for this saturation was proposed in ref 18. At low cellulose concentrations, the sample contains numerous of crystallized NMMO monohydrates that are not bound to cellulose. During regeneration, water enters the solid cellulose−NMMO sample and dilutes free NMMO monohydrates to the state when NMMO becomes fluid, and then NMMO can diffuse from the sample into the water bath. At low cellulose concentrations NMMO behaves almost as if there are no cellulose chains around. The increase of cellulose concentration decreases the amount of free NMMO molecules, and NMMO "detachment" from cellulose chains becomes noticeable. This is reflected by the decrease of D_{NMMO} at $C_{cell} > 5-6\%$ (or $f_{cell} > 0.04$).

As suggested in ref 18, the extrapolation of the plateau to $f_{cell} = 0$ should give the value of D_{NMMO} in a dissolving-in-water NMMO monohydrate: It is around 1.4×10^{-10} m/s^2. This value is 5 times smaller as compared with the calculated one according to eq 4 at $C_{cell} = 0$ (Table 2). This difference in $D_{NMMO}(C_{cell} = 0)$ obtained experimentally and calculated with the Einstein approach was expected and is explained by the high NMMO concentration in the sample (see discussion of the applicability of eq 4 to the case of a pure NMMO solution). Some other reasons complicating the interpretation of NMMO diffusion can also be given. First, NMMO forms different types of hydrates, depending on its concentration in water, and thus NMMO is dragging water molecules during diffusion. This is not taken into account in the calculation of NMMO size and thus in the calculation of the diffusion coefficient at $C_{cell} = 0$. Second, the initial states of NMMO, calculated or real, are different: Equation 4 takes into account only the size of the solute free moving in water, while real NMMO has to change the phase state during regeneration, from solid to liquid, which slows down the calculated diffusion coefficient values.

3.3. Influence of Regenerating Bath (Water) Temperature. The influence of bath temperature on regeneration kinetics of 5% Avicel−NaOH−water gels and 3% Solucell−NMMO solutions was studied. An example of NaOH release from 5% Avicel−NaOH−water gels into the water bath at 25, 50, and 80 °C is shown in Figure 7.

As expected, the higher the bath temperature, the quicker the NaOH release from cellulose gels, and thus the quicker cellulose regeneration. The same occurs for the regeneration of 3% Solucell−NMMO solutions in water baths of different temperatures. The diffusion coefficients D_{NaOH} and D_{NMMO} were calculated for 25, 50, and 80 °C, and Arrhenius law was applied to obtain the activation energy for each system. Figure 8 shows that the values of D_{NaOH} and D_{NMMO} at the same temperature T practically coincide, and so do the values of the activation energy: $E_{NaOH} = 21 \pm 2$ kJ/M and $E_{NMMO} = 19 \pm 2$ kJ/mol.

The value of E_{NaOH} obtained for 5% Avicel−7.6% NaOH−water gels was compared with two other NaOH activation energy values that were obtained with rheological measurements of pure 7.6% NaOH−water solutions and of Avicel−NaOH−water solutions. For 7.6% NaOH−water solutions, measurements of solution viscosity at different temperatures were performed, and Arrhenius law was applied, which gave 19 kJ/mol. As for cellulose−NaOH−water solutions (at cellulose concentrations and solution temperatures far from gelation), the activation energy is known for Avicel dissolved in 9% NaOH−water.[5] It is equal to 21 kJ/M and does not depend on cellulose concentration, which means that cellulose−NaOH−water solutions are not real solutions but rather suspensions.[5] The value of E_{NaOH} obtained with the measurements of NaOH diffusion

Table 2. Diffusion Coefficients of NaOH and NMMO during Regeneration of Avicel-NaOH−Water Gels and Solucell−NMMO Solutions in a Water Bath of 25 °C

cellulose concentration (wt %)	0	3	5	6	7				
D_{NaOH} ($\times 10^{-10}$ m^2/s)	15.1[a]	2.09	1.42	1.21	1.10				
cellulose concentration (wt %)	0	0.3	1.1	2.3	3	6[c]	8[c]	10[c]	12[c]
D_{NMMO} ($\times 10^{-10}$ m^2/s)	7.04[b]	1.42	1.31	1.20	1.25	1.10	0.98	0.81	0.50

[a] Reference 22. [b] Calculated from the size of NMMO, using the Stokes−Einstein formula in eq 4. [c] Reference 18.

Table 3. Summary of Diffusion Models Tested[a]

gel type	model	expression	reference
heterogeneous	obstruction	$\frac{D}{D_0}=\left[1+\frac{2}{3}\left(\frac{R_{cell}+R}{R_{cell}}\right)^2 f_{cell}\right]^{-1}$	27
heterogeneous	hydrodynamic	$\frac{D}{D_0}=\left[1+k^{0.5}+\frac{1}{3}k\right]^{-1}; k=\frac{f_{cell}^{1.17}}{0.31}\left(\frac{R}{R_{cell}}\right)^2$	28
heterogeneous	combined obstruction and hydrodynamic	$\frac{D}{D_0}=\left[1+\frac{2}{3}\left(\frac{R+R_{cell}}{R_{cell}}\right)^2 f_{cell}\right]^{-1}\exp(-\pi f_{cell}^{0.174\ln(59.6R_{cell}/R)})$	29
heterogeneous	obstruction	$\frac{D}{D_0}=\exp\left[-\frac{(R_{cell}+R)}{R_{cell}}\sqrt{f_{cell}}\right]$	30
heterogeneous	obstruction	$\frac{D}{D_0}=\exp\left(-\pi\left[\frac{R_{cell}+R}{af_{cell}^{-0.5}+2R_{cell}}\right]^2\right)$ *a* is a scaling constant depending on the flexibility of the polymer chain	23
homogeneous (curve 1 in Figure 4)	hydrodynamic	$\frac{D}{D_0}=\exp(-bRf_{cell}^{0.75})$ *b* is a constant	32
homogeneous (curve 2 in Figure 4)	free volume for hydrogels	$\frac{D}{D_0}=\exp\left[-cR^2\frac{f_{cell}}{(1-f_{cell})}\right]$ *c* is a constant	23 and 33

[a] Here D and D_0 are solute diffusion coefficients in the sample and in water, respectively. R is the solute radius.

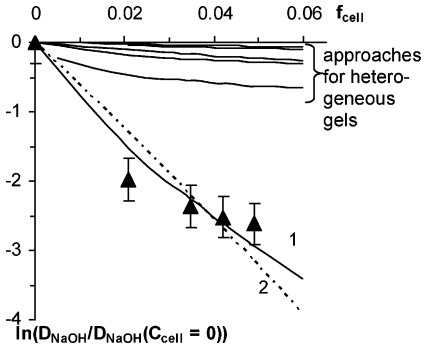

Figure 4. Reduced NaOH diffusion coefficient as a function of the cellulose volume fraction in the gel during regeneration at 25 °C. Curve 1 corresponds the to hydrodynamic approach, and curve 2 corresponds to the free volume approach. For details, see Table 2.

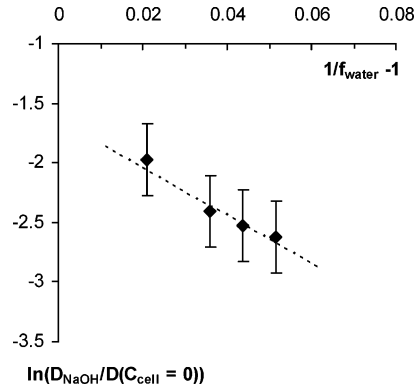

Figure 5. Reduced NaOH diffusion coefficient as a function of water volume fraction in Avicel−7.6% NaOH−water gel during regeneration at 25 °C; dashed line corresponds to the free volume theory approximation. The line is the best fit with $R^2 = 0.94$.

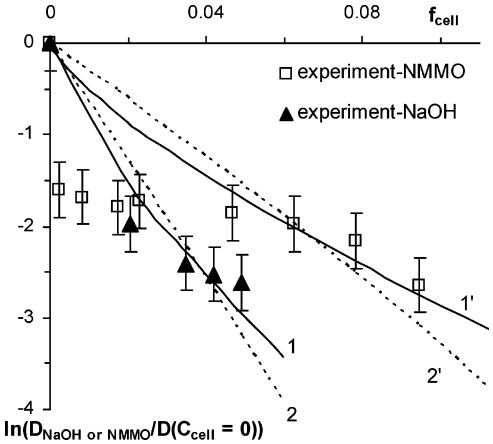

Figure 6. Comparison of NaOH and NMMO reduced diffusion coefficients during cellulose regeneration in water at 25 °C. Curves 1 and 2 correspond to hydrodynamic and free volume models for NaOH (1 and 2) and NMMO (1′ and 2′), respectively (see equations in Table 3).

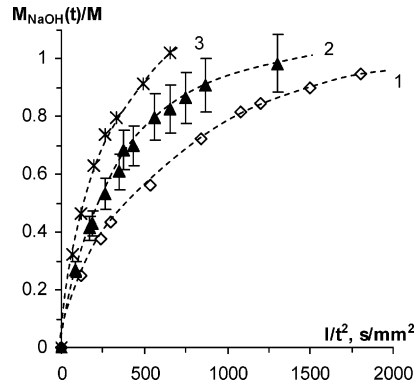

Figure 7. Diffusion of NaOH from 5% Avicel−7.6% NaOH−water gels into the water regenerating bath at (1) 25, (2) 50, and (3) 80 °C. The lines are shown to guide the eye.

during Avicel regeneration in water is the same as that compared with the previously found values of the activation energy with rheological measurements.[5] This means that whatever the system is, pure NaOH solution, cellulose−NaOH−water solution, or cellulose−NaOH−water gel, it is NaOH hydrate with or without cellulose, which is moving in the system. The presence of cellulose, in either the solution or the gel state, does not change the motion mechanics.

The same comparison of the activation energy obtained from diffusion and rheological experiments was performed for the

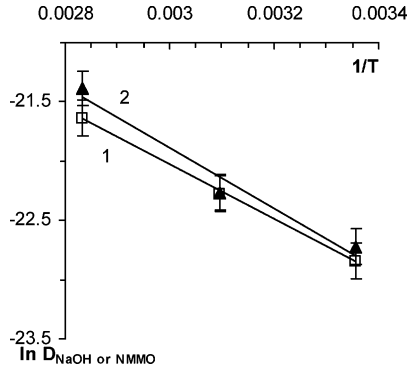

Figure 8. Arrhenius plot for (1) NMMO and (2) NaOH diffusion coefficients for 3% Solucell−NMMO solutions and 5% Avicel−7.6% NaOH−water gels, respectively. Lines are least-squares linear approximations.

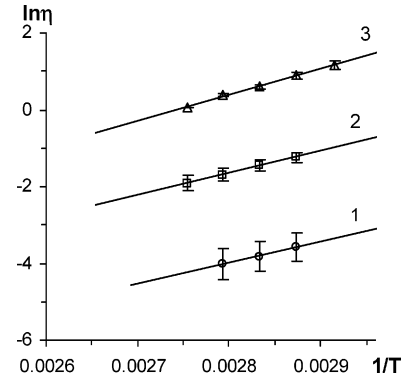

Figure 9. Viscosity vs inverse temperature for (1) NMMO monohydrate and Solucell−NMMO solutions of (2) 1% and (3) 3% cellulose concentrations. Lines are least-squares approximations.

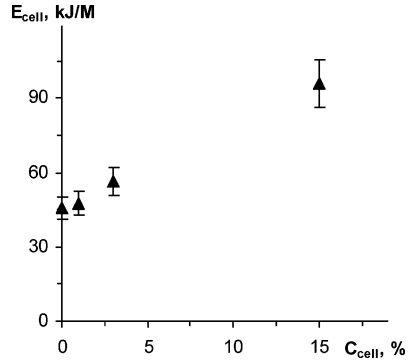

Figure 10. Activation energy of Solucell−NMMO solutions as a function of cellulose concentration.

Solucell−NMMO system. The viscosities of NMMO monohydrate and 1% and 3% Solucell−NMMO solutions in the temperature interval of 70−90 °C were measured; the Arrhenius plot is shown in Figure 9. The activation energy varies from 46 and 57 kJ/mol, correspondingly. For more concentrated solutions, for example, 15% cellulose−NMMO,[34] the activation energy is 90−100 kJ/mol. The increase of the activation energy with the increase of cellulose concentration is a normal trend for polymer solutions (Figure 10).

There is a large difference in the activation energy values obtained from the rheological and diffusion coefficient (19 kJ/mol) measurements. This discrepancy should be expected, and in fact, the "rheological" and "diffusion" activation energies correspond to very different moving entities. In the rheological measurements we are dealing with real solutions of cellulose in NMMO, and the activation energy corresponds to the motion

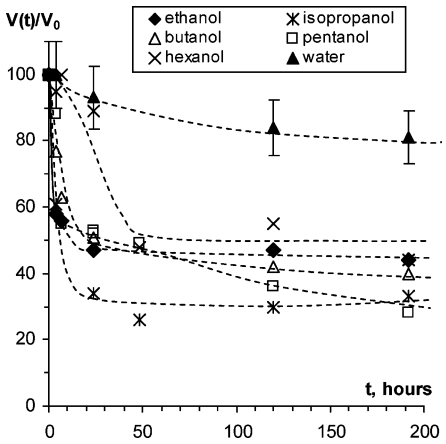

Figure 11. Reduction of 5% Avicel−7.6% NaOH−water sample volume in regenerating bath of different liquids. Lines are given to guide the eye.

of cellulose chains. During cellulose regeneration, the initial state of the sample is a crystallized cellulose−NMMO solution, and in the course of regeneration a two-phase system appears: a swollen-in-water cellulose and a dissolving-in-water NMMO. The mechanics of the moving entities in the rheological and regeneration experiments are very different, and the only prediction that could be made is that the rheological activation energy should be higher than the diffusion one. This is what was obtained in the experiments. What is much more surprising is that NaOH activation energy obtained from the rheological and diffusion coefficient measurements coincide and do not depend on cellulose concentration. This means, as said above and suggested in ref 5, that the NaOH solution is a suspension of NaOH hydrates in water and cellulose−NaOH−water is not a real solution.

3.4. Influence of Regenerating Bath Type. In the previous sections the regenerating (or nonsolvent) bath was water. The type of nonsolvent used for cellulose regeneration strongly influences the structure and morphology of regenerated cellulose fibers or membranes and, as a consequence, their properties (see, for example, refs 19, 35, and 36). Here we investigate the influence of the bath type on the behavior of Avicel−NaOH−water gels and on the NMMO diffusion coefficient.

Figure 11 shows the kinetics of 5% Avicel−7.6% NaOH−water gel contraction in regenerating baths of different alcohols and in water. The smallest volume reduction occurs in water, $V(t)/V_0 > 85\%$, where V_0 and $V(t)$ are the initial sample volume and in the course of regeneration, respectively. In alcohol baths, Avicel−7.6% NaOH−water gels are contracting more than twice. In most of the cases, the fastest contraction occurs during the first 10−20 h after sample immersion into the regenerating bath; during the following 30−40 h the sample slowly approaches its equilibrium size.

Due to the fact that samples were strongly contracting, the application of the Fick approach was impossible. Thus general thermodynamic reasoning will be used for the analysis of the contraction of Avicel−NaOH−water gels in alcohol regenerating baths.

When an Avicel−7.6% NaOH−water gel is placed in a regenerating bath, cellulose coagulates due to the phase separation, leading to a swollen-in-nonsolvent cellulose sample. The degree of swelling of cellulose depends on the miscibility of cellulose with a given liquid. The notion of a solubility parameter can thus be used to explain cellulose sample contraction. The solubility or Hildebrand parameter δ describes the attractive strength between the molecules of the material.

Table 4. Solubility Parameters, Molar Mass, and Viscosity of Materials Used, at 25 °C

material	solubility parameter[37] $\delta \pm 1$ (MPa$^{0.5}$)	molar mass	viscosity $\pm 10^{-3}$ (Pa s)
cellulose	39.0		
water	47.5	18	1.0
ethanol	26.0	46	1.2
isopropanol	23.9	60	2.27
butanol	23.8	74	3.0
penthanol	21.7	88	3.68
hexanol	21.9	102	4.0

For a polymer−solvent system, the simplest way to predict polymer miscibility is to compare its solubility parameter with that of the solvent. A rule of thumb says that the closer the solubility parameters, the better the polymer miscibility in a given liquid. Being a very rough approximation, this approach gives a certain overview of the dissolution and/or swelling of a polymer in a solvent. In our case, the solubility parameters of water and alcohols will be compared with that of cellulose.

The solubility parameters of cellulose, water, and alcohols are summarized in Table 4.[37] Figure 12 shows the value of the sample reduced volume at equilibrium $(V/V_0)_{eq}$, taken from Figure 11, as a function of the solubility parameters difference $\Delta\delta = \delta_{cell} - \delta_{bath}$, where δ_{cell} and δ_{bath} are cellulose and regenerating liquid solubility parameters, respectively. The smallest $\Delta\delta$ corresponds to the cellulose/water system; indeed the sample volume decreased less than 15%. The larger the solubility parameter difference, the higher the volume reduction. If plotting the reduced volume at equilibrium as a function of a molar mass of regenerating liquid (see the inset of Figure 11), then the trend is not that clear (except that in water the contraction is the lowest). It is the cellulose−liquid miscibility and thus the solubility parameter that governs cellulose swelling in a regenerating bath.

The behavior of Solucell−NMMO solutions in regenerating baths of different alcohols was also examined. The volume reduction of the samples was rather low, not more than 10−15%. With refractometry, it was possible to measure the release of NMMO into the regenerating bath, as described in section 2.2, and to calculate the diffusion coefficients with the Fick approximation. The results were compared with NMMO diffusion coefficients in pure liquids that were calculated by using the Stokes−Einstein in eq 4 and knowing the liquid viscosities, summarized in Table 4. The results are presented in Figure 13.

As expected, the diffusion coefficient decreases with the increase of the regenerating bath viscosity (Figure 13). This was

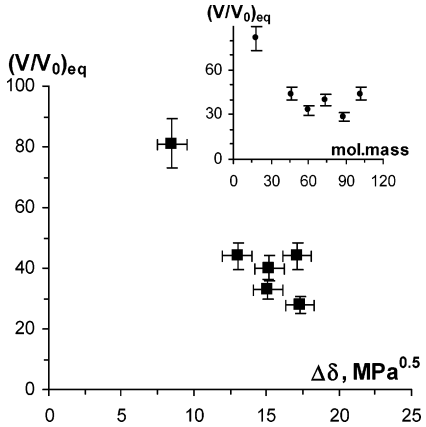

Figure 12. Contraction of a 5% Avicel−7.6% NaOH−water gel at equilibrium as a function of the solubility parameter difference. Inset: The same as a function of regenerating liquid molecular mass.

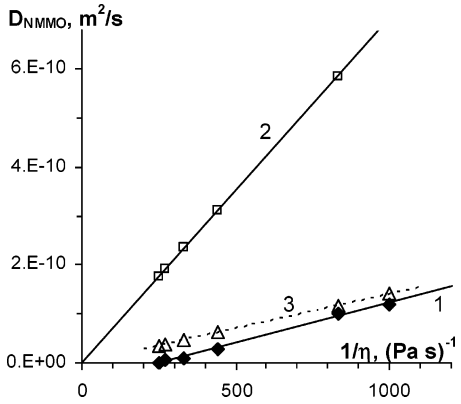

Figure 13. NMMO diffusion coefficients, measured (dark points), from 3% Solucell−NMMO solution into different regenerating liquids and in the same pure liquids, calculated (2 and 3), as a function of inverse viscosity, at 25 °C. Lines are least-squares linear approximations. See details in the text.

also predicted in ref 19 for the regeneration of cellulose−NMMO solutions in different alcohol baths. The values of NMMO diffusion coefficients measured during regeneration are much lower than those calculated using eq 4 (line 2 in Figure 13). This cannot be explained by the influence of the cellulose concentration (measured for 5% Solucell−NMMO and calculated for $C_{cell} = 0$, i.e., diffusion of NMMO in pure liquids) because in section 3.2 it was shown that the diffusion coefficient practically does not vary for cellulose concentrations from 0% to 5% (Figures 3 and 6). The reason for the difference between the measured and calculated diffusion coefficients is the same as that discussed in the first paragraph of section 3.2: In reality, NMMO concentration in the sample is high, but the Einstein approach is valid for low solute concentrations; thus the diffusion coefficient measured must be lower than the calculated one. D_{NMMO} obtained during regeneration of cellulose in water (Figure 6) was 5 times smaller than that calculated as the diffusion of one NMMO molecule in pure water, eq 4. It was interesting to check if the same ratio is valid for measured (during cellulose regeneration) and predicted (calculated with eq 4) NMMO diffusion coefficients in alcohols. To do this, the values of D_{NMMO} predicted were divided by 5; the result is shown by triangles and the corresponding line 3 in Figure 13. These "new" diffusion coefficients are now much closer to the experimental results. This confirms the conclusion made in section 3.2: Equation 4 is not applicable to predict D_{NMMO} at low cellulose concentrations during regeneration because the NMMO concentration in the sample is high.

4. Conclusions

The diffusion of NaOH during regeneration of cellulose−NaOH−water gels in water and alcohols was studied and compared with the diffusion of NMMO from cellulose−NMMO solutions into the same regenerating liquids. At 5%−7% cellulose, NaOH and NMMO diffusion coefficients are practically the same.

The analysis of the influence of cellulose concentration on NaOH diffusion coefficients shows that the "porous membrane" (i.e., free volume or hydrodynamic approach) and not the "hydrogel-obstruction" approach must be used for understanding and interpreting of cellulose regeneration from cellulose−NaOH−water gels. The applicability of a free volume or hydrodynamic approach is caused by the phase separation process occurring during regeneration of cellulose from cel-

lulose−NaOH gels placed in a nonsolvent liquid. The interpretation of NMMO diffusion and thus of cellulose regeneration should also be with the "porous membrane" approach, but it is complicated by the high concentration of NMMO in the sample, the presence of NMMO not linked to cellulose at low cellulose concentrations, and the change of the NMMO phase state during regeneration. An increase of the size of the diffusing entity due to NMMO dragging water molecules during diffusion should also be considered.

NaOH activation energy obtained from diffusion experiments coincides with the activation energy calculated from the rheological experiments for cellulose−NaOH−water and pure NaOH−water solutions. This result confirms the suggestion made in ref 5 that cellulose−NaOH−water solutions are in fact suspensions of NaOH hydrates with or without cellulose.

Finally, the swelling of cellulose in different nonsolvents can be explained by the solubility parameter.

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