Dissolution Behavior of Cellulose In The Binary Solvent of Polar Aprotic Solvent And TBAA

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Research Article

Keywords: Cellulose, dissolution, tetrabutylammonium acetate, TBAA, polar aprotic solvent, solubility, solvation

Posted Date: May 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-445982/v1>

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Abstract

We have found that cellulose could be dissolved rapidly in the binary solvent of polar aprotic solvents (PAS) and tetrabutylammonium acetate (TBAA) in a high solubility. The polar aprotic solvents includes dimethyl sulfoxide, pyridine, dimethylacetamide, dimethylformamide and N-Methyl-2-pyrrolidone. The factors affecting the dissolution behavior of cellulose was investigated and it is indicated that the solubility and dissolution rate of cellulose in the binary solvent are significantly dependent on the species of PAS and the molar ratio of PAS/TBAA. Among all the polar aprotic solvents, dimethyl sulfoxide is the best one, being attributed to its high diffusivity and strong solvation ability. The optimal molar ratio of PAS/TBAA was determined by donor number of the polar aprotic solvents. The dissolution of cellulose in the binary solvent was proposed to involve three processes, namely solvent diffusion, solvation of TBAA as well as disruption of the intermolecular or intramolecular hydrogen bonds (H-bonds) of cellulose.

Introduction

Cellulose is the most abundant renewable organic resource on Earth. It is also an excellent natural homopolymer with high mechanical properties and high heat resistance. However, it neither dissolves in the general solvents nor melts on heating due to its strong intermolecular or intramolecular H-bonds, which thus greatly limits its application areas.

Except to the traditional paper field, the most important applications of cellulose is the formation of fiber and film. Conventional processes for the cellulose formation are composed of dissolution through derivation of cellulose such as viscose and cupper amine processes, and regeneration to film (cellophane) or fiber (rayon). However, the conventional processes have been found to cause serious environmental pollution, due to the use of volatile and odiferous CS_2 and the by-products. In despite of this, the viscose process is still commonly used because no solvent could completely replace it with respective to the process cost.

Since 1970, several organic solvent systems have been developed for the direct dissolution of cellulose, such as lithium chloride/dimethylacetamide ($\text{LiCl}/\text{DMAc}/$) (Charles et al. 1980; Morgenstern and Berger 1993), N-methylmorpholine oxide/water ($\text{NMMO}/\text{H}_2\text{O}$) (Borbely 2008), and 1-butyl-3-methylimidazolium (BMIMCL) (Swatloski et al 2002; Swatloski et al 2002) etc.

LiCl/DMAc has a low solubility, thus its commercial application is greatly limited. $\text{NMMO}/\text{H}_2\text{O}$ has a high solubility and has already been used in the commercial production of cellulose fiber. However, the instability of NMMO may cause a safety risk due to its possible spontaneous decomposition (Liebert 2010).

BMIMCL was found to dissolve cellulose with high solubility (Remsing et al 2006; Liebner et al 2010; Mikkola et al 2007). However, its overall dissolution process is very long, typically extending for a period of several hours. Furthermore, the dissolution is conducted at a temperature higher than 100°C , so cellulose is usually unstable and tends to decompose during dissolution. It was found that addition of a

polar aprotic solvent to BMIMCL could increase the dissolution rate and improve the rheology of the obtained cellulose solution (Lin 2013).

In 2011, we discovered a completely new solvent for cellulose, which is a binary solvent of a polar aprotic solvent (PAS) and tetrabutylammonium acetate (TBAA) (Lin et al 2015). It is capable of providing an optically clear solution of cellulose without chemical modification, and the obtained cellulose solution could be regenerated to cellulose film and fiber by precipitation into a variety of nonsolvents, such as water, alcohols, or acetone. The cellulose solution could also be used for the preparation of cellulose derivation.

In this paper, it was attempted firstly to investigate the dissolution behavior as well as the affecting factors, and secondly to propose a dissolution mechanism of cellulose in this new binary solvent.

Experimental

Materials

TBAA was used as purchased from Tokyo Chemical Industry Co., Ltd. Four kinds of cellulose were used, that is, microcrystalline cellulose powder (Merck, 250 DP), NPI's powdered cellulose (W-100G, 400DP), needle bleached Kraft pulp (NBKP, 1300DP, thickness of approximately 1mm) sheet and absorbent cotton, each of which was used without any treatment such as drying. All the solvents used were purchased from NACALAI TESQUE, INC.

Dissolution of cellulose

The dissolution experiments were carried out in a 10ml transparent sample vial with a heating magnetic stirrer to aid the dissolution. The temperature of the heating magnetic stirrer was set at 50°C for all the dissolution experiments except where indicated. A given amount of cellulose was placed into the binary solvent of TBAA/PAS and stirred until an optical transparent solution was obtained and the necessary time was defined as dissolution time. During the dissolution, 0.1 ml samples were collected at regular time intervals for the polarization microscope observation to make sure whether cellulose was completely dissolved. The same agitation speed (600rpm) and sample vial (10ml) were used in all the dissolution experiments.

Determination of the solubility

The solubility of cellulose was defined as the maximum amount of cellulose that ultimately dissolve in a given quantity of solvents. It was expressed in the unit of g/100g and was measured according to the following procedure.

To 2g binary solvent of TBAA/PAS, a certain amount (0.05-0.5g) of cellulose was added and stirred for 3hr, following by observation by the polarization microscope to make sure whether cellulose completely dissolved. If the solution was optically clear, the same dissolution experiment was done except for adding

more amount of cellulose, and the solubility was determined by simply repeating the same experiment over and over until the cellulose solution began to become optically unclear.

Determination of the dissolution rate

Dissolution rate was expressed as time (minute) that was required for dissolving a given amount of cellulose in the binary solvent of TBAA/PAS. It is the period from adding cellulose to the binary solvent of PAS/TBAA until an optically clear solution was obtained.

Measurement of solvent retention value (SRV) in pulp sheet

SRV is an indication of cellulose fiber's ability to take up solvent. It was defined as the ratio of the solvent mass to the dry mass of NBKP sheet and was measured according the following procedure.

NBKP sheet was cut into a 15mm square and weighted (W_0) before the measurement of SRV. To a 30 ml sample vial, 10 ml polar aprotic solvent was added, followed by placing into the pulp sheet. After covering the vial, it was kept at room temperature for a given time, and then the NBKP sheet was taken out from the solvent and the excessive solvent retained on the surface of pulp sheet was removed by touching with KimWipes and then it was weighted (W). SRV is calculated in according the equation shown below.

$$SRV = (W - W_0) / W_0 \times 100\%$$

Results And Discussion

Dissolution of cellulose in TBAA/DMSO

The dissolution of cellulose in the binary solvent of TBAA/DMSO with a molar ratio of 10/1 was conducted at 50°C. The solubility and dissolution rate were determined and the results are shown in Figs. 1 and 2.

They indicate that a large amount of cellulose can be dissolved in the binary solvent of TBAA/DMSO regardless to the crystalline degree, shape or size of cellulose. The solubility and dissolution rate increases with a decrease in the degree of polymerization (DP) of cellulose. In the case of microcrystalline cellulose, the cellulose solution became optically unclear if the cellulose concentration was higher than the solubility shown in Fig. 1. However, in the case of NBKP or absorbent cotton, the solubility was limited not due to the optical opacity but the excessive viscosity which makes it impossible to stir.

The effect of temperature on the dissolution time was evaluated and the results are shown in Fig. 3. Even cellulose could be dissolved at room temperature, the dissolution rate increased considerably with increasing temperature up to 50°C, and then dissolution rate becomes less dependent on temperature. It is suggested that an increase in temperatures do not only promote the solvent diffusivity or accessibility but also affect the solvation of TBAA.

Effect of DP or temperature on viscosity of cellulose solution are investigated and the results are shown in Figs. 4 and 5. It can be seen that viscosity increases with an increase in DP or a decrease in temperature, revealing an opposite tendencies to those of solubility and dissolution rate. This result is suggested to be attributed to the fact that an increase in viscosity could reduce the diffusion and in turn hinder the cellulose dissolution.

The above results indicates that the dissolution of cellulose in the binary solvent seems to be a diffusion-determining process. Therefore, any factor increasing the viscosity can extend the dissolution time, such as, the concentration and DP of cellulose, as well as temperature etc.

Dissolution of NBKP in various binary solvents

In order to understand what roles the polar aprotic solvent and TBAA play in dissolution, the dissolution of cellulose in various binary solvents containing 15wt% TBAA was conducted and the results are shown in Table 1.

It can be seen that a large amount of cellulose could be dissolved in all the polar aprotic solvents (PAS) in Group A which are large in both donor number (DN) and acceptor number (AN), and slightly dissolved in the polar aprotic solvents in Group B which DN are large but AN are small. However, cellulose could not be dissolved but swelled in the polar aprotic solvents in Group C which have are low in both DN and AN. It is interesting to find that cellulose could neither be dissolved nor swelled in all the protic solvents such as water and alcohol, etc. The results suggest that solubility be affected not only the donor ability but also the acceptor ability of PAS.

In order to verify the cellulose solubility in various binary solvents containing the PAS in Group A and Group B, the relationship between the molar ratio (MR) of PAS/TBAA and solubility was investigated and result is shown in Fig. 6.

It demonstrates that solubility increase with an increase in MR of binary solvents to a maximum value and then turn to decrease regardless the species of PAS. The MR for obtaining the max solubility is expressed as the optimal molar ratio (OMR) and was plotted with DN as shown in Fig. 7. It reveals an increasing tendency with an increase in DN. One except is only pyridine, being due probably to its basicity which may diminish the solvation of TBAA.

On the other hand, the max solubility did not simply increase with an increase in the DN value, suggesting that there exist other factors affecting the solubility.

Solvent retention value (SRV)

Usually, the dissolution of a polymer into a solvent involves two transport processes, namely solvent diffusion and chain disentanglement. SRV could provide a measure of solvent diffusivity or accessibility for the cellulose, which in turn enables prediction of the contribution of polar aprotic solvents to dissolution of cellulose.

The SRV of NBKP sheet in various PAS was measured and the results are shown in Table 3 and Fig. 8.

It is seen that SRV of DMSO increased to 500% within 15 minutes, approximately five times of other PAS in Group A and ten times of those in Group B and C. It means that PAS of large DN and AN has a high SRV. Furthermore, by plotting SRV with maximum solubility, it is interesting to see that the solubility has a good relation with SRV, as shown in Fig. 9, revealing an increasing tendency with an increase in SRV.

A proposal for the dissolution mechanism

The results mentioned above indicate that solubility is affected by SRV and the optimal molar ratio (OMR) is determined by donor number. In fact, both of SRV and OMR decisively affect the valid amount of TBAA that really access to cellulose. The higher SRV or the lower OMR, the larger the valid amount of TBAA.

It is known that the dissolution of cellulose is quite different from the common homopolymer because it consists of a huge amount of intermolecular and intramolecular H-bonds. A good solvent for cellulose involves not only the solvent diffusion, but also the capability of disrupting the H-bonds.

Cellulose could not dissolve in DMSO, even though it has an exceedingly high diffusivity. Therefore, TBAA is suggested to be the determinant factor of H-bond disruption, and a comprehensive understanding of TBAA solvation phenomena in the binary solvent system is essential for investigating the disruption of H-bonds of cellulose.

Solvation or ionization is mostly commonly found in electrolyte. There are many experimental and computational studies (Cox et al 1974; Mayer 1975; Sebastien 2015; Izutsu 1980) have been reported for the solvation of alkali cations in various organic solvents especially the polar aprotic solvents.

It have been indicated that solvent with stronger donor ability has higher solvation ability. That is, the solvation ability increases with an increase in DN. It was also reported that tetraalkylammonium cation (R_4N^+) is stable in polar aprotic solvents but unstable in water.

Based on the reports, it was suggested that in those binary solvents that contain PAS of high DN, TBAA could be solvated or ionized to cation TBA^+ and anion Ac^- . Anion Ac^- could form strong interactions with hydroxyl groups of cellulose, leading to the disruption of H-bonds between inter or intra cellulose chains. In order to verify the suggestion, pH of various TBAA solution was measured regarding with the effect of DN. In this experiment, the TBAA concentration was fixed to 30wt%, and the mass ratio of PAS/water is faxed to 3/1 to facilitate the pH testing. The results are shown in Fig. 10.

It can be seen that pH of TBAA solution in water and methanol are respectively 6.5 and 7.5, being close to neutral. However, it is interesting to see that pH value increase remarkably after adding a polar organic solvents and showing an increasing tendency with an increase in DN. The results indicate that in the polar aprotic solvent, TBAA could be solvated into TBA^+ and Ac^- and the solvation ability increase with an increase in DN.

Based on these results, it is proposed that dissolution of cellulose in the binary solvent of PAS/TBAA involves three processes, namely solvent diffusion, solvation of TBA⁺ to give rise anions Ac⁻, and disruption of H-bonds. The higher the solvation ability, the easier the disruption of H-bonds. DMSO is the optimal solvent for cellulose dissolution, being attributed to its high diffusivity and strong solvation of TBA⁺.

Declaration

Author declaration

KRI, Inc. is my employer from 2005 to present. I have engaged in the study related to submitted work from 2009. The submitted work was supported by KRI, Inc.

- Conflicts of Interest / Competing Interests: Lianzhen Lin state that there are no conflicts of interest or competing interests.
- Patients' rights and animal protection statements: Lianzhen Lin state that this article does not contain any studies with human or animal subjects.
- Funding: Lianzhen Lin state that all the submitted work was support by KRI, Inc. No funding was received for this work.
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- I contributed to the study conception and design. All material preparation, data collection and analysis were performed by me. The manuscript was also written by me.
- I confirm that the manuscript has been read and approved by all named authors.
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I agree with all of the above.

Author's name (Fist, Last) Signature Date

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Tables

Table1 Solubility of cellulose (NBKP) in various binary solvents of TBAA

Group	Solvent ^a	DN ^b	AN ^b	Solubility of NBKP
A	DMSO	29.8	19.3	Soluble (7g/100g or more)
	pyridine	33.1	14.2	
	DMF	26.6	16.0	
	NMP	27.3	13.3	
	DMA	27.8	13.6	
B	DMI	27.8	-	Slightly soluble (Less than 1g/100g)
	TMU	31.2	9.2	
	HMPA	38.8	10.6	
	DMPU	29.3	-	
C	THF	20	8	Insoluble but swelled
	Acetone	17	12.5	
	Acetonitrile	14.1	18.9	
D	water	18.0	54.8	neither swelling or soluble
	methanol	19.0	41.5	
	ethanol	19.2	37.9	

^aDMI: 1,3-dimethyl-2-imidazolidinone; TMU: N,N,N',N'-Tetramethylurea; HMPA: hexamethylphosphoramide; DMPU: N,N'-dimethylpropyleneurea.

^bGutmann Acceptor and Donor number

Table 2. SRV of various PAS for NBKP sheet

solvent	DN	AN	dielectric constant	SRV (%)
DMSO	29.8	19.3	47	561
pyridine	33.1	14.2	12.3	115
DMA	27.8	13.6	37.8	101
NMP	27.3	13.3	32	112
DMF	26.6	16.0	36.7	125
TMU	31.2	9.2	23.1	45
HMPA	38.8	10.6	30	40
DMPU	29.3	-	37	35
Acetone	17	12.5	21	37
Acetonitrile	14.1	18.9	37.5	30

Figures

Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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Figure 7

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Figure 8

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Figure 9

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Figure 10

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