

Dissolution Mechanism of Cellulose in SO₂-Amine-Dimethylsulfoxide

AKIRA ISOGAI, ATSUSHI ISHIZU, and JUNZO NAKANO,
*Department of Forest Products, Faculty of Agriculture, University of
Tokyo, Bunkyo-ku, Tokyo 113, Japan*

Synopsis

The dissolution mechanism of cellulose in SO₂-amine-dimethylsulfoxide systems was studied by using ¹H- and ¹³C-NMR spectroscopy. SO₂ and amine (diethylamine or triethylamine) were found to form a complex in DMSO, and the SO₂-amine complex, in turn, reacts with an alcoholic hydroxyl group of methanol to produce a new complex. In the case of cellulose, it was proved that all hydroxyl groups in cellulose react with the SO₂-amine complexes and form the same complexes in the solution state as those formed in methanol.

INTRODUCTION

Recently, many types of nonaqueous cellulose solvents have been found, which made it possible to prepare cellulose derivatives in homogeneous and nonaqueous systems. We have succeeded in the quantitative preparation of approximately 30 types of tri-*O*-substituted cellulose ethers by using the nonaqueous cellulose solvent system, SO₂-diethylamine (DEA)-dimethylsulfoxide (DMSO).¹⁻⁴ These new cellulose derivatives not only have chemically reactive groups, such as aromatic rings, double bonds or halogens, but also unique physical properties such as liquid crystals behavior.^{4,5}

The SO₂-amine solvents for cellulose were first found by Hata and Yokota.⁶⁻⁸ They reported that DEA, triethylamine (TEA), triisooamylamine, or piperidine can be used in combination with liquid SO₂ for the dissolution of cellulose. Yamazaki and Nakao⁹ reported that DMSO and 37 other organic solvents containing small amounts of SO₂ and amine dissolve cellulose. As to the dissolution mechanism of cellulose in this system, several papers have been published by Hata and Yokota,⁶⁻⁸ Yamazaki and Nakao,⁹ Philipp et al.,¹⁰ Turbak,¹¹ and Hudson and Cuculo.¹² However, their proposals were somewhat different from one another, and details of the dissolution mechanisms of cellulose in SO₂-amine systems have not been clarified.

In this paper, the dissolution mechanism of cellulose in SO₂-amine systems was studied by using ¹H- and ¹³C-NMR spectrometry.

EXPERIMENTAL

Sample and Reagents. Avicel (commercially available cellulose powder, DP_v = 250) was used as a cellulose sample. Pure grade DMSO was dried over molecular sieve 3A. A SO₂/DMSO solution (ca. 0.3 g SO₂/mL) was prepared according to the previous papers.¹⁻⁴ DMSO-d₆ and tetramethylsilane were

used as the NMR solvent and an internal standard, respectively. Other pure grade reagents and solvents were used without any purifications.

NMR Measurements. JEOL JNM 4H-100 and JNM FX-100 were used as ^1H - and ^{13}C -NMR spectrometers, respectively. ^{13}C -NMR spectra of cellulose solutions were obtained by using NNE (nonnuclear overhauser effect) mode and 2 s of the pulse delay.

RESULTS AND DISCUSSION

Reaction of Methanol with SO_2 and Amine

Methanol / SO_2 -DEA-DMSO System

Figure 1 shows the chemical shifts of signals in ^1H -NMR spectra of the methanol/ SO_2 -DEA-DMSO and related systems. The $-\text{OH}$ proton of methanol and the $-\text{NH}$ proton of DEA appeared at 4.1 and 1.3 ppm, respectively, in DMSO solutions. Since the $-\text{OH}$ proton of methanol and the $-\text{NH}$ proton of DEA are exchangeable with each other, it is natural that a single peak due to the $-\text{OH}$ and $-\text{NH}$ protons of methanol and DEA, respectively, was observed at an intermediate position (3.9 ppm) when methanol and DEA were mixed in DMSO. The chemical shift of the $-\text{OH}$ proton of methanol did not change by the addition of SO_2 in the methanol/DMSO. These results show that both SO_2 and DEA have no significant influence individually on the $-\text{OH}$ proton of methanol.

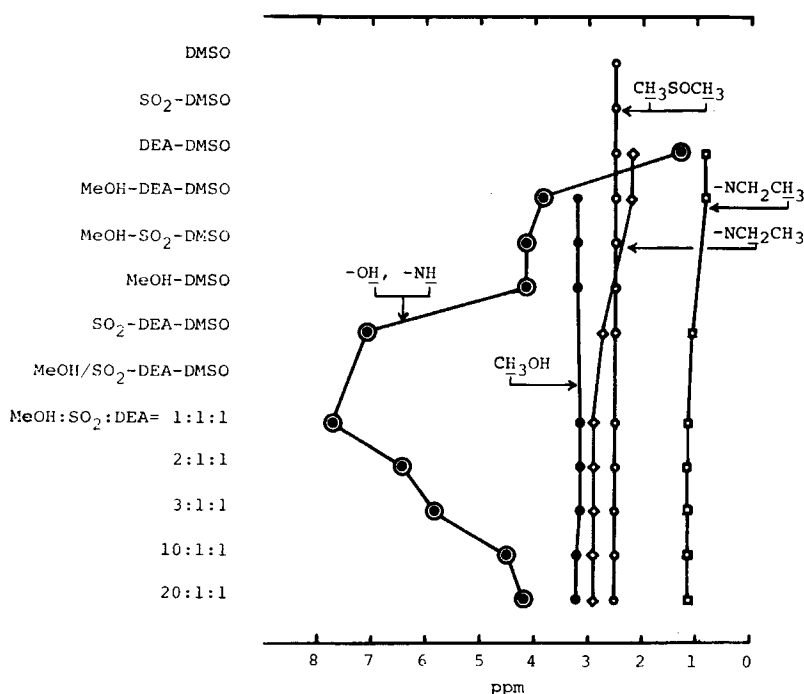


Fig. 1. Chemical shifts of signals in ^1H -NMR spectra of the methanol/ SO_2 -diethylamine-DMSO and related systems.

When SO₂ and DEA were mixed in DMSO, the chemical shift of the —NH proton of DEA appeared at 7.1 ppm, and also the methylene and methyl protons of DEA were affected. The chemical shift (7.1 ppm) of the —NH proton of DEA has been reported as that of the tertiary ammonium salt.¹³ Thus, SO₂ and DEA were found to react with each other in DMSO to form a complex.

By the addition of methanol equimolar with respect to the SO₂-DEA complex, a single peak from the —OH proton of methanol and the —NH proton of DEA appeared at lower magnetic field (7.8 ppm) than that from the —NH proton of the SO₂-DEA complex. These results indicate that the —OH of methanol reacts quantitatively with the SO₂-DEA complex to form a new complex or a new derivative consisting of a methanol molecule and a SO₂-DEA complex.

The single broad signal at 7.8 ppm moved to 4.1 ppm with the increase in the ratio of methanol to the SO₂-DEA complex, but the chemical shifts of the signals of methyl and methylene protons of DEA did not change. The latter result shows that a complex or a derivative produced by mixing methanol with the SO₂-DEA complex in the same ratio was not destroyed by the addition of excess methanol. However, the methyl proton of methanol bound to the SO₂-DEA complex shifted as a single peak from 3.1 to 3.3 ppm or to the chemical shift of methanol in the methanol/DMSO solution. This result indicates that a complex rather than a derivative was formed. If a derivative such as a sulfite ester were formed, two peaks from the methyl proton of the derivatized methanol and from those of excess free methanol should have been detected in the ¹H-NMR spectrum. The appearance of the methyl protons as a single peak irrespective of the addition of excess methanol can be explained by the rapid exchange between the methanol bound in a complex and free methanol. Figure 1 shows, furthermore, that the chemical shift of the methyl proton of DMSO remained constant in every system, indicating that DMSO itself has no direct role in complex formation.

Figure 2 shows chemical shifts of signals in ¹³C-NMR of the methanol/SO₂-DEA-DMSO system and related systems. The methyl carbon of

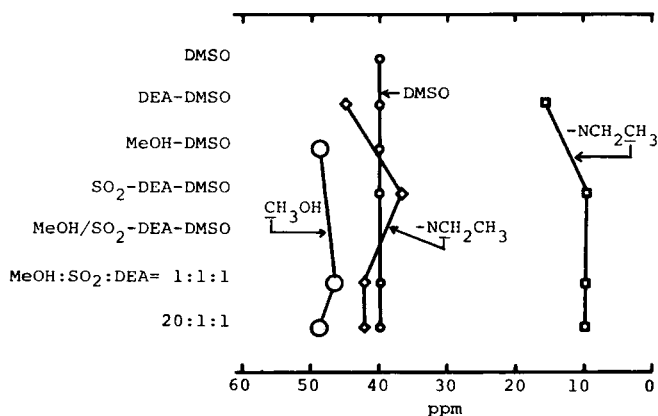


Fig. 2. Chemical shifts of signals in ¹³C-NMR spectra of the methanol/SO₂-diethylamine-DMSO and related systems.

methanol shifted from 46 to 48 ppm as a single peak with the increase in the ratio of methanol to the SO_2 -DEA complex from 1:1 to 20:1. This also supports the formation of a complex between methanol and the SO_2 -DEA complex in DMSO.

Methanol / SO_2 -TEA-DMSO System

Figure 3 shows $^1\text{H-NMR}$ spectra of the methanol/ SO_2 -TEA-DMSO and related systems. Although TEA has no $-\text{NH}$ proton, the signals of the methyl and methylene protons of TEA are shifted downfield by the addition of SO_2 to a TEA-DMSO solution. This phenomenon, which was also observed for the DEA-DMSO solution, suggests the formation of a complex between SO_2 and TEA. When methanol equimolar to the SO_2 -TEA complex (SO_2 :TEA = 1:1 by mol) in DMSO was added, the $-\text{OH}$ proton of methanol appeared at 7.8 ppm, which is the same value as the chemical shift observed in the methanol/ SO_2 -DEA-DMSO system with the molar ratio of 1:1:1 for methanol, SO_2 , and DEA. The behavior of the signals of the $-\text{OH}$ protons, methyl protons of methanol, and methyl and methylene protons of TEA upon the addition of excess methanol are also quite similar to those observed in the methanol/ SO_2 -DEA-DMSO system. These data together with those of $^{13}\text{C-NMR}$ spectra, which was not shown here because of the similarity to those of the methanol/ SO_2 -DEA-DMSO system (Fig. 2), indicate the formation of a complex between methanol, SO_2 , and TEA in DMSO.

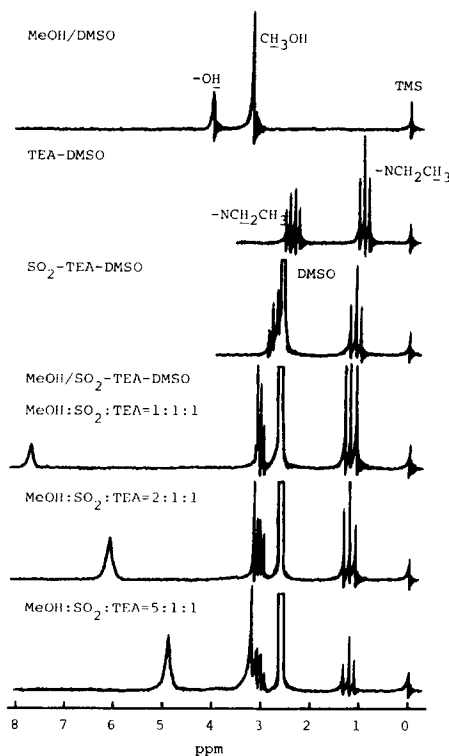


Fig. 3. $^1\text{H-NMR}$ spectra of the methanol/ SO_2 -diethylamine-DMSO and related systems.

Chemical Structure of the Complex between Methanol, SO₂, and Amine in DMSO

On the basis of the above discussion, SO₂ and DEA or TEA were found to form a complex as shown in Figure 4(a) in DMSO. The NMR data shown in the previous sections indicate that the mechanism of complex formation between methanol, SO₂, and DEA is almost the same as that between methanol, SO₂, and TEA. Namely, the —N⁺H proton of DEA forming the complex with SO₂ does not participate directly in the formation of the new complex with methanol, because TEA, which has no —NH proton, also has the same tendency to form a complex with methanol and SO₂. Furthermore, it is difficult to consider from a steric point of view that the ammonium cation of the SO₂-amine complex has direct interaction with the —OH of methanol. This is because the nitrogen atom forms the quaternary ammonium salt with a sp³ molecular orbital with not only TEA but also with DEA, which behaves similarly to TEA in terms of complex formation. Therefore, the sulfur and oxygen atoms of the SO₂-amine complex have more than likely some direct interaction with the —OH of methanol.

As described previously, SO₂ itself had no influence on methanol; only SO₂ complexed with DEA or TEA reacted with methanol (Figs. 1 and 3). Special steric and/or electronic factors of the sulfur and oxygen atoms of the SO₂-amine complex seems to have caused the new complex formation with the —OH of methanol. The ¹H-NMR data (Figs. 1-3) indicate that the —OH proton of methanol increased its acidity by the formation of a complex with the SO₂-amine complex.

The fact that the chemical shift became the lowest when methanol was mixed with the SO₂-amine complex in the molar ratio of 1 : 1 indicates that

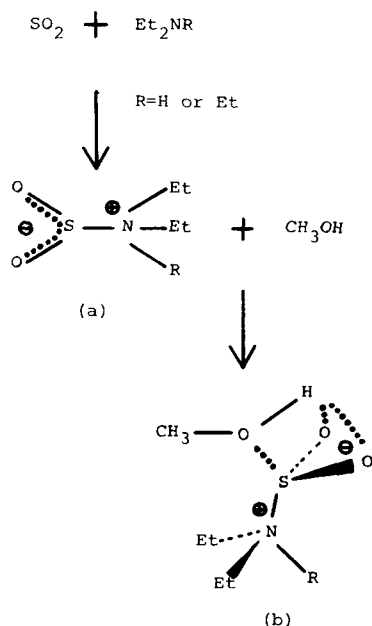


Fig. 4. Reaction of methanol with SO₂ and amine in DMSO.

the —OH of methanol reacts quantitatively with the SO_2 -amine complex to form the new complex, as shown in Figure 4(b).

Dissolution Mechanism of Cellulose in SO_2 -Amine-DMSO Systems

Figure 5 shows $^1\text{H-NMR}$ spectra of cellulose solutions of SO_2 -DEA-DMSO and SO_2 -TEA-DMSO systems, in which the SO_2 -amine complex equimolar to the —OH of cellulose was mixed. The chemical shifts of the methylene and methyl protons of the amines were equal to those observed in the methanol/ SO_2 -amine-DMSO systems (Figs. 1 and 3). The chemical shift of the —OH protons of cellulose in both solutions also coincides with those (7.8 ppm) observed in the model experiments. This result indicates that all hydroxyl groups in cellulose form complexes as shown in Figure 7. If cellulose had some free hydroxyl groups in solution, the chemical shifts of the —OH proton of cellulose would have been shifted to a magnetic field higher than 7.8 ppm. It is known that more than 3 mol of SO_2 -amine (SO_2 : amine = 1:1 by mol) per glucose residue of cellulose are required to prepare a completely clear solution, when the SO_2 -amine-organic solvent systems are used as cellulose solvents. This supports the stoichiometric reactions among the —OH of cellulose, SO_2 , and amine in DMSO.

Figure 6 shows $^{13}\text{C-NMR}$ spectra of the two cellulose solutions. No apparent difference was detected in the chemical shifts of the cellulose carbons between the two cellulose solutions, indicating that the same type of complexes are formed. The peaks from the C-1 and C-4 carbons appear at 102 and 79 ppm, respectively, as single peaks, and these values are almost equal to those of cellulose oligomers.¹⁴ The peaks from the C-6 carbons of the two cellulose solutions appear at 59 ppm as single peaks, and the difference of the chemical shift due to C-6 carbons between cellulose in the SO_2 -amine-DMSO systems and cellulose oligomers in DMSO (61 ppm)¹⁴ is 2 ppm. As shown in Figure 2, the difference in the chemical shift between the methyl carbon of methanol in the methanol/ SO_2 -DEA-DMSO ($\text{MeOH}:\text{SO}_2:\text{DEA} = 1:1:1$)

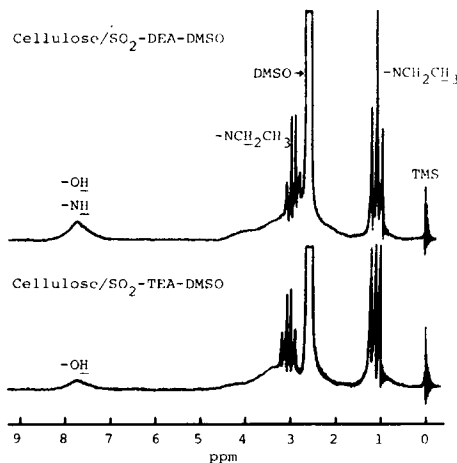


Fig. 5. $^1\text{H-NMR}$ spectra of cellulose/ SO_2 -diethylamine-DMSO and cellulose/ SO_2 -triethylamine-DMSO solutions.

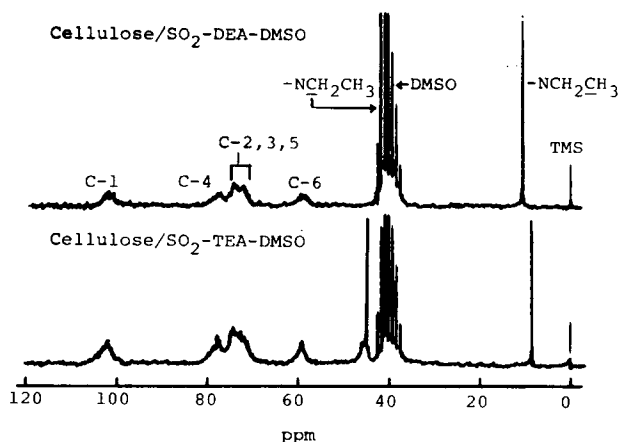


Fig. 6. ¹³C-NMR spectra of cellulose/SO₂-diethylamine-DMSO and cellulose/SO₂-triethylamine-DMSO solutions.

and that in the DMSO solution was also 2 ppm. Although the signals from the C-2 carbons of cellulose overlap with those of the C-3 and C-5 carbons, the chemical shift of the C-2 carbons were detected clearly at higher magnetic fields than that (74 ppm) of cellulose oligomers in DMSO.¹⁴

These NMR analyses, therefore, prove that the reactions among the —OH of cellulose, SO₂, and amine in DMSO are completely equal to those in methanol/SO₂-amine-DMSO systems. Furthermore, the above data indicate

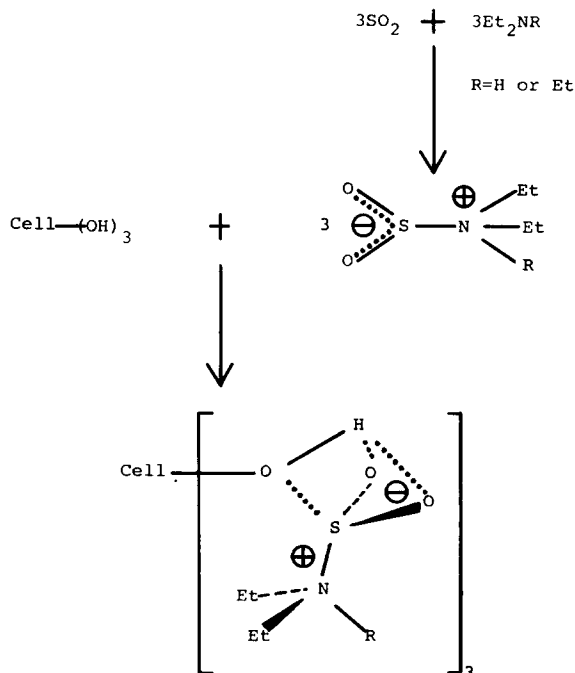


Fig. 7. Dissolution mechanism and state of cellulose in SO₂-amine-DMSO systems.

that almost all hydroxyl groups in cellulose form complexes as shown in Figure 7.

As reported in the previous paper,¹⁵ the SO₂-DEA-DMSO system dissolves native celluloses and their mercerized samples, but not regenerated celluloses, amylose, starch, glucomannan, xylan, and pectin. These phenomena support the idea that the sulfur and oxygen atoms of the SO₂-amine complex, which contribute sterically and/or electronically, react only with the —OH of native and mercerized celluloses. These celluloses, which have specific intra- and intermolecular hydrogen bonds, produce a complex between the —OH of cellulose, SO₂, and amine in DMSO.

References

1. A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.*, **29**, 2097 (1984).
2. A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.*, **29**, 3873 (1984).
3. A. Isogai, A. Ishizu, J. Nakano, S. Eda, and K. Kato, *Carbohydr. Res.*, **138**, 99 (1985).
4. A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.*, **31**, 341 (1986).
5. A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.*, **30**, 345 (1985).
6. K. Hata and K. Yokota, *Sen-i Gakkaishi*, **22**, 96 (1966).
7. K. Hata and K. Yokota, *Sen-i Gakkaishi*, **24**, 415 (1968).
8. K. Hata and K. Yokota, *Sen-i Gakkaishi*, **24**, 420 (1968).
9. S. Yamazaki and O. Nakao, *Sen-i Gakkaishi*, **30**, T234 (1974).
10. B. Philipp, H. Schleicher, and W. Wagenknecht, *Cellulose Chem. Technol.*, **9**, 265 (1975).
11. A. B. Turbak, *Chemtech.*, **10**, 51 (1980).
12. S. M. Hudson and J. A. Cuculo, *J. Macromol. Sci.*, **C18**, 1 (1980).
13. R. M. Silverstein, G. C. Bussler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1981, p. 198.
14. D. Gagnaire, D. Mancier, and M. Vincenden, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 13 (1980).
15. A. Isogai, A. Ishizu, J. Nakano, and R. H. Atalla, *Solid State Characterization of Cellulose*, ACS Symposium Series, Am. Chem. Soc., Washington, DC, 1986, to appear.

Received June 11, 1986

Accepted July 22, 1986