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# <sup>1</sup>H NMR analysis of cellulose dissolved in non-deuterated ionic liquids

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## Abstract

<sup>1</sup>H NMR spectroscopy of cellulose in a non-deuterated polar ionic liquid (IL) was carried out to analyze specific interaction between cellulose and ILs. We applied a polar IL, 1,3-dimethylimidazolium methyl methylphosphonate, as a cellulose solvent for <sup>1</sup>H NMR spectroscopy. To prevent vanishing the signals of hydroxyl groups (C-OHs) by hydrogen-deuterium exchange, a non-deuterated IL was utilized and both signals for C-OHs and backbone protons were successfully detected with the aid of no-deuterium NMR technique and a solvent suppression technique. It was confirmed that C-OHs were interacted with ILs stronger, rather than backbone protons. Furthermore, the signals of the C-OHs at 2-, 3-, and 6-position were independently observed. Strong interaction between C-OH at the 6-position and ILs was confirmed to be a key step for dissolution of cellulose.

**Keywords** *ionic liquids · <sup>1</sup>H NMR · No-D NMR · hydrogen bond*

## Introduction

While cellulose materials and their derivatives have been widely used, insolubility of cellulose has suppressed the advancement of cellulose technology. Some kinds of solvents such as LiCl/dimethylacetamide (DMAc) and *N*-methylmorpholine-*N*-oxide have been developed and used for reactions and regeneration (Vaca-Garcia et al. 1998; Liebert 2010). In spite of increasing development in cellulose processing, there are few reports on the

profiles of dissolved cellulose for revealing mechanisms of dissolution and reaction. Especially,  $^1\text{H}$  NMR of dissolved cellulose has not been performed despite the great advantages of  $^1\text{H}$  NMR including direct detection of the protons which form hydrogen bonds with solvents. The reason of it is that there is no good solvent for  $^1\text{H}$  NMR analysis. Only LiCl/DMAc and LiCl/1,3-dimethyl-2-imidazolidinone are known to solubilize cellulose without degradation and derivatization while *N*-methylmorpholine-*N*-oxide dissolves cellulose with degradation. However, these solvents require a few days and multi-step treatments to dissolve cellulose without degradation.

As another type of solvents, ionic liquids (ILs), organic salts with melting point below 100 °C, have been recently expected as solvents for cellulose (Swatloski et al. 2002; Armand et al. 2009; Ohno et al. 2009; Sun et al. 2011; Wang et al. 2012), and recently we have reported novel ILs which dissolve cellulose under mild condition (Fukaya et al. 2006, 2008). Since polar ILs can dissolve cellulose without degradation and derivatization, these polar ILs are considered to be suitable for the analysis of the dissolved cellulose. We have reported HPLC with polar ILs as eluents (HPILC) as a method for analysis of molecular weight distribution of cellulose in the ILs (Fukaya et al. 2011). HPILC also revealed change of molecular weight distribution of cellulose in ILs during depolymerization by ultrasonication (Kuroda et al. 2013).  $^{13}\text{C}$  NMR measurement has been tried to detect signals of cellulose in ILs (Moulthrop et al. 2005).

However,  $^1\text{H}$  NMR of dissolved cellulose has not been analyzed even in ILs. This is attributed to large proton signals derived from large excess amount of ILs compared to cellulose. They give rise to dropping sensitivity and overlapping signals of cellulose. General solution for these problems is deuteration of ILs. However, deuteration of ILs is not desirable because ILs have structural diversity; deuteration of various ILs causes troublesome processes and consuming enormous time. Furthermore, deuteration sometimes leads to vanishing OH signals due to hydrogen-deuterium exchange. For example, fully deuterated pyridinium chloride makes OH signals undetectable (Jiang et al. 2009), and it is known that the proton at 2-position of imidazolium ring is also exchangeable (Handy et al. 2005). Whereas use of deuterated additives for shimming, lock, and decreasing viscosity is one of the potential methods to obtain  $^1\text{H}$  NMR spectrum, it disrupts the interaction between cellulose and ILs. Considering these facts, development of direct  $^1\text{H}$  NMR analysis of cellulose dissolved in non-deuterated pure ILs should be quite beneficial.

To this end,  $^1\text{H}$  NMR measurement with no-deuterium (No-D) NMR technique (Hoye et al. 2004, 2004; Creary et al. 2005) and a solvent suppression technique (water suppression enhanced through  $T_1$  effect: WET) are quite attractive for this purpose. In this study,  $^1\text{H}$  NMR using No-D NMR and WET was performed in a non-deuterated ILs, 1,3-dimethylimidazolium methyl methylphosphonate (IL **1**; shown in Fig. 1).

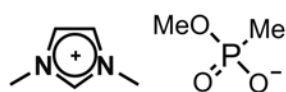


Fig. 1 Structure of IL **1**.

# Experimental

## Materials and Instruments

1-Methylimidazole was purchased from Kanto Chemical Co., Inc., and dried over KOH and distilled before use. Dimethyl methylphosphonate was purchased from Tokyo Chemical Ind. Co., Ltd. and distilled before use. Toluene was purchased from Kanto Chemical Co., Inc. and used as received. Microcrystalline cellulose powder (cellulose powder C) was purchased from Advantec Toyo Co. and used after drying under reduced pressure. Chitosan (Chitosan 100) was purchased from Wako Pure Chemical Industries, Ltd. and used as received. Xylan was purchased from Tokyo Chemical Ind. Co., Ltd. It was dissolved in DMSO and precipitated by water. The precipitation was washed with excess amount of water and dried before use. Deuterium oxide and DMSO- $d_6$  were purchased from Acros Organics and used as received. 3-(Trimethylsilyl)-propanesulfonic acid sodium salt was purchased from Merck KGaA and used as received. The amounts of water of IL samples were confirmed by Karl Fischer coulometric titration (Kyoto Electronics; MKC-510N).

$^1\text{H}$ - and  $^{13}\text{C}$  NMR measurements of saccharides were carried out on a JEOL ECX-400 ( $^1\text{H}$  base frequency 400 MHz) with a NM-40TH5AT/FG2 autotunable gradient probe (JEOL Ltd.). The analysis of NMR spectra was carried out with JEOL Delta (version 5.0.1).

## Synthesis of IL 1

IL 1 was synthesized as follows. Dimethyl methyl phosphonate (50 g; 0.40 mol) and 1-methylimidazole (36.4 g; 0.44 mol) were added into 100 ml of toluene under an argon gas atmosphere at room temperature. The reaction mixture was stirred at 120 °C for 48h. The resulting liquid was dried *in vacuo* at 80 °C and washed repeatedly with excess dehydrated diethyl ether. The residual liquid was dissolved in dichloromethane, and the resulting solution was passed through a column filled with neutral activated alumina. After removal of dichloromethane, the residual liquid was dried *in vacuo* at 100 °C for 8h to give IL 1 with water content below 400 ppm. Structure of IL 1 was confirmed by  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra (JEOL ECX-400; JEOL Ltd.) and elemental analysis (Elementar vario EL III; Elementar Analyzensysteme GmbH).

$^1\text{H}$ -NMR (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  = 1.26 (3H, d,  $J$  = 15.6 Hz,  $\text{PCH}_3$ ), 3.57 (3H, d,  $J$  = 10.1 Hz,  $\text{POCH}_3$ ), 4.05 (6H, s,  $\text{NCH}_3$ ), 7.57 (2H, d,  $J$  = 1.8 Hz,  $\text{NCHCHN}$ ), 10.73 (1H, s,  $\text{NCHN}$ ).  $^{13}\text{C}$ -NMR (100 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  = 11.47, 12.79 ( $\text{PCH}_3$ ), 36.06 ( $\text{NCH}_3$ ), 51.18 ( $\text{POCH}_3$ ), 123.26 ( $\text{NCHCHN}$ ), 139.79 ( $\text{NCHN}$ ).

Elemental analysis: Found: C, 39.22, H, 7.77, N, 13.18. Calc. for  $\text{C}_7\text{H}_{15}\text{N}_2\text{O}_3\text{P}_0.5\text{H}_2\text{O}$ : C, 39.07, H, 7.49, N, 13.02 %. IL 1 absorbed small amount of water during elemental analysis because it is very hygroscopic.

## Analysis of cellulose with No-D NMR and WET

Cellulose (30 mg) was added into 1.0 g of dried IL 1. The mixture was stirred gently 80 °C until the solution became homogeneous and clear. The resulting solution was transferred to 5 mm NMR tubes. The sample tube

was capped with plastic lids, then the top was wrapped in a parafilm. All treatments were processed under an atmosphere of dry nitrogen gas. The sample was analyzed at 100 °C with 240 scans.

WET method: the measurements were performed based on the standard pulse sequence purchased by JEOL Ltd. The WET pulse of 11 ms and WET attenuator of 50 dB were used. The attenuation level required for a hard 90 degree proton pulse was 4.5 dB and the duration of the pulse was 12.8  $\mu$ s. For suppression of  $^{13}\text{C}$  satellite peaks, MPF8 was applied as a decoupling sequence.

## Analysis of deuterated cellulose and xylan and chitosan

We measured deuterated cellulose because the types of the protons of cellulose should be distinguished. Protons of cellulose are generally identified as backbone protons ( $\text{CHs}$ ) or protons of hydroxyl groups ( $\text{C-OHs}$ ). The signals of  $\text{C-OHs}$  of deuterated cellulose are thought to be invisible.

Cellulose (30 mg) was dissolved into IL 1 (1.0 g) and deuterium oxide (40  $\mu\text{L}$ ) was added to the sample solution. The resulting solution was heated 150 °C for 5min and transferred to 5 mm NMR tubes. This sample was measured by No-D NMR and WET as described above.

We measured xylan and chitosan dissolved in IL 1 to assign  $\text{C-OHs}$ . Because xylan has no  $\text{C-OH}$  at 6-position and chitosan has no  $\text{C-OH}$  at 2-position, we assigned these  $\text{C-OHs}$  by comparing these spectra and that of cellulose.

Xylan (30 mg) and chitosan (30 mg) were respectively added into 1.0 g of IL 1s and the samples were stirred until homogeneous and clear. The resulting solutions were transferred to 5 mm NMR tubes, and coaxial inserts containing 3-(trimethylsilyl)-propane sulfonic acid sodium salt/DMSO- $d_6$  mixtures (1.2 wt%) were subsequently fitted as external standards (0 ppm). The sample tubes were capped with glass lids, then the tops were wrapped in parafilms. The resulting solutions were measured by No-D NMR and WET as described above.

## Analysis of chemical shifts for cellulose in IL 1 and IL 1/DMSO- $d_6$ mixtures

Chemical shift of cellulose in IL 1 was measured after adding DMSO- $d_6$  as a poor solvent for cellulose. By measuring the chemical shifts with increasing the concentration of DMSO- $d_6$  until cellulose turned to precipitate, it should clarify the most important  $\text{C-OH}$  site in cellulose for dissolution.

The mixtures of IL 1 and DMSO- $d_6$  in mixing ratio from 1:0 to 1:25 (mol/mol) were prepared. Cellulose (30 mg) was added into 1.0 g of IL 1/DMSO- $d_6$  mixtures. The mixtures were stirred gently 80 °C until the solutions became homogeneous and clear. The resulting solutions were transferred to 5 mm NMR tubes, and coaxial inserts containing 3-(trimethylsilyl)-propane sulfonic acid sodium salt/DMSO- $d_6$  mixtures (1.2 wt%) were subsequently fitted as external standards (0 ppm). The sample tubes were capped with glass lids, then the tops were wrapped in parafilms. All treatments were processed under an atmosphere of dry nitrogen gas. The resulting solutions were measured by No-D NMR and WET as described above. While DMSO- $d_6$  was used as an additive, shimming and lock with deuterium were not used.

## Measurement of $\beta$ values of Kamlet-Taft parameters

$\beta$  value of Kamlet-Taft parameters represents hydrogen bond basicity of ILs, and it is frequently used as the index of the strength of hydrogen bond between ILs and solvents. We compared the  $\beta$  values of IL 1/DMSO-*d*<sub>6</sub> mixtures with the chemical shifts of C-OHs to analyze the relation between hydrogen bonds of C-OHs and  $\beta$  values of the solutions.

$\beta$  values of Kamlet-Taft parameters were measured as follows. The solvatochromic dyes, 4-nitroaniline (from Tokyo Chemical Industries Co., Ltd) and *N,N*-diethyl-4-nitroaniline (from Kanto Chem.), were used as received. These dyes were added to 0.2 ml of sample solutions. These solutions were placed into quartz cells with 1 mm light-path length. From the wavelength at the maximum absorption ( $\lambda_{\max}$ ) determined by UV-*vis* spectrophotometer (UV-2450; Shimadzu), the  $\beta$  values were calculated by use of the following equations:

$$\nu_{(\text{dye})} = 1/(\lambda_{\max(\text{dye})} \times 10^{-4})$$
$$\beta = (1.035 \nu_{(\text{N,N-diethyl-4-nitroaniline})} + 2.64 - \nu_{(4\text{-nitroaniline})})/2.80$$

## H,H-COSY of glucose

For further investigation on the interactions of C-OHs and ILs, two-dimensional (2D) NMR is an excellent candidate. 2D NMR can analyze compounds in view of interaction, conformation, spatial configuration and so forth. As a popular 2D NMR, H,H-correlation spectroscopy (H,H-COSY) of glucose in IL 1 was performed using No-D NMR and WET.

Glucose (0.10 g) was added into 1.0 g of dried IL 1. The mixture was stirred gently 80 °C until the solution became homogeneous and clear. The resulting solution was transferred to a 5 mm NMR tube. The sample tube was capped with a plastic lid, then the top was wrapped in a parafilm. This sample was analyzed at 60 °C with 60 scans.

WET method: the measurement was performed based on the standard pulse sequence purchased by JEOL Ltd. The WET pulse of 14 ms and WET attenuator of 50 dB were used. For suppression of <sup>13</sup>C satellite peaks, MPF8 was applied as a decoupling sequence.

COSY method: the correlation experiment was performed using a standard gradient-selected COSY pulse sequence purchased from JEOL Ltd.

## Results and discussion

### Observation of <sup>1</sup>H signals of cellulose

Fig. 2 shows <sup>1</sup>H NMR spectra of the IL 1/cellulose solution using No-D NMR and WET. In the spectrum obtained by the standard method (Fig. 2a), no peaks of cellulose but those for IL 1 were observed. To improve resolution, the solution was measured with No-D NMR (Fig. 2b). While all peaks became relatively sharp and their intensities increased, any peaks of cellulose were not found. WET was applied to the peak of IL 1 at 2.7 ppm for confirmation of suppression of IL peaks in IL 1/cellulose solution (Fig. 2c). It was found that the peak and its satellite peaks were suppressed locally even in the IL/cellulose solution, which is highly viscous. Then, all peaks for IL 1 at 0.3, 2.7, 3.5, 7.7, and 9.6 ppm were suppressed (Fig. 2d). The peaks of cellulose were observed including overlapped peaks at 2.4, 2.9, 3.1, 4.0, 5.2,

6.1, and 6.4 ppm. In the spectrum, since sufficient signal to noise ratio was obtained, a diluted solution was measured using No-D NMR and WET.  $^1\text{H}$  signals of cellulose in 0.5 wt% solution were detected by the accumulation of only 12 scans. In the case of  $^{13}\text{C}$  NMR, detection of signals of cellulose requires over 5000 scans (several hours) even in 5 wt% cellulose/IL solutions. Integrals of peaks near the suppressed peaks were not in stoichiometric ratio. Sharp peaks without arrows in Fig. 2d were attributed to impurities of IL 1 in spite that the IL 1 was confirmed to be sufficiently pure by elemental analysis; C/N ratio was found to be 2.98 (3.00 in calculation).

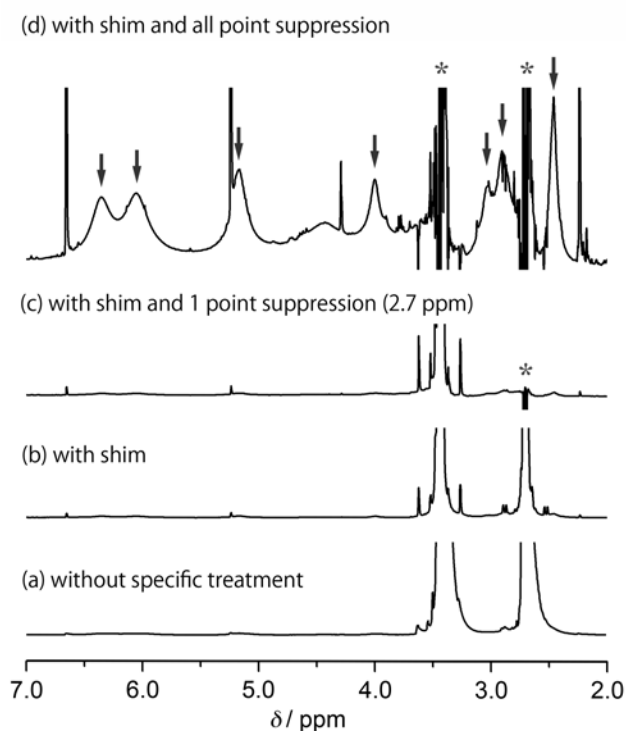


Fig. 2  $^1\text{H}$  NMR spectra of cellulose in IL 1 at 100 °C. Arrows indicate the signals of cellulose. \*:suppressed signal

In Fig. 2d, seven peaks for cellulose were observed. Generally, protons of cellulose are categorized into two types based on  $\text{CHs}$  and  $\text{C-OHs}$ . To assign the signals, we preliminarily measured the spectra of cellulose in IL 1 before and after adding deuterium oxide (Fig. 3). After addition of deuterium oxide, the intensities of the peaks at 5.2, 6.1, and 6.4 ppm decreased, showing that the three peaks should be assigned to  $\text{C-OHs}$ . Four remained peaks at 2.4, 2.9, 3.1, and 4.0 ppm should therefore be assigned to  $\text{CHs}$  while the peak at 4.0 ppm was not observed due to overlapping with the signal of water. For further assignment of  $\text{C-OH}$  signals, we have measured  $^1\text{H}$  NMR spectra of xylan and chitosan which lack the  $\text{C-OH}_{(2)}$  and  $\text{C-OH}_{(6)}$ , respectively. The signal at 5.2 ppm can be assigned to  $\text{C-OH}_{(6)}$  which was not observed in the spectrum of xylan. The signal at 6.4 ppm was assigned to  $\text{C-OH}_{(2)}$  considering the spectrum of chitosan. Therefore, we believe that the  $\text{C-OH}$  signal at 6.1 ppm is assigned to  $\text{C-OH}_{(3)}$ .

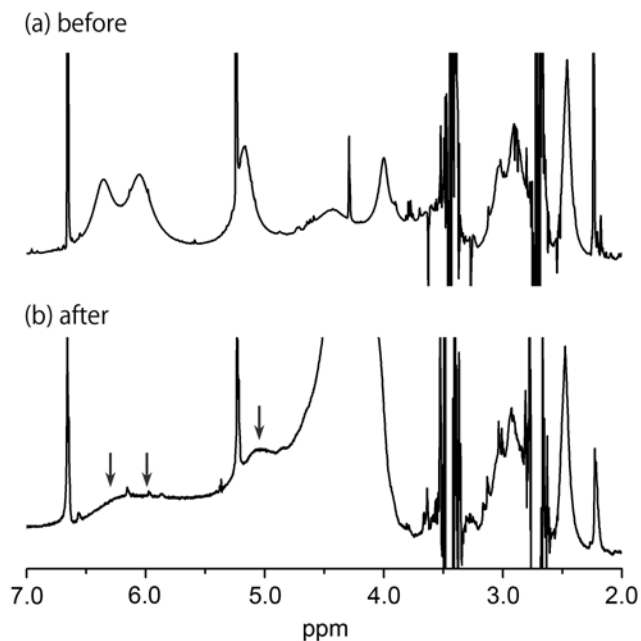


Fig. 3  $^1\text{H}$  NMR spectra of cellulose in IL 1 (a) before and (b) after adding deuterium oxide. Arrows indicate the signals of C-OHs

### Interaction between cellulose and ILs

$^1\text{H}$  NMR is one of the most suitable techniques for investigating hydrogen bonds unlike other indirect techniques including  $^{13}\text{C}$  NMR. The results in Fig. 2d show that both CHs and C-OHs were observed by  $^1\text{H}$  NMR, and hence the interaction between ILs and two types of protons can be analyzed. To confirm that ILs interact strongly with C-OHs, rather than CHs, we compared the chemical shifts of cellulose in IL 1 and those of cellobiose in DMSO- $d_6$  (Online Resource 1, Fig. S1). The signals for C-OHs of cellulose in IL 1 (see Fig. 2d, 5.0 to 6.6 ppm) were observed on much lower magnetic field side than those of cellobiose in DMSO- $d_6$  (4 to 5 ppm). On the other hand, the signals of CHs in both solutions were observed in the similar chemical shifts. From these results, it was confirmed that IL 1 interacted with C-OHs stronger than with CHs. IL 1 interacted with C-OHs due to a high hydrogen bond basicity of IL 1 ( $\beta$  value of Kamlet-Taft parameter of IL 1 was 1.10). This high  $\beta$  value of IL 1 is the proof of high solubility of cellulose in IL 1. This was confirmed by comparing its  $\beta$  value with that of DMSO- $d_6$  studied (0.71).

It is known that C-OH<sub>(6)</sub> plays an important role to make cellulose insoluble in ordinary molecular solvents (Kondo 1997). To solubilize cellulose, interchain hydrogen bonds among C-OH<sub>(6)</sub>s therefore should be destroyed by highly polar solvents. The  $^1\text{H}$  NMR spectra of cellulose in IL 1 before and after adding different amounts of DMSO- $d_6$  were measured. Cellulose was found to be insoluble in IL 1/DMSO- $d_6$  mixture with the mixing ratio of 1:25 (by mol) or more. As shown in Fig. 4, by increasing DMSO- $d_6$  fraction, the peaks for C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub> shifted to higher magnetic field side. On the other hand, no shift of the peak for C-OH<sub>(6)</sub> was found. These data pointed out that the interacted IL 1s to C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub> were gradually replaced with DMSO- $d_6$ , or C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub> formed



intrachain hydrogen bond by increasing DMSO- $d_6$  fraction. Against these, the signals for C-OH<sub>(6)</sub> did not show any shift, suggesting solubilization of cellulose by the strong interaction of IL 1 and C-OH<sub>(6)</sub> even in the presence of excess DMSO- $d_6$ . Through these experiments, it was confirmed that the strong interaction between IL 1 and C-OH<sub>(6)</sub> was the key step to dissolve cellulose. This is the first report about experimental proof related to the importance of interaction between C-OH<sub>(6)</sub>s and ILs because thus far there are not any other methodologies for direct detection of hydrogen bonds between specific C-OHs and ILs. This is supported by the report that both C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub> are known to contribute to form *intrachain* hydrogen bonds whereas C-OH<sub>(6)</sub> leads to the formation of *interchain* hydrogen bonds (Nishiyama et al. 2002). It is worthily noted that reactivity of the respective hydroxyl groups should be different depending on the mixing ratio of IL 1 and DMSO- $d_6$  due to the difference of their hydrogen bonds. As shown here, it can be estimated by <sup>1</sup>H NMR.

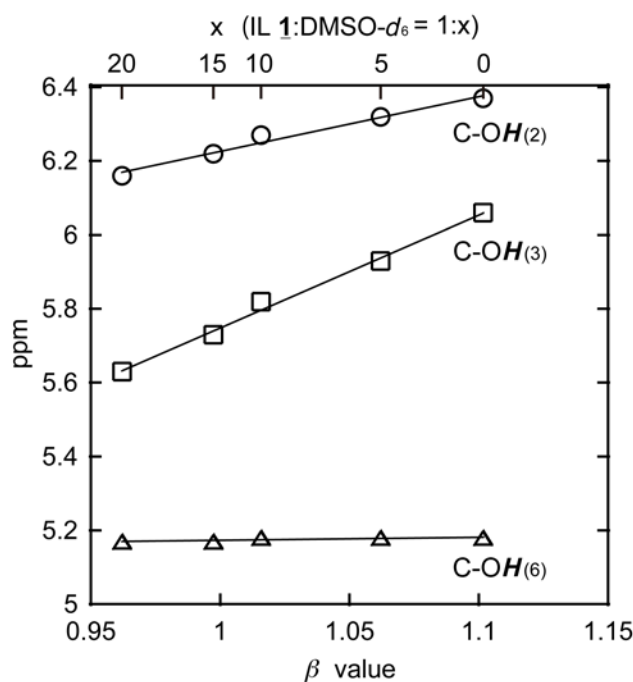


Fig. 4 The relationship between  $\beta$  values of IL 1/DMSO- $d_6$  mixtures and chemical shifts of C-OHs in cellulose/IL 1/DMSO- $d_6$  mixtures

Kamlet-Taft parameter is commonly used for estimating hydrogen bond acidity, hydrogen bond basicity, and dipolarity/polarizability of ILs (Kamlet et al., 1983), and it is well known that ILs which have high  $\beta$  values can form hydrogen bonds with cellulose and dissolve it. Using the <sup>1</sup>H NMR studied, the  $\beta$  values were compared with behavior of hydrogen bonds. Fig. 4 shows the relations between  $\beta$  values of IL 1/DMSO- $d_6$  solutions and the chemical shifts of C-OHs. As increasing the fraction of DMSO- $d_6$ ,  $\beta$  value gradually decreased from 1.1 to 0.96, and the relations of C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub> were linear. It was reconfirmed that  $\beta$  value is available for estimating intensity of hydrogen bond between ILs and C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub>. According to C-OH<sub>(6)</sub>, the shift of the  $\beta$  value may suggest that IL 1 interacted strongly to C-OH<sub>(6)</sub> when the  $\beta$  value was higher than 0.96. Therefore, it was confirmed that the results about hydrogen bonds from <sup>1</sup>H NMR and solvatochromism were similar, especially concerning C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub>. These results indicate that potential factors which affect estimation did not

appear in the case of cellulose and IL 1. In some cases, there are potential factors affecting estimation such as steric hindrance. It is important to mention that  $\beta$  value of Kamlet-Taft parameter was useful even in mixtures due to reflection of the preferential solvation of ILs. From  $\lambda_{\max}$  of dyes related to the  $\beta$  value in IL 1/DMSO- $d_6$  solutions, it was confirmed that  $\beta$  value depended on the interaction with 4-nitroaniline (4N) more strongly rather than *N,N*-diethyl-4-nitroaniline. Because the relationships between  $\lambda_{\max}$  of 4N and the chemical shifts of C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub> were also linear, it was confirmed that  $\lambda_{\max}$  of 4N indicated the behavior of hydrogen bond with C-OH<sub>(2)</sub> and C-OH<sub>(3)</sub>. This is the first report about relations between hydrogen bonds of specific C-OHs and  $\beta$  value quantitatively.

It is important to mention that when  $\beta$  value was higher than 0.96 (at least), ILs strongly interacted to C-OH<sub>(6)</sub> and destroyed interchain hydrogen bonds. When  $\beta$  value is over 0.8, the effect of  $\beta$  value on degree of solubility is now under discussion. This result should be clue to clarify it.

## 2D NMR of glucose in ILs

As a method for further investigation on the interactions of C-OHs and ILs, 2D NMR is an excellent candidate. 2D NMR is capable of analyzing compounds in view of interaction, conformation, spatial configuration and so forth. As a problem of 2D NMR, however, high sensitivity is essential for detection of correlation peaks. Therefore, even 2D NMR of glucose was only analyzed in deuterated ILs until now, in the case of pure ILs (Youngs et al. 2011). As a popular 2D NMR, H,H-correlation spectroscopy (H,H-COSY) of 10 wt% glucose in IL 1 was performed using No-D NMR and WET (Fig. 5). Some correlation peaks for the coupling between CHs were detected due to the attenuation of the signals for IL 1 by WET, though the signals of IL 1 still remained. The structural identification was not completed because some correlation peaks were not observed between the anomeric proton and CHs. However, no correlation peaks were observed in the case of usual H,H-COSY without No-D NMR and WET. Observation of the correlation peaks on 2D NMR spectra should contribute to investigating the profile of cellulose in ILs with various 2D NMR measurements including NOESY.

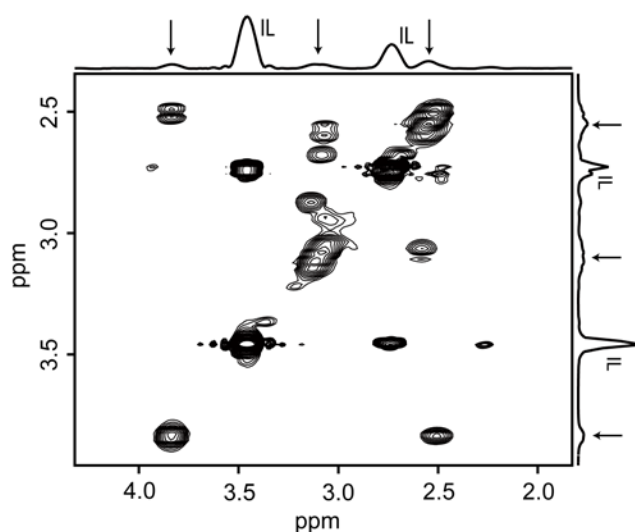


Fig. 5 H,H-COSY spectrum of glucose in IL **1** (number of scans: 60, temperature 60 °C). Arrows indicate the signals of  $\text{C-H}$ s of glucose

## Conclusion

$^1\text{H}$  NMR spectroscopy of cellulose in a non-deuterated IL was performed with No-D NMR and WET. We successfully detected signals of cellulose dissolved in ILs, which dissolve cellulose without degradation and derivatization. Both signals of  $\text{C-H}$ s and  $\text{C-OH}$ s were observed in non-deuterated ILs. From chemical shifts of the signals, hydrogen bonds between ILs and  $\text{C-OH}$ s were confirmed. Interaction between ILs and  $\text{C-OH}_{(6)}$  was confirmed to be the key step for dissolution of cellulose.

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## References

- Armand M, Endres F, MacFarlane DR, Ohno H, Scrosati B (2009) Ionic-liquid materials for the electrochemical challenges of the future. *Nature Mater* 8: 621-629 doi: 10.1038/nmat2448
- Creary X, Willis ED, Gagnon M (2005) Carbocation-forming reactions in ionic liquids. *J Am Chem Soc* 127: 18114-18120
- Fukaya Y, Sugimoto A, Ohno H (2006) Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates. *Biomacromolecules* 7: 3295-3297 doi:10.1021/bm060327d
- Fukaya Y, Hayashi K, Wada M, Ohno H (2008) Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. *Green Chem* 10: 44-46. doi:10.1039/b713289a
- Fukaya Y, Tsukamoto A, Kuroda K, Ohno H (2011) High performance "ionic liquid" chromatography. *Chem Commun* 47: 1994-1996 doi:10.1039/c0cc05307d
- Hoye TR, Eklov BM, Voloshin M (2004) No-D NMR Spectroscopy as a Convenient Method for Titering Organolithium (RLi), RMgX, and LDA Solutions. *Org Lett*, 6: 2567-2570 doi: 10.1021/ol049145r

- Hoye TR, Eklov BM, Ryba TD, Voloshin M, Yao LJ (2004) No-D NMR (No-Deuterium Proton NMR) Spectroscopy: A Simple Yet Powerful Method for Analyzing Reaction and Reagent Solutions. *Org Lett*, 6: 953-956 doi: 10.1021/ol049979+
- Jiang N, Pu Y, Samuel R, Ragauskas AJ (2009) Perdeuterated pyridinium molten salt (ionic liquid) for direct dissolution and NMR analysis of plant cell walls. *Green Chem*, 11: 1762 doi: 10.1039/B913609F
- Handy ST, Okello M (2005) The 2 Position of Imidazolium Ionic Liquids: Substitution and Exchange. *J Org Chem* 70: 1915-1918 doi: 10.1021/jo0480850
- Kamlet MJ, Abboud JLM, Abraham MH, Taft RW (1983) Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters,  $\rho^*$ ,  $\alpha$ , and  $\beta$ , and some methods for simplifying the generalized solvatochromic equation. *J. Org. Chem.* 48:2877-2887 doi: 10.1021/jo00165a018
- Kondo T (1997) The relationship between intramolecular hydrogen bonds and certain physical properties of regioselectively substituted cellulose derivatives. *J Polym Sci Part B Polym Phys*, 35: 717-723 doi: 10.1002/(SICI)1099-0488
- Kuroda K, Fukaya Y and Ohno H (2013) Direct HPILC analysis of cellulose depolymerisation in ionic liquids. *Anal Methods*, 5: 3172-3176 doi: 10.1039/C3AY40182K.
- Liebert T (2010) Cellulose Solvents - Remarkable History, Bright Future. In: Liebert TF, Heinze TJ, Edgar KJ (ed) *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*, American Chemical Society, Washington DC, pp 3-54 doi: 10/1021/bk-2010-1033
- Nishiyama Y, Langan P, Chanzy H (2002) Crystal Structure and Hydrogen-Bonding System in Cellulose I $\beta$  from Synchrotron X-ray and Neutron Fiber Diffraction. *J Am Chem Soc* 124: 9074-9082 doi: 10.1021/ja0257319
- Moulthrop JS, Swatloski RP, Moyna G, Rogers RD (2005) High-resolution  $^{13}\text{C}$  NMR studies of cellulose and cellulose oligomers in ionic liquid solutions. *Chem Commun*, 12: 1557-1559
- Ohno H, Fukaya Y (2009) Task Specific Ionic Liquids for Cellulose Technology. *Chem Lett* 38: 2-7 doi:10.1246/cl.2009.2
- Sun N, Rodriguez H, Rahman M, Rogers RD (2011) Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass? *Chem Commun* 47: 1405-1241 doi:10.1039/c0cc03990j
- Swatloski RP, Spear SK, Holbrey JD, Rogers RD (2002) Dissolution of cellose with ionic liquids. *J Am Chem Soc* 124: 4974-4975 doi:10.1021/ja025790m
- Vaca-Garcia C, Thiebaud S, Borredon ME, Gozzelino G (1998) Cellulose esterification with fatty acids and acetic anhydride in lithium chloride/N,N-dimethylacetamide medium. *J Am Oil Chem Soc* 75:315-319 doi: 10.1007/s11746-998-0047-2

Wang H, Gurau G, Rogers RD (2012) Ionic liquid processing of cellulose. *Chem Soc Rev* 41: 1519-1537 doi:10.1039/c2cs15311d

Youngs TGA, Holbrey JD, Mullan CL, Norman SE, Lagunas MC, D'Agostino C, Mantle MD, Gladden LF, Bowron DT, Hardacre C (2011) Neutron diffraction, NMR, and molecular dynamics study of glucose dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Chem Sci*, 2: 1594-1605 doi: 10.1039/C1SC00241D