

INVESTIGATIONS ON SOLUTION OF CELLULOSE IN COMPLEX PHOSPHORIC ACID SOLVENT AND ITS STABILITY

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Cotton cellulose pulp was dissolved in phosphoric acid (PA) complex solvent and properties of the subsequent solution were discussed. Equivalent P_2O_5 concentration was calculated to clarify theoretically the compositions in the dissolution media. The resulting dark yellow solution confirmed Boerstoel's suggestion that cellulose must be degraded when temperature of solution is higher than 42 °C. Cholesteric lyotropic liquid crystalline solutions prepared at 72%, 73% and 74% P_2O_5 were observed. The clearing temperature of corresponding solutions was determined by hot-stage polar light microscope (PLM). The complex PA solvent prepared with P_2O_5 concentration of 73% had stronger dissolution power than those prepared with other concentrations. Phosphorus molar ratio data showed that tetraphosphoric acid (TPA) can result in indirect dissolution of cellulose, once P_2O_5 concentration of the complex solvent reaches 74%. Solution stability through DP analysis of cellulose solutions revealed significant results on the intrinsic sensitivity of this complex solvent to cellulose.

Keywords: cellulose, complex phosphoric acid solvent, dissolution behavior, liquid crystalline solution, dissolution power, stability

INTRODUCTION

New environmentally friendly and recycled materials have attracted attention with the rapid utilization of petroleum sources. Researchers have concentrated on cellulose dissolution and preparation of the corresponding solution. Results indicate the possibility and convenience of cellulose coagulation and regeneration. Owing to the intrinsic property of strong reactions of hydrogen bonding in cellulose, determining a proper solvent or solvent system to break this reaction and accomplish the dissolution has become an interesting and necessary proposition.

Extensive studies on solvents for cellulose have been conducted, including a recent work on ionic liquid (IL)¹⁻⁵ and NaOH complex solvent system.⁶⁻⁹ Phosphoric acid (PA) is one of the favored solvents for cellulose dissolution. The acid represents common mineral acids, such as

orthophosphoric acid (OPA, pure H_3PO_4), pyrophosphoric acid (PPA, pure $H_6P_2O_7$), tetraphosphoric acid (TPA, pure $H_6P_4O_{13}$), and so on. To evaluate the concentration of different acids conveniently, wt% P_2O_5 and wt% H_3PO_4 were introduced (wt% $H_3PO_4 = 1.38$ wt% P_2O_5),¹⁰ which is consistent with Ullman's Encyclopedia.¹¹ Empirically, it was reasonable to believe that P_2O_5 (P_4O_{10}) was an equivalent material in the evaluation of the concentration of PA in different forms because phosphorus atom is unchangeable regardless of reactions. For example, the wt% P_2O_5 for pure orthophosphoric acid (H_3PO_4) could be calculated by the molar mass ratio of 0.5 P_2O_5/H_3PO_4 , which is approximately 72.4%. For more than 80 years, PA has been the most popular solvent among inorganic mineral acids for the dissolution of crystalline cellulose owing to its

non-corrosive and non-toxic properties, safety, and low cost. The dissolution of cellulose in concentrated acids has been shown to undergo decrystallization/swelling prior to dissolution by forming cellulose-acid complexes.¹² Low crystalline cellulose was regenerated from PA solutions at different agitation rates.¹³ Other studies have employed pretreated cellulose with OPA to enhance enzymatic hydrolysis,¹⁴⁻¹⁶ 85% PA aqueous solution to improve saccharification,¹⁷ 83% aqueous PA solutions¹⁸ and OPA,¹⁹ which have been used in the fermentation of cellulose to bioethanol. OPA has been demonstrated to have the capacity to break intra-molecular hydrogen bonds in cellulose through formation of phosphor-ester linkages.¹⁹ Butera *et al.*¹⁹ referred to cellulose dissolution in OPA, and achieved a homogeneous liquid solution because OPA was able to withdraw intra-molecular hydrogen bonds in cellulose through formation of phosphor-ester linkages. The dissolution mechanisms of cellulose in OPA are accompanied by molecular packing density of cellulose in specific concentrations of aqueous PA solutions²⁰ and reaction between OPA and cellulose to form C-O-P bridges.²¹

After the first report of liquid crystalline solution of hydroxypropyl cellulose,²² the dissolution of acetoxypropyl cellulose in acetone,²³ and acetyl-ethyl-cellulose in chloroform,²⁴ as well as cellulose in DEA-DMSO²⁵ and NMMO-H₂O,²⁶ has been developed for liquid crystalline cellulose and cellulose derivatives. Relationships between P₂O₅ content and solvent, cellulose concentration, and degree of polymerization and clearing temperature, as well as correlative kinetic theories of the relationship, have been investigated separately.²⁷ However, minimal illustration of or result on the phenomenon of liquid crystalline solution has been put forward. Additionally, the molecular weight distribution of cellulose in solution and viscosimetry of regenerated cellulose samples redissolved in copper II ethylene diamine have been less accurate than those of viscosimetry of solution prepared by raw cellulose dissolved in complex PA solvent used to evaluate the stability of cellulose solution. Thus, for more than a decade, there had been no similar investigation on the dissolution of cellulose by this acidic solvent, the consequent liquid crystalline solution properties and its stability.

This work aimed to study the complex solvent system composed of orthophosphoric acid (OPA) and tetraphosphoric acid (TPA) in terms of intrinsic dissolution sensitivity to cellulose with the relatively higher crystallinity of 70% and polymerization degree of 1000.

Moreover, the formation and stability of the corresponding liquid crystalline solution were studied by XPS, PLM and viscometer measurements, and the degree of polymerization was calculated.

EXPERIMENTAL

Materials

Cotton cellulose with a degree of polymerization (DP) of 1000 (Xiangtai Cell. Co., Ltd. Hubei, China) was dried at 65 °C in vacuo for 24 h. For further use, the cellulose was dried with desiccant at ambient temperature. Phosphoric acid aqueous solution (85% purity) composed of orthophosphoric acid, OPA, H₃PO₄, (1.685 g/cm³ density) and tetraphosphoric acid H₆P₄O₁₃ (TPA, 80% P₂O₅ concentration, 2.0 g/cm³ density) were supplied by Guoyao Reagent Co., Ltd. (Shanghai, China).

Complex solvent preparation

To improve the accessibility of this complex solvent to crystalline cellulose, structures of OPA and TPA were eliminated. To maintain equilibrium, PA aqueous solution and TPA were proportionally stirred at 43 °C for 2 h according to the pre-determined average P₂O₅ concentration. Subsequently, 72.4% P₂O₅ concentration of pure OPA was calculated from the formula weight ratio P₂O₅/H₃PO₄. The TPA used in this study contained 80% P₂O₅. After that, this solvent was stored at 0 °C for 24 h.

Cellulose dissolution

Cellulose pulps and prepared complex PA solvent at 17 cellulose-to-liquor wt% were poured into a 10 L kneader at 0 °C, and agitated at 40 rad/min, according to a range of pre-determined time to prepare the cellulose solution.

Solid content in cellulose solution

Cellulose solution was spread on a glass slide, coagulated by immersing in acetone for 5 min, washed in distilled water to remove any remnant acid, and dried at 42 °C in vacuum for 2 h. Regenerated cellulose content in solution was calculated as $\frac{C}{B-A}$, with the mass of the glass slide, glass slide coated with cellulose solution and the prepared membrane denoted as *A*, *B* and *C*, respectively.

Characterization

Polar Light Microscope (PLM) measurement

The dissolving process of cellulose in complex PA solvent was observed on a XPR-500C Polar Light Microscope (PLM, with a hot stage, Caikon Optical Instrument Company, China). Each cellulose solution was sandwiched between a cover slip and a glass slide and observed under elevated temperatures until the disappearance of the liquid crystalline phenomenon. The first temperature at which the liquid crystalline phenomenon disappeared was called the clearing temperature of this solution.

X-ray photoelectron spectra (XPS) measurement

Spectra of regenerated cellulose membranes were obtained with a vacuum PHI 5000 Versaprobe spectrometer, using monochromated AlK α radiation. Peak fitting was carried out for high resolution C1 signals (after Shirley type background subtraction), using curve fitting SURFSOFT programs with a 6040 Gaussian-Lorentzian ratio.

Viscosity measurement

Viscosity of solvents was measured at 25 °C and 50% relative humidity using a NDJ-7 type rotary viscometer (Precision & Scientific Instrument Ltd. Co., Shanghai, China). Each 15 mL specimen of either homogeneous complex PA solvents or cellulose solution prepared with P₂O₅ concentrations of

72%-74% was degassed in vacuum, stored in a desiccator before viscosity measurement. The range of viscosity value was 1-10⁶ mPa·s.

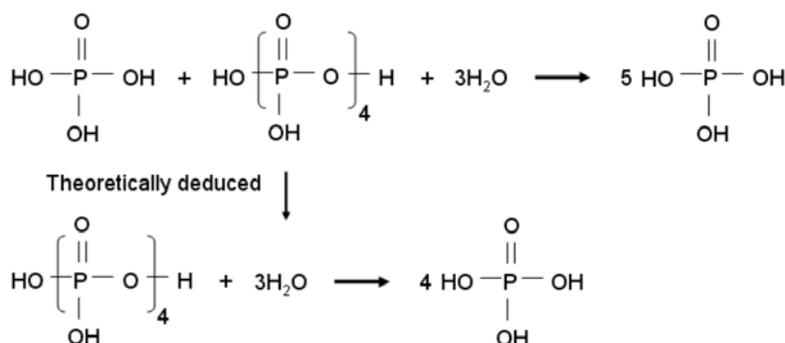
RESULTS AND DISCUSSION

P₂O₅ concentration definition and complex solvent composition analysis

Phosphoric acid refers to any polyphosphoric acid having a H₂O/P₂O₅ ratio of three or less. When the H₂O/P₂O₅ ratio is three, the polyphosphoric acid is orthophosphoric acid (H₃PO₄, OPA).²⁸ Pure OPA contains 72.4% P₂O₅ as calculated from the formula weight ratio P₂O₅/H₃PO₄.²⁹⁻³² The TPA used in the study contains 80% P₂O₅. To confirm the concentration of the complex solvent more conveniently, average P₂O₅ concentration is defined as its concentration. The calculating method is shown in equation 1. The composition of the solvent system should be clarified. According to the components and parameters of complex PA solvent, H₃PO₄, H₆P₄O₁₃ and water are present in the solvent system at the beginning of stirring. Scheme 1 shows the reaction formula.³³

$$P_2O_5(\%) = \frac{\sum P_2O_5 \text{ concentration of composition}_{(i)} \times \text{mass of composition}_{(i)}}{\text{Total mass of solvent}} \quad (1)$$

*composition*_(i) – Number *i* composition of solvent



Scheme 1: Reaction formula of H₃PO₄, H₆P₄O₁₃ and H₂O

Assuming that the mass of pure H₃PO₄ in PA aqueous solution is W , therefore, the mass of the rest of H₂O is $\frac{3}{17}W$. The mass of H₆P₄O₁₃ is

$\frac{12}{11}W$ according to Eq. (1). Thus, there is no water in the solvent system and the P₂O₅ concentration is 70.5%, on condition that the mass ratio of OPA

to TPA is 1:1.1 based on Eq. (2):

$$P_2O_5(\%) = \frac{W \times 72.4\% + 1.1 \times W \times 80\%}{\frac{100}{85}W + 1.1 \times W} = 70.5\% \quad (2)$$

Since the demarcation point of P_2O_5 concentration is determined, pure H_3PO_4 and H_2O coexist in the solvent, because P_2O_5 concentration is less than 70.5% (or the mass ratio of OPA to TPA is more than 1:1.1). In contrast, H_3PO_4 coexists with $H_6P_4O_{13}$ in the solvent when P_2O_5 concentration is more than 70.5% (or the mass ratio of OPA to TPA is less than 1: 1.1).

Fig. 1 shows the optical photographs of complex PA solvents filled with white powder of anhydrous $CuSO_4$. Since $CuSO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O$ and the color of the product is blue, the introduction of anhydrous $CuSO_4$ discriminates the water content in this solvent system. With the increase in P_2O_5 concentration, the fading tendency of the solvent color is strengthened due to the decrease in H_2O content in the complex PA solvent. Practically, the slight moisture in the air, which these solvents can easily absorb, turns the color to light blue. All the solvents were stored at 0 °C. Clearly, the solvents prepared with P_2O_5 concentrations of 68% and 69% are frozen by their internal water and non-transparent. However, the solvents prepared at and above 70% P_2O_5 are transparent, indicating that slight or no water was present in these solvents. Specifically, the solvents prepared at 70%, 70.5% and 71% P_2O_5 are composed of H_3PO_4 and contain a slight amount of water or

$H_6P_4O_{13}$. Thus, they can be ranked together. Moreover, the solvents prepared at 72%, 73% and 74% P_2O_5 , which contain $H_6P_4O_{13}$ and H_3PO_4 , are homogeneous.

Boerstael³⁴ pointed out that even a slight amount of water molecules would compete for the interaction with OPA during the dissolution of cellulose. Thus, cellulose could probably swell or not dissolve completely. To ensure that cellulose will be absolutely dissolved, the P_2O_5 concentration of the complex solvent should be equal to or above 72%.

Dissolution behavior

Combining previous research³⁵ with repeated experiments, we could focus on the dissolution behavior of cellulose dissolving in complex PA solvents at the P_2O_5 concentration range from 72% to 76%.

In Fig. 2, the hatched quadrate area at each P_2O_5 concentration represents the corresponding cellulose dissolving condition ranges. The average dissolution temperature is elevated from 38.5 °C to 58 °C as the P_2O_5 concentration increases from 72% to 76%. The highest dissolution temperature when cellulose dissolves in the complex PA solvent prepared at 76% P_2O_5 is 58 °C. Samuel³⁶ suggested that the optimal temperature range for the dissolution of cellulose in OPA is from 40 °C to 50 °C. Boerstael²⁷ found that the rapid degradation of cellulose might occur at temperatures above 42 °C.

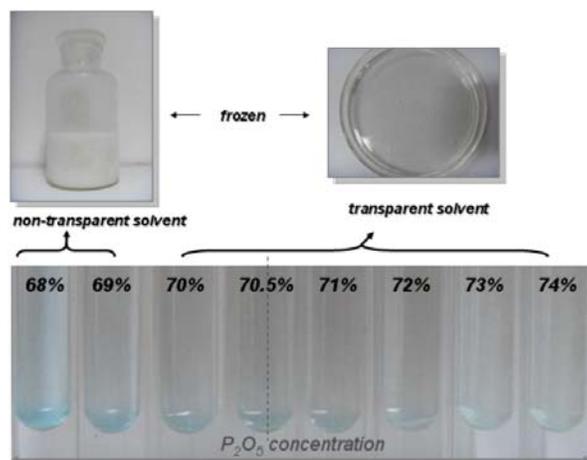


Figure 1: Complex PA solvents prepared with different P_2O_5 concentrations

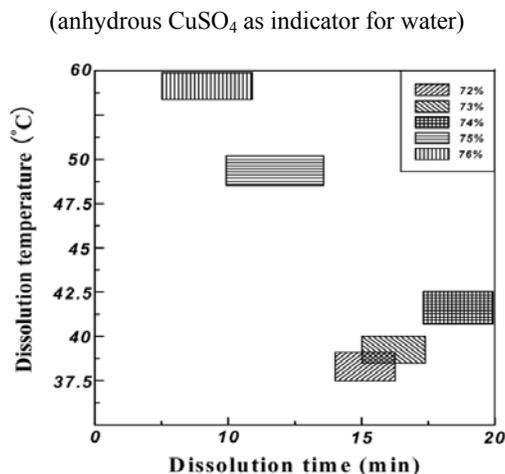


Figure 2: Dissolution of cellulose in complex PA solvent under parameters of concentration, temperature and time

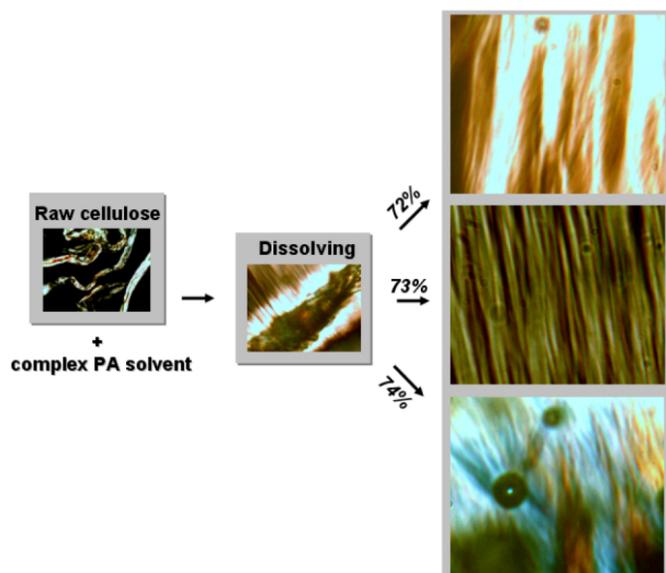


Figure 3: PLM micrographs (x600 magnifications) of liquid crystalline solutions prepared with different P_2O_5 concentrations

The dark yellow color of cellulose solutions prepared at 75% and 76% P_2O_5 suggests that cellulose in these solutions has been degraded.

Therefore, it could be speculated that the disappearance of cellulose solids in complex PA solvents at and above 75% P_2O_5 is due to degradation rather than dissolution. Additionally, the discrepancy between the maximum and minimum time of dissolution of cellulose in complex solvent prepared at 72% P_2O_5 , as well as that prepared at 73% P_2O_5 , is nearly 2 to 3 min.

The narrower the fluctuation of dissolution time, the more convenient the experiment becomes.

Formation of anisotropic cellulose solution

Cellulose solution that showed the absence of birefringence under crossed polarized light is considered isotropic. In Fig. 3, cellulose solutions possess the anisotropic property when the P_2O_5 concentration ranges from 72% to 74%. The fingerprint patterns can be observed as well. These are characteristics of cholesteric liquid

crystals.³⁷ Obscure fingerprint patterns appear at 72% and 74% P₂O₅ while those that appear at 73% P₂O₅ are clear. Furthermore, the light strikes the cholesteric liquid crystal in a right angle to the helicoidal axis; alternating retardation minima and maxima, corresponding to 90° rotations of the molecules around the helicoidal axis, are presented as alternating light and dark lines. Each distance between the light line and the adjacent dark line represents a 180° rotation of the molecules and is equal to half the pitch of the cholesteric liquid crystal on the average.³⁸ The solution prepared at 74% is iridescent, showing Bragg-like reflections in visible light. When white light is directed onto the solution samples, only characteristic wavelengths,³⁹ such as blue and red lights are reflected. Therefore, blue and red regions could be observed in the liquid crystalline solution. The presence of the fingerprint patterns in these solutions confirms their lyotropic cholesteric liquid crystalline nature.

Fig. 4 indicates that the clearing temperature of the cellulose solution is elevated from 103 °C to 137 °C, when the P₂O₅ concentration changed from 72% to 74%. Clearing temperature is another characteristic property of liquid crystalline solutions.²⁷ Based on this, the higher the clearing temperature of the liquid crystalline solution, the more stable the liquid crystalline property of this solution might be. Moreover, once the liquid crystalline solution with higher clearing temperature has formed, destruction by reactions through thermal methods rarely occurs. Considering the thermal stability of the cellulose solution, the clearing temperature should be as high as possible.

Dissolution power of complex PA solvents

Evaluating the solubility of the cellulose dissolving in complex PA solvent is difficult because the extra viscose cellulose solution could not be centrifuged to allow separation from solutions. For this reason, cellulose solid content is introduced. Consequently, the dissolution power of various complex solvents can be discerned.

Fig. 5 shows the changes of cellulose solid content versus dissolving time at P₂O₅

concentrations of 72%, 73% and 74%. Drastic degradation of cellulose dissolved in complex solvent prepared with P₂O₅ concentrations of 75% and 76% results in slight or absence of precipitation of cellulose from these two solutions. This renders cellulose solid content insignificant; thus, this is not discussed in this paper. When cellulose is dissolved in the complex solvent at 72% P₂O₅, the cellulose solid content ranges from 10% to 12%, while the maximum value of cellulose solid content in the solution prepared at 73% P₂O₅ approaches 15.5%, which is proximal to the theoretical value of 17%. This observation indicates that the latter solvent exhibits better dissolution power on cellulose. Furthermore, the average value of solid content in solution prepared at 73% P₂O₅ is higher than those prepared at 72% and 74% P₂O₅ as dissolving time is less than 3 h. Thus, the strongest solvent prepared at 73% P₂O₅ seems the most adaptive to the preparation of cellulose solution, which could be readily available to fiber manufacture in the future.

Effect of composition in complex PA solvent on dissolution

A novel and classic analysis on dissolution mechanism of cellulose in H₃PO₄ (PA) was reported by Conte and his co-workers²¹ in 2009. On the basis of ¹³C, ³¹P and ¹H NMR measurements, they put forward a possible dissolution mechanism: an alternation of the three-dimensional structure of the liquid OPA in concomitance with the disruption of the microfibrillar structure of cellulose was achieved as a consequence of a solute-solvent reaction. This reaction involved formation of C-O-P bridges between OPA and cellulose. Another systematic and detailed study³⁶ illustrated that cellulose was protonated by OPA as protic acid and this new positively charged cellulose was dissolved in OPA solvent. In accordance with these viewpoints, it is feasible that OPA can be employed to dissolve cellulose effectively. According to Eq. (1) and Scheme 1, the actual TPA content in complex PA solvent can be easily figured out. Fig. 5 shows that the increase in the actual TPA content from 17% to 57.5% is nearly

linear, as the P_2O_5 concentration increases. At the same time, the values of phosphorus molar ratio in regenerated cellulose samples increase from 0.25% to 4.42%. No data were obtained at 75% and 76% on the phosphorus curve, as slight or no cellulose sample was obtained. This resulted from the drastic degradation of raw cellulose in these two complex solvents. As shown in Fig. 4, the solvent prepared at 73% possesses a stronger

dissolution power than those prepared at 72% and 74%. The above results illustrate that the introduction of TPA enhances the dissolution capacity of the complex solvent on cellulose. However, the P_2O_5 concentration of the dissolution power of this solvent system as well as the cellulose samples regenerated therein are sensitive.

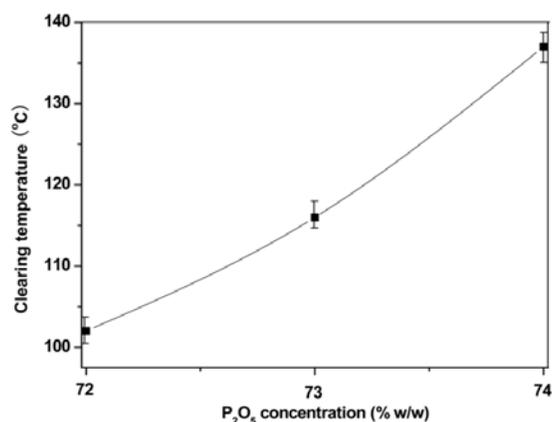


Figure 4: Effect of P_2O_5 concentration on clearing temperature for cellulose (17% w/w) solution

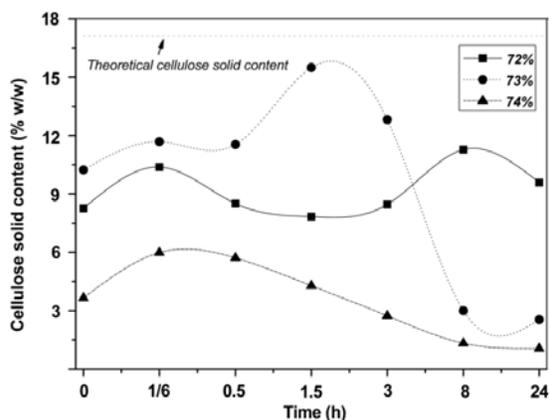


Figure 5: Changes of solid content of cellulose solution against dissolution time at different P_2O_5 concentrations

When P_2O_5 concentration reaches 74%, the intrinsic dissolution capacity of the solvent system is impaired and the molar ratio of phosphorus in regenerated cellulose sharply increases to 4.42%, nearly 9 times that of 0.48%

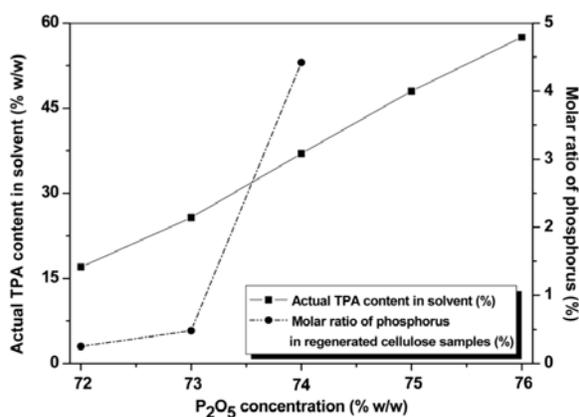


Figure 6: Changes of TPA content in solvent, and of molar ratio of phosphorus in regenerated cellulose sample prepared from solutions with different P_2O_5 concentrations

at P_2O_5 concentration of 73%. More functional groups carrying phosphorus element must be grafted on the cellulose molecular chains. TPA reveals its negative effect on dissolving cellulose. Based on this, the complex solvent might be

considered as an indirect solvent system in the dissolution of cellulose.

Stability analysis of the cellulose solutions

Cellulose can be considered as a classic polymer. Thus, DP of cellulose in dilute solutions [0.5%, 1%, 1.5% and 2% selected as cellulose content (% w/w) for dilute solutions] could be calculated by Wei's method. The degree of polymerization is determined from measurements of viscosity η at 25 ± 0.5 °C, according to Eq. (3):¹²

$$DP = 190 \times [\eta] \quad (3)$$

Parameter $[\eta]$ is the intrinsic viscosity calculated from the plot between $(\eta_{sp}/C)_{c \rightarrow 0}$ and C , where C is the cellulose content in g/100 mL. The value conversion between cellulose content (% w/w) and cellulose content (g/100 mL) is shown in Table 1. Suppose cellulose with a fixed mass assumed as L (2 g, 1.5 g, 1 g, or 0.5 g) was dissolved in 100 g complex PA solvent. Since the mass ratio between OPA and TPA could be calculated according to Eq. (1) at any fixed P_2O_5 concentration (72%, 73%, or 74%), the volumes of OPA and TPA in the corresponding complex PA solvent are determined and assumed as M and N , respectively. The cellulose content (g/100 mL) in solution was consequently obtained by $\frac{100 \times L}{M+N}$.

The specific viscosity of a cellulose solution can be written as:

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 \quad (4)$$

and the reduced viscosity is:

$$\frac{\eta_{sp}}{C} = \frac{\eta - \eta_o}{\eta_o C} \quad (5)$$

where η is the viscosity of cellulose solution, and η_o is the viscosity of the corresponding complex solvent.⁴⁰ The η_o values of the complex PA

solvents prepared at 72%, 73% and 74% P_2O_5 are of 400 mPa·s, 700 mPa·s and 1100 mPa·s, respectively. All data of η are obtained and finally converted into $\frac{\eta_{sp}}{C}$ with η_o , separately.

Fig. 7 exhibits a linear dependence between $\frac{\eta_{sp}}{C}$ and C in the entire range of cellulose content. By extrapolating $\frac{\eta_{sp}}{C}$ to zero, the intrinsic viscosity $[\eta]$ can be obtained. The relationship between $[\eta]$ and DP is shown in Eq. (3). Subsequently, the DP values of cellulose in dilute solutions are deduced.

Fig. 8 displays the curves of DP of cellulose in dilute solution prepared with different P_2O_5 concentrations versus storage time. DP values of cellulose dissolved in solution prepared at 72% and 73% fluctuate between 780 and 950, and 820 and 910. The starting DP of cellulose in 74% solution is 713, which is lower than those of cellulose in solutions prepared at 72% P_2O_5 (DP 949) and 73% P_2O_5 (DP 913). Fig. 6 indicates that the DP of cellulose at the beginning decreases as TPA content in the complex solvent increases. In general, all curves of DP of cellulose in complex PA solvent (72%, 73% and 74%) exhibit a tendency to decline as time increases.

A similar acidic solvent system was utilized by Boerstoele²⁷ in 2001. The author showed that DP of cellulose changes from 800 to 600 on the average. Thus, it is reasonable to believe that cellulose could be stored in the solvents prepared at 72% and 73% for 3 h, since its DP varies between 950 and 550. The powerful complex PA solvent can successfully dissolve cellulose with high crystallinity and polymerization degree and can be processed into liquid crystalline solutions with high cellulose contents. These characteristics highlight the potential of the process to effectively produce cellulose fibers with a high orientation degree and predominant mechanical properties at an industrial level.

Table 1
Value conversion of cellulose content in corresponding solutions

Cellulose content (g/100 mL)	Cellulose content (% w/w)			
	2%	1.5%	1%	0.5%
72%	3.78	2.82	1.87	0.93
73%	3.81	2.85	1.89	0.94
74%	3.85	2.87	1.90	0.95

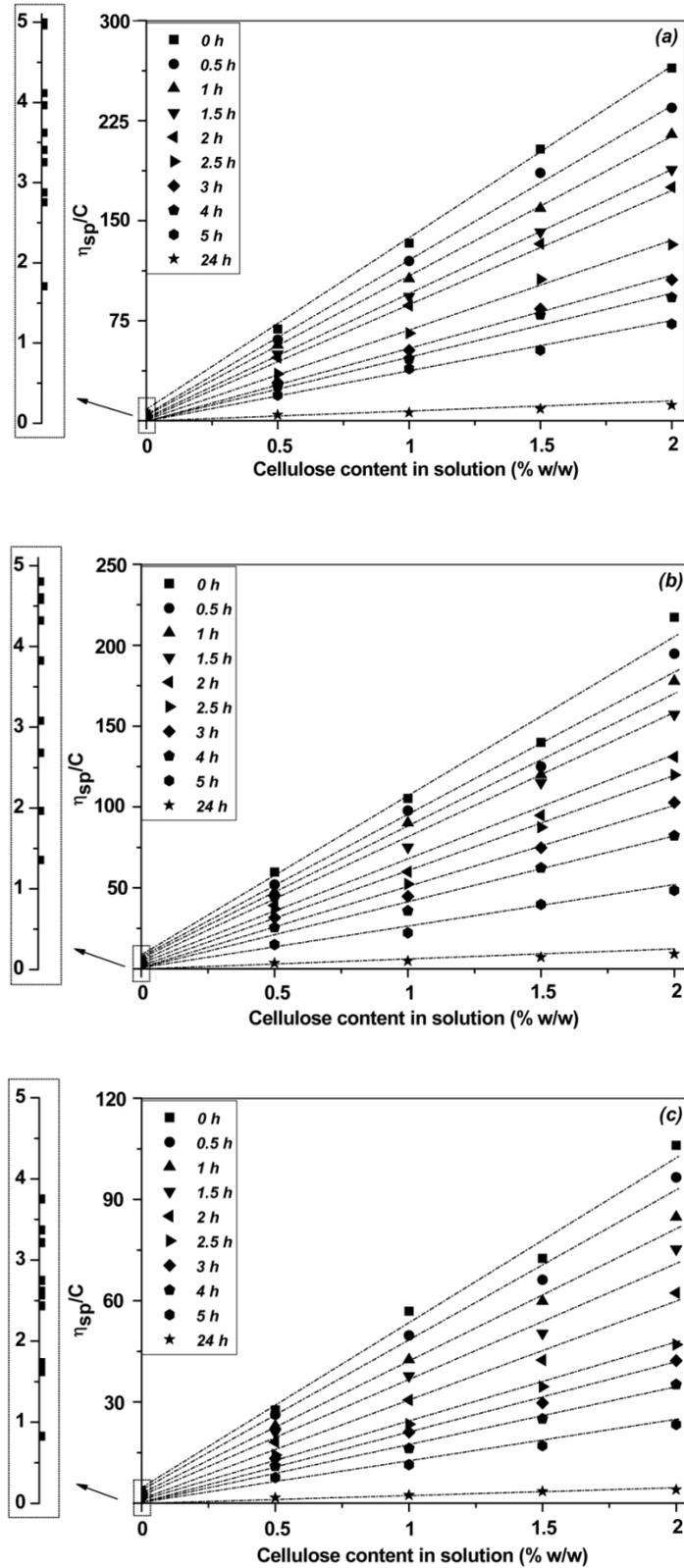


Figure 7: Viscosity as a function of cellulose content in solution at different storage times as prepared with P_2O_5 concentrations of: (a) 72%, (b) 73% and (c) 74%

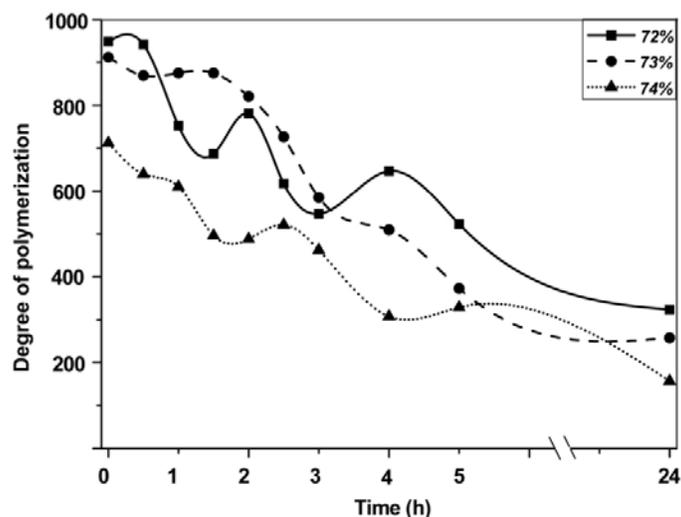


Figure 8: Curves of polymerization degrees of cellulose in solution versus storage time prepared at different P₂O₅ concentrations

CONCLUSION

Theoretically, anhydrous complex PA solvent could be obtained when its P₂O₅ concentration surpasses 70.5%. The range in which good solubility and anisotropy was found is rather narrow; performance is optimal between 72% and 76% P₂O₅ concentrations in the solvent. However, this concentration range, which remains adaptive to the dissolution of cellulose, has not been validated yet since the polymerization degree of raw cellulose increased from 620 to 1000. The P₂O₅ concentration showed sensitivity for complex PA solvent in relation to cellulose dissolution and the optimal range was from 72% to 74%. It is relevant to note that the complex solvents at 72%, 73% and 74% P₂O₅ could be successfully processed into the lyotropic cholesteric liquid crystalline solutions. Fingerprint patterns in solutions were clearly observed particularly at the P₂O₅ concentration of 73% by PLM. At the same time, 15.5% of cellulose solid content in solution prepared at 73% P₂O₅, which was the highest obtained, indicates that the solvent at this concentration possesses the strongest dissolution power. Phosphorus molar ratio in regenerated cellulose samples increased from 0.25% to 4.42% as the actual TPA content in the complex solvent increased. If the P₂O₅ concentration is lower than

74% P₂O₅, this solvent system could be considered as a direct dissolution medium for cellulose. The stability analysis of resulting solutions demonstrated that the complex solvents prepared at 72% and 73% P₂O₅, which could also be processed into liquid crystalline solutions, can provided the prerequisite for spinning of fibers with potentially predominant mechanical properties. In summary, to avoid or minimize degradation, cellulose can favor the lower P₂O₅ concentration of complex PA solvent if its dissolution could be realized.

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REFERENCES

- ¹ J. M. Zhang, H. Zhang, J. Wu *et al.*, *Own. Soc.*, **12**, 1941 (2009).
- ² R. Rinaldi, *Chem. Commun.*, **47**, 511 (2010).
- ³ P. Andre, N. M. Kenneth and S. S. Pang, *Ind. Eng. Chem. Res.*, **49**, 11809 (2010).
- ⁴ H. Ute, K. Mirjana, A. Borgards *et al.*, *Biomacromol.*, **12**, 871 (2011).
- ⁵ B. Zhao, L. Greiner and W. Leitner, *Roy. Soc. Chem.*, **2**, 2476 (2012).
- ⁶ N. L. Moigne and P. Navard, *Cellulose*, **17**, 31 (2010).
- ⁷ S. Zhang, F. X. Li, J. Y. Yu, Y. L. Hsieh, *Carbohydr.*

- Polym.*, **81**, 668 (2010).
- ⁸ A. L. Yang, H. Qi and A. Lue, *Carbohydr. Polym.*, **83**, 1185 (2010).
- ⁹ C. Qian, *Adv. Avail. Res.*, **383**, 3998 (2012).
- ¹⁰ M. Feki, M. Stambouli, D. Pareau and H. F. Ayedi, *Chem. Eng. J.*, **88**, 71 (2002).
- ¹¹ H. W. Voges, B. Elvers and S. Hawkins, *VCH Wein., Germany*, **A19**, 466 (1991).
- ¹² S. Wei, V. Kumar and G. S. Banker, *Int. J. Pharm.*, **142**, 175 (1996).
- ¹³ K. Vijay, H. K. Sanjeev and S. B. Gilbert, *AAPS PharmSciTech*, **2**, 1 (2001).
- ¹⁴ Y. H. P. Zhang and L. R. Lynd, *Biomacromolecules*, **6**, 1510 (2005).
- ¹⁵ Y. H. P. Zhang, J. B. Cui, L. R. Lynd and L. R. Kuang, *Biomacromolecules*, **7**, 644 (2006).
- ¹⁶ J. H. Zhang, B. X. Zhang, J. Q. Zhang *et al.*, *Biotechnol. Adv.*, **28**, 613 (2010).
- ¹⁷ K. Chiahung and L. Chengkang, *Carbohydr. Polym.*, **77**, 41 (2009).
- ¹⁸ J. H. Zhang; J. Q. Zhang, L. Lin *et al.*, *Molecules*, **14**, 5027 (2009).
- ¹⁹ G. Butera, C. De Pasquale, A. Maccotta *et al.*, *Cellulose*, **18**, 1499 (2011).
- ²⁰ V. V. Vinogradov, L. N. Mizerovskii and O. P. Akaev, *Fiber Chem.*, **34**, 167 (2002).
- ²¹ P. Conte, A. Maccotta, C. D. Pasquale *et al.*, *Agric. Food Chem.*, **57**, 8748 (2009).
- ²² R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **34**, 97 (1976).
- ²³ S. L. Tseng, A. Valente and D. G. Gray, *Macromolecules*, **14**, 715 (1981).
- ²⁴ J. X. Guo and D. G. Gray, *Macromolecules*, **22**, 2082 (1989).
- ²⁵ V. Dave, C. E. Frazier and W. G. Glasaer, *J. Appl. Polym. Sci.*, **49**, 1671 (1993).
- ²⁶ B. Laszkiewicz, *Mol. Cryst. Liq. Cryst.*, **353**, 127 (2000).
- ²⁷ H. Boerstael, J. B. Maatman and B. M. K. Westerink, *Polymer*, **42**, 7371 (2001).
- ²⁸ F. E. Alan and P. Murrsville, U.S. Patent 3562302 (1971).
- ²⁹ C. C. Chen and N. J. Belleville, U.S. Patent 3072660 (1963).
- ³⁰ K. Beltz *et al.*, U.S. Patent 3272597 (1966).
- ³¹ W. D. Cao, S. T. Liu and H. L. Mao, *Adv. Mater. Res.*, **152**, 288 (2011).
- ³² R. A. Wiesboeck, S. Mountain and J. D. Nickerson, U.S. Patent 3768387 (1973).
- ³³ H. X. Xu, D. X. Zhang, Z. G. Li *et al.*, *Syn. Fiber*, **3**, 5 (2007).
- ³⁴ H. Boestoel, H. Maatman, S. J. Picken *et al.*, *Polymer*, **42**, 7363 (2001).
- ³⁵ M. G. Northolt, H. Boestoel, H. Maatman *et al.*, *Polymer*, **42**, 8249 (2001).
- ³⁶ S. M. Hudson and J. Cuculo, *J. Macrom. Sci.*, **18**, 1 (2007).
- ³⁷ W. P. Pawlowski and R. D. Gilbert, *J. Polym. Sci.*, **26**, 1101 (1998).
- ³⁸ C. Robinson, *Tetrahedron*, **13**, 1 (1961).
- ³⁹ J. F. Revol, D. L. Godbout and D. G. Gray, U.S. Patent 005629055A (1997).
- ⁴⁰ M. Ramzix, G. J. Vroege and H. N. W. Lekkerkerker, *Macromol. Symp.*, **166**, 209 (2001).