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VISCOMETRIC STUDY OF CELLULOSE IN PF/DMSO SOLUTION

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Key Words: Cellulose, Intrinsic Viscosity, Dilute Solution

ABSTRACT

Cellulose samples were found to be soluble in PF/DMSO to form a genuine dilute solution without suffering obvious degradation under adequate conditions. The Mark-Houwink-Sakurada equation for cellulose in PF/DMSO at 30°C obtained here was $[\eta]=3.01 \times DP^{0.81}$ where $[\eta]$ is in the unit of $cm^3 \cdot g^{-1}$. The intrinsic viscosity of cellulose in Cadoxen, FeTNa, PF/DMSO and DMAc/LiCl was in the following order: $[\eta]_{DMAc\ LiCl} > \eta]_{PF/\ DMSO} > [\eta]_{FeTNa} > [\eta]_{Cadoxen}$, and the same tendency for the values of the parameter α. The intrinsic viscosity can be considered as an indication of the dimension of cellulose macromolecular chains in different solvent systems.

INTRODUCTION

In recent years, much attention has been paid to cellulose due to the shortage of petroleum resources as well as its absolutely reproducible properties. Unfortunately, reliable knowledge of cellulose macromolecular characteristics is still very poor and even no stable and "simple" solvent for forming a genuine

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cellulose solution has been found hitherto. If strong acids or alkalis are used as its solvents the macromolecular decomposition can not be well avoided. If cellulose is first converted into cellulose nitrate before further processing, it is also difficult to avoid the decomposition of cellulose during nitration. When using metal complex alkali solvents, e.g. cupriammonium hydroxide, the cellulose solutions are still easy to decompose and to change color. N-methyl morpholine N-oxide can dissolve cellulose, but it is expensive and sometimes explosive [1, 2]. Therefore, all these above-mentioned solvents are not good for dissolving cellulose, particularly for characterizing its macromolecular behavior.

Johnson *et al.* [3-7] found that the natural cellulose could dissolve easily in paraformaldehyde with dimethyl sulfoxide as a co-solvent (PF/DMSO) to form a middle concentrated solution without any significant decomposition. Here we intended to show that the natural and regenerated cellulose could dissolve in PF/DMSO system to form a genuine dilute solution without significant decomposition and the macromolecular characteristics of cellulose, e.g. the average molecular weight could be determined by the intrinsic viscosity measurement of this solution system. In addition, we also measured the intrinsic viscosity of cellulose samples in other three kinds of solvents Cadoxen, iron sodium tartrate (FeTNa) and N,N-dimethylacetamide/lithium chloride (DMAc/LiCl).

EXPERIMENTAL

Materials

Cellulose sample A was cotton linter and cellulose samples B-E were wood pulps, whose degree of polymerization (DP) were determined by light scattering measurement. The cellulose samples were heated at 105°C until constant weight was reached and dried over phosphorus pentoxide in a desiccator. All reagents used were of the reagent-grade supplied by Shanghai Feida Chemical Co., China. Paraformaldehyde (PF) was ground into powders and dried over phosphorus pentoxide in a desiccator before use. Dimethyl sulfoxide (DMSO) was distilled and then dehydrated using a molecular sieve process for at least 24 hours before use. DMSO also acted as a diluent in the determination of molecular weight of the cellulose samples before and after dissolution in PF/DMSO solution. N, N-dimethylacetamide (DMAc) was stored over potassium hydroxide for more than 1 week before use. Lithium chloride (LiCl) was dried at 100-105°C overnight and then stored in a desiccator before use.

Preparation of Cellulose Solution

PF/DMSO Solution

The mixture of about 70 mg cellulose, a certain amount of PF and 20ml DMSO was under mechanical stirring heated to 60°C for 15 minutes, to 85°C for 20 minutes, and then 115°C for 15 minutes. Thus, after filtered through a 60-80 porosity Danney funnel, a transparent and stable PF/DMSO solution of 0.3 wt% cellulose was then obtained. In order to determine the optimum weight ratio of PF to cellulose for preparing this solution, the solubility of cellulose was investigated in the range of 1-8 of the ratio. Table 1 showed the experimental results for the solubility behavior of cellulose I and cellulose II in PF/DMSO under various PF-to-cellulose ratios (wt/wt).

Obviously, cellulose I and cellulose II were insoluble in PF/DMSO at the PF-to-cellulose ratio less than 1 and partially dissolved or swelled at the ratio above 2. At the ratio equal to or greater than 6, a transparent solution could be obtained. Thus, the PF-to-cellulose ratio of 6 was chosen here for the viscosity measurement system and a series of about 0.3 wt% solutions (with PF to DMSO ratio of 6) of various cellulose samples in PF/DMSO were prepared by the procedure as just described.

Cadoxen Solution [8]

100 mg cellulose was put into 20 ml Cadoxen and kept under stirring for 12 hours at room temperature and the cellulose in Cadoxen solution was then obtained.

TABLE 1. Dependence of Solubility of Cellulose (0.3 wt% solution) on the Ratio of PF to Cellulose (wt/wt ratio)

PF/cellulose(wt/wt)	1	2-5	≥6
		solubility	
Cellulose I	Insoluble	Partly soluble , partly swelled	Soluble
Cellulose II	Insoluble	Partly soluble , partly swelled	Soluble

Cellulose I: natural cellulose; Cellulose II: regenerate cellulose

FeTNa Solution [1]

The dissolution operation for the cellulose in FeTNa solution was similar to that for the cellulose in Cadoxen.

DMAc/LiCl Solution [9]

70mg cellulose was put into 6 ml DMAc in a 10 ml vial under stirring via a magnetic stirrer, the mixture was heated to 150°C for 30 minutes, then cooled to 100°C and LiCl of 9 wt% DMAc was then added into the system. The resulted mixture was then kept at 50°C for about 15 hours under stirring, and thus the cellulose in DMAc/LiCl solution was obtained.

Solution Viscosity

The following Mark-Houwink-Sakurada equation was used:

$$[\eta]=K' \text{ x } DP$$

where $[\eta]$ is the intrinsic viscosity in the unit of $cm^3 \cdot g^{-1}$, K' and α are two parameters which depend on the solution system used and DP is the degree of polymerization of the sample. Every prepared solution for cellulose samples A-E was diluted to 5 different concentrations and kept at 30°C (for PF/DMSO or DMAc/LiCl solution) or 25°C (for Cadoxen or FeTNa solution) for 15 minutes using a water bath before the intrinsic viscosity measurement. The intrinsic viscosity $[\eta]$ was determined using a Ubbelodhe viscometer via Huggins' plot, i.e. plot of η_{sp}/c versus c, where η_{sp} is the specific viscosity in unit of $cm^3 \cdot g^{-1}$ and c is the polymer concentration in unit of $g \cdot cm^3$.

RESULTS AND DISCUSSION

Cellulose in PF/DMSO Solution

The Weight Ratio of PF to Cellulose

As we know, the weight ratio of PF to cellulose in the concentrated solution is usually one to one. While in the dilute solution here, the cellulose concentration was much lower (0.3 wt%), the amount of cellulose macromolecules per volume was rather low and thus the chance of their interaction with PF molecules was low too. Therefore, cellulose wouldn't interact sufficiently with PF in the system to form a good solution until the PF-to-cellulose ratio reached

TABLE 2. Dependence of Degree of Polymerization DP on Dissolution Time

Sample	DP
Cellulose before dissolution	495
Cellulose precipitated from cellulose solution just after dissolution in PF/DMSO	493
Cellulose precipitated from cellulose solution 2 years after dissolution in PF/DMSO	489

a certain value. We chose the weight ratio of PF to cellulose at 6 for preparing this solution system.

The Change of Molecular Weight during Dissolution in PF/DMSO Solution

In our previous experiment, we measured the DP of natural cellulose sample A before dissolution, just after dissolution and two years after dissolution, the result was shown in Table 2.

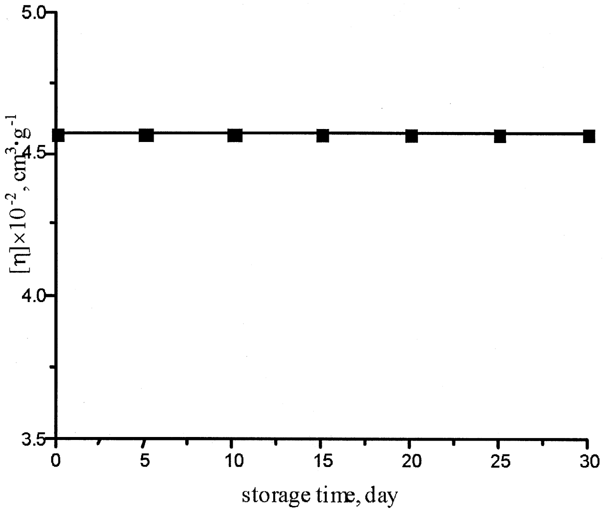

Figure 1. Dependence of intrinsic viscosity on storage time.

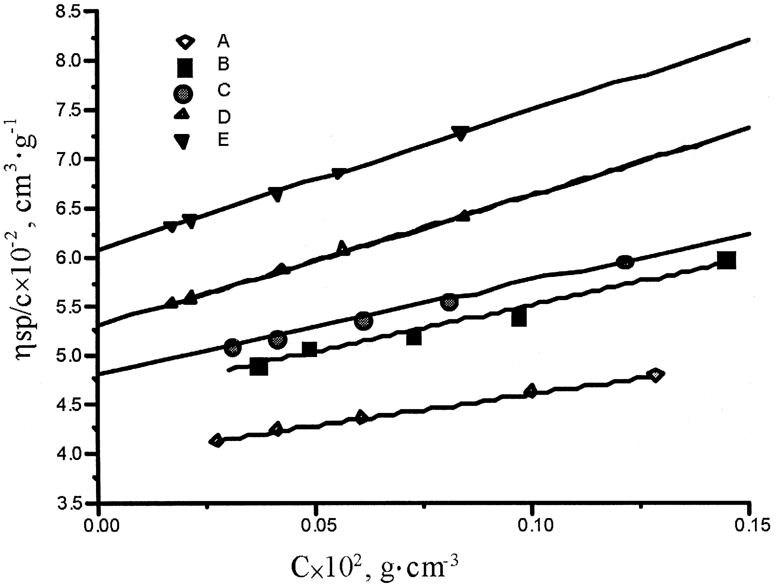

Figure 2. Dependence of specific viscosity on concentration.

From the data obtained, we could consider that cellulose did not decompose in the PF/DMSO solution and the solution was stable. Here, we also measured the dependence of the intrinsic viscosity of sample B in PF/DMSO solution on the storage time, as shown in Figure 1. It was obvious that the intrinsic viscosity [η] did not change with the storage time which meant that the solution was stable. Thus, the method of viscometric measurement could well be applied for the determination of DP of cellulose.

The Values of K' and α

Figure 2 gave the dependence of the specific viscosity sp on the cellulose concentration. The values of the intrinsic viscosity [η] and the corresponding Huggins' constant k' (in the equation of $\eta_{sp}/c=[\eta] + k' [\eta]^2 c$) for the various cellulose samples were listed in Table 3.

Figure 3 gave the dependence of the intrinsic viscosity [η] on DP in the relation $[\eta]=3.01 \times DP^{0.81}$ where [η] is in the unit of $cm^{-3}\cdot g^{-1}$, which was somewhat different from Swenson's result [10].

TABLE 3. Intrinsic Viscosity [η] and Huggins' Constant k'of Cellulose Samples in PF/DMSO Solution at 30°C

Sample	$[\eta]\times10^{-2}$, $cm^3\cdot g^{-1}$	k'
A	3.94	0.47
B	4.57	0.46
C	4.80	0.42
D	5.31	0.474
E	6.09	0.38

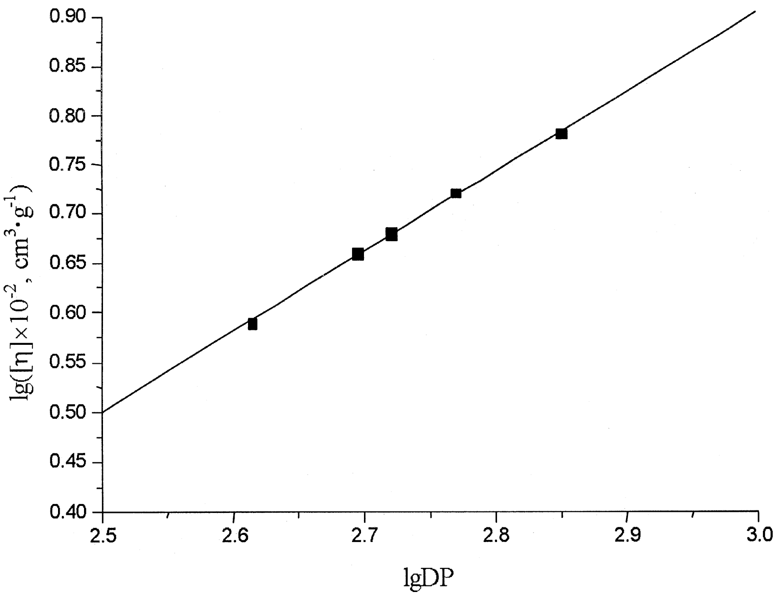

Figure 3. log-log Plot of [h] vs. DP of cellulose in PF/DMSO.

Intrinsic Viscosity in Various Solvents

The values of the intrinsic viscosity of the five cellulose samples measured in Cadoxen, FeTNa, DMAc/LiCl and PF/DMSO solutions were also determined and the results were listed in Table 4, which showed that the intrinsic viscosity for each given sample in the four various solvent systems variedaccording to the following order: $[\eta]$DMAc/LiCl>$[\eta]$PF/DMSO>$[\eta]$FeTNa >$[\eta]$Cadoxen, and the same tendency for the values of the parameter α as shown in Table 5, which gave parameters in the Mark-Houwink-Sakurada equation for cellulose in various solvents systems.

The results obtained can be explained through the theory of hydrodynamics of macromolecules in dilute solution. According to Fox and Flory' treatment, $[\eta]=\phi[h^2]^{3/2}/M$[12], where ϕ is a universal constant, $[h^2]$ is the mean-square end-to-end distance of macromolecular chain. The stronger the interaction between cellulose and solvent molecules, the more extended the macromolecular chain or the bigger dimension of the chain or the bigger value of α. Thus, from Table 4, the intensity of interaction between cellulose and solvent molecules was in the following order: DMAc/LiCl>PF/DMSO >FeTNa>Cadoxen, which also meant the same tendency for the dimension of cellulose macromolecules in these solvents, i.e., cellulose extended to a greater extent in PF/DMSO than in Cadoxen and in FeTNa, although smaller than in DMAc/LiCl. In a word, the intrinsic viscosity can be considered as an indication of the dimension of cellulose macromolecular chains in different solvent systems.

TABLE 4. Intrinsic Viscosity of Cellulose Samples in Cadoxen, FeTNa, PF/DMSO and DMAc/LiCl

Sample	$[\eta]\times10^{-2}$, $cm^3\cdot g^{-1}$			
	Cadoxen	FeTNa	PF/DMSO	DMAc/LiCl
A	1.99	2.89	3.76	4.32
B	2.33	3.47	4.71	5.68
C	3.20	4.21	5.83	6.28
D	3.79	4.89	6.21	6.98
E	4.21	5.54	7.12	7.56

TABLE 5. Parameters for the Mark-Houwink-Sakurada Equation [η]=K' x DP$^{\alpha}$ of Cellulose in Various Solvents

Solvent	Temperature ℃	K' $cm^3 \cdot g^{-1}$	α	Method for DP determination	Reference
PF/DMSO	30	3.01	0.81	LS[1]	this work
Cadoxen[a]	25	1.8	0.77	LS	8
Cuoxam[b]	25	0.8	0.81	LS	1
Cuen[c]	25	1.7	0.8	OS[2]	1
FeTNa[d]	25	2.74	0.78	LS	1
DMAc/LiCl	30	0.054	1.19	LS	11

a: Triethylenediamine cadmium

b: Cupriammonium hydrate

c: Cupriethylenediamine hydroxide

d: Iron sodium tartrate

1: Light scattering

2:Osmotic Pressure

CONCLUSION

Cellulose samples were found to be soluble in PF/DMSO to form a genuine dilute solution without suffering obvious degradation under adequate conditions.

The Mark-Houwink-Sakurada equation for cellulose in PF/DMSO at 30°C obtained was [η]=3.01DP0.81 where [η] is in the unit of $cm^3 \cdot g^{-1}$.

The intrinsic viscosity of cellulose in Cadoxen, FeTN, PF/DMSO and DMAc/LiCl was in the following order:
[η]DMAc/LiCl>[η]PF/DMSO>[η]FeTNa>[η]Cadoxen, the same tendency for the value of the parameter α. The intrinsic viscosity can be considered as an indication of the dimension of cellulose macromolecular chains in different solvent systems.

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