ESRF	**Experiment title:** **X-ray scattering of cellulose in alkali-urea aqueous solution and its coagulation process**	**Experiment number**: **02-01-843**
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Report:

1. Aim of the experiments

Cellulose is not soluble in common solvents and only a few types of complex solvent system are used in the industry today such as $Cu(OH)_2/NH_3$, N-methylmorpholine oxide (NMMO) or viscose process. However, these are all toxic or hazardous, and thus new cellulose solvents have been pursued for years. Recently, aqueous alkali/urea solution was discovered to dissolve cellulose efficiently. Several research groups are pursuing new industrial process based on this solvent. However, fundamental aspects of this solvent system such as molecular behavior during dissolution/regeneration are still not well understood.

Our recent study (Isobe et al., *J. Colloid. Interf. Sci.* **359**, 2011) showed that the structure and surface property of cellulose hydrogels from alkali/urea solution are strongly dependent on the types of coagulating bath: non-aqueous coagulating bath gave rod-like structure with hydrophobic surface, and aqueous bath gave membrane-like structure with hydrophilic surface.

To observe the structural formation of this gel, we performed wide angle X-ray diffraction (WAXD) at SPring 8 (Isobe et al., *Carbohyd. Polym.* **89**, 2012). The experimental setup was as follows. First, cellulose solution was filled in glass capillary and on the top of it 5wt% sodium sulfate aqueous solution was added as non-solvent. Then, synchrotron X-ray was irradiated at several points by moving the capillary vertically. In this setup, as non-solvent penetrated the solution by diffusion, dissolved cellulose molecules underwent transformation to gel. With this capillary arrangement, we successfully monitored the time-dependent phenomenon: First, (110) plane of Na-cellulose IV (hydrated form of cellulose II), and then (020) plane appeared. This means that the primary structure of cellulose gel is hydrophobically-stacked molecular sheet, and then these sheets line up with hydrogen bonding. However, the experiment was performed only by using one non-solvent.

Our objective of this experiment was to obtain systematically the time-dependent X-ray scattering data of coagulating cellulose in the Q-range of 0.01-2.0 (A^{-1}) with various types of

coagulants. In addition, as a control solvent, 8wt% LiCl/DMAc solution was also employed. This organic solvent is also known to give transparent and completely amorphous cellulose hydrogel in its regeneration.

2. Experiments

Cellulose sample with degree of polymerization of 200 (acid hydrolyzed wood pulp) was dissolved in two solvent systems: 1) aq. 4.6wt% LiOH/15wt% urea and 2) 8wt% LiCl/DMAc solution. Cellulose concentrations were 10wt% and 8wt%, respectively. Capillary setting was the same as our previous experiment described above. As coagulants, Water, 5wt% Sulfuric acid, Methanol, and Ethanol were employed. The capillary was mounted sample exchanger and diffraction data was recorded on CCD camera with 2 different camera lengths (163 cm and 14.5 cm). For each capillary, scattering was measured at 10~15 vertical positions corresponding with typically 10 seconds exposure.

3. Results and discussion

3.1 WAXD

3.1.1 LiCl/DMAc solvent

In the diffraction profiles with the use of EtOH as a coagulant, no peak from cellulose crystalline region was observed. This corresponds well to the fact that cellulose gel from LiCl/DMAc solvent has totally amorphous structure. The halo centered at q = 1.4 $Å^{-1}$, which is considered to be a scattering of DMAc, slightly shifted to higher angle as the coagulant (EtOH) diffused into cellulose solution.

3.1.2 LiOH/urea solvent

In the gelation with Water and 5wt% Sulfuric acid solution (Figure 1), both of them showed the similar tendency: First, (110) plane of Na-cellulose IV (q = 1.42 $Å^{-1}$) appeared (Fig. 1A), and the appearance of (020) plane (q = 1.58 $Å^{-1}$) followed (Fig. 1B). This result corresponds to our previous study with using 5wt% Na_2SO_4 as a coagulant. Therefore, we concluded that in the case of aqueous coagulant, hydrophobically-stacked cellulose molecular sheets are formed in the first stage and then these sheets line up with hydrogen bonding.

Also, non-aqueous coagulants were tested. In the gelation with Ethanol, the formation of (110) plane (q = 1.42 $Å^{-1}$) was observed as in aqueous coagulants. However, no further formation of (020) plane was observed. In addition, two unfamiliar peaks centered at q = 0.3 $Å^{-1}$ and 0.63 $Å^{-1}$ gradually stood out. These peaks are thought to result from the alkali / urea / cellulose complex (Isobe et al. *Cellulose* **21**, 2014).

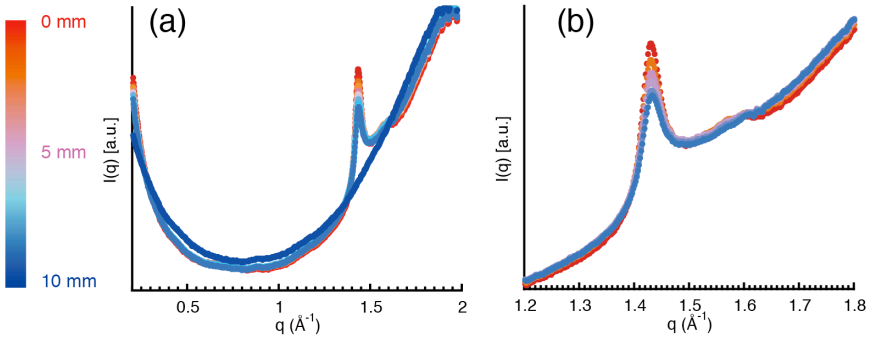

Figure 1. (a) WAXD profiles of LiOH/Urea (solvent) and 5wt% H_2SO_4 (coagulant) system. Scale bar shown on the left is depth of capillary. Gelation proceeds from blue to red. (b) Profiles in higher magnification of (a).

In the case of gelation with Methanol, while the formation of (110) plane without further formation of (020) plane was observed as in the case of EtOH, two peaks from alkali/urea/cellulose complex had once appeared and gradually disappeared as the gelation proceeded. This can be explained as follows. In the first contact with MeOH, alkali precipitated with its lower solubility in MeOH in the form of alkali/urea/cellulose complex. However, as the diffusion of MeOH proceeded (namely MeOH concentration increased), precipitated alkali was gradually dissolved in MeOH and washed out.

From these results, we concluded that in the LiOH/urea solvent, the primary structure of cellulose gel is hydrophobically-stacked molecular sheets, independent of the types of coagulants used. While with the use of aqueous coagulants these molecular sheets line up with hydrogen

bonding, no further linear alignment of these sheets occurs with the use of non-aqueous coagulants. Also, with the use of EtOH, alkali/urea/cellulose complex is formed.

3.2 SAXS

3.2.1 Linear plot

While in LiOH/urea system all plots linearly increased toward small q region, the plot of LiCl/DMAc system showed an appearance of correlation peak at q = 0.015 $Å^{-1}$, which corresponds to the spinodal decomposition with the periodicity of around 40 nm.

3.2.2 Log plot

In the log plots (Figure 2), LiOH/urea system showed no Guinier region. This is because structural feature could be present in smaller q region than we observed. Also, the transition from blue to red was dependent on coagulants: As the size of the molecule of coagulant used got bigger, the transition got wider. This can result from the diffusion coefficient of coagulant molecule.

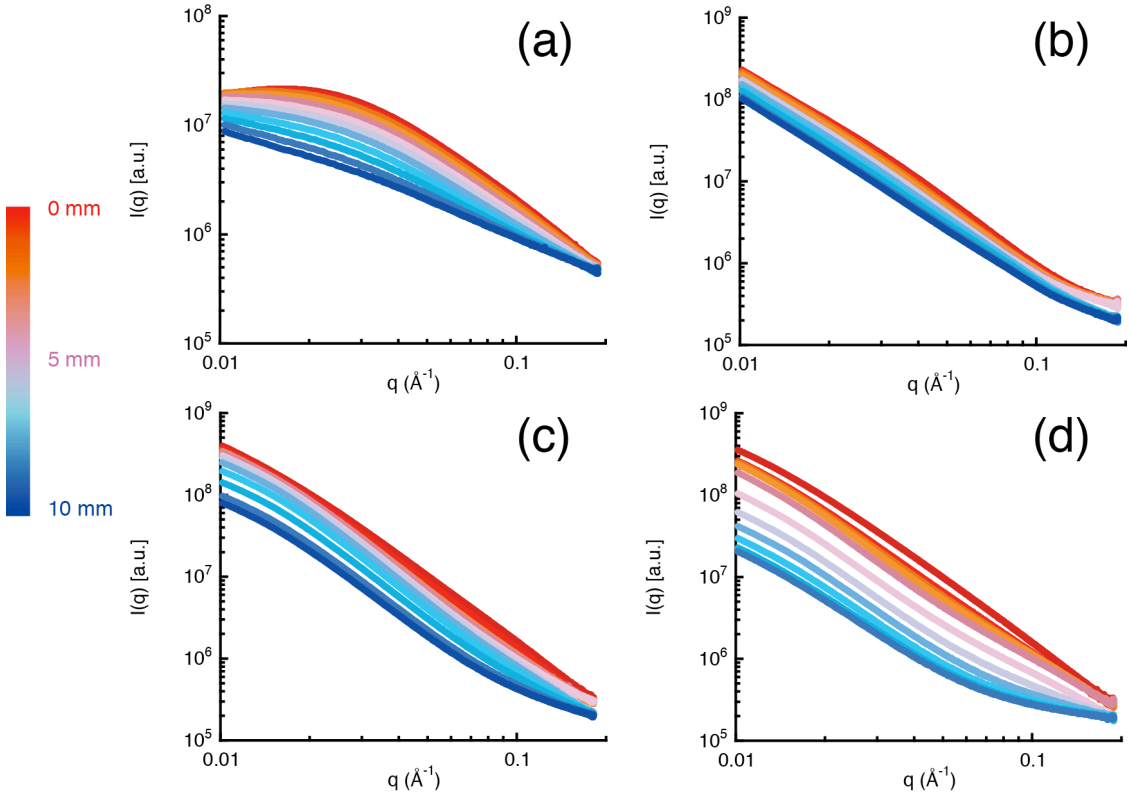

Figure 2. Log-log plots of SAXS profiles of LiCl/DMAc system (a) and LiOH/Urea system (b ~ e). Their coagulants are (a) EtOH, (b) Water, (c) 5wt%H_2SO_4, (d) MeOH, and (e) EtOH. Scale bar shown on the left is depth of capillary. Gelation proceeds from blue to red.

3.3 Proposed mechanism of cellulose gel formation

The probable mechanism of cellulose gelation was depicted in Figure 3.

In the case of LiCl/DMAc solvents, the mode of coagulation is the spinodal decomposition: Concentric fluctuation is gradually enhanced with the periodicity of 40 nm and complete phase separation occurs.

In the case of LiOH/urea solvent, the mode of coagulation is nucleation and its growth. The nucleus is hydrophobically-stacked molecular sheet. With the use of aqueous coagulants, these molecular sheets line up with hydrogen bonding. With the use of non-aqueous coagulants, no further linear alignment of these sheets occurs. However, with the use of EtOH, alkali/urea/cellulose complex is also formed as indicated in dotted circle in Figure 3.

4. Perspective

Although we observed successfully the growth of gel structure in molecular scale, the structural information such as diameter or shape of the primary gel structure is still missing. And also, the dependency of structural growth on degree of polymerization and concentration is still unclear. Therefore, it is necessary to observe much lower q region with using cellulose solution of different concentration and degree of polymerization.

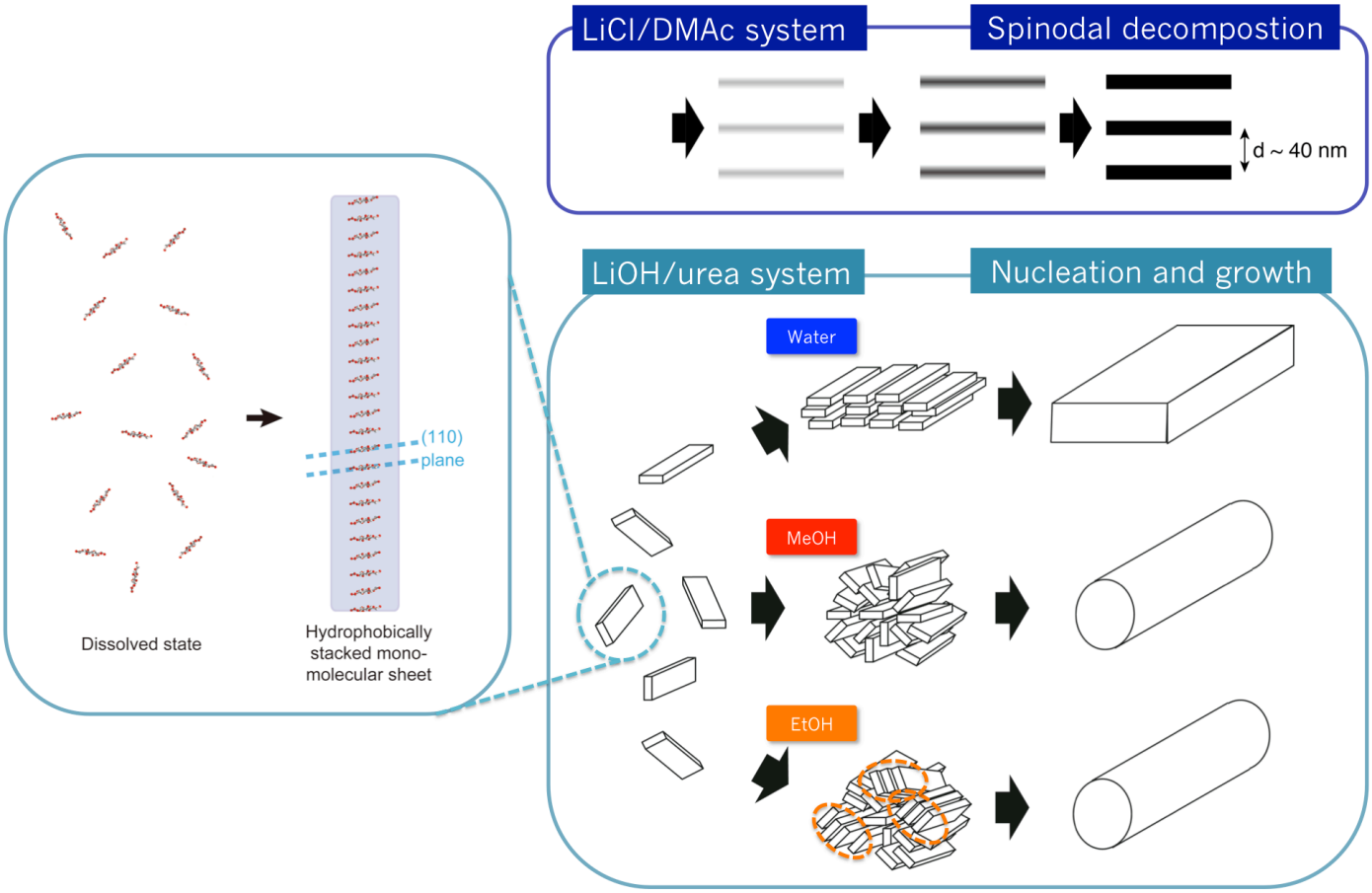

Figure 3. Schematic depiction of cellulose gelation with different solvents and coagulants. Dotted circles represent the alkali/urea/cellulose complex.