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VISCOSITY MEASUREMENTS OF CELLULOSE/SO₂-AMINE-DIMETHYLSULFOXIDE SOLUTION

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ABSTRACT

Viscosity measurements of cellulose in SO₂-diethylamine-dimethylsulfoxide were studied in order to examine the applicability of this cellulose solvent system for molecular weight measurement of cellulose in wood pulp.

Microcrystalline cellulose powder, pulp for filter paper, bleached kraft pulp, linter, cotton and low molecular weight regenerated celluloses are dissolved rapidly in this system. Limiting viscosity numbers were obtained from the Huggins plots, and the relationship between the limiting viscosity numbers and the concentrations of cellulose was proposed. The Mark-Houwink-Sakurada equations for cellulose in SO₂-diethylamine-dimethylsulfoxide corresponding to those in cupriethylenediamine hydroxide were proposed. The parameters a in the equations are 1.04–1.23, which means that cellulose chains expand in the dissolution state.

Although the cellulose/SO₂-diethylamine-dimethylsulfoxide solution is not stable for long time, this cellulose solvent system is applicable to evaluation of molecular weight of cellulose in wood pulp because cellulose sample are dissolved in this system very rapidly without degradations.

1. INTRODUCTION

Molecular weight of cellulose has remarkable influence on quality of cellulosic materials such as paper, fiber and membranes. Especially since cellulose in wood pulp is subjected to severe physical and chemical history through pulping processes, molecular weight of cellulose in pulp is one of the important standards for evaluation of pulp quality.

Usually molecular weight of pulp is obtained from viscosity measurements of cellulose solution such as cupriethylenediamine hydroxide (Cuen)¹⁾ or other Jayme's reagents, which are strong basic solvents. Thus wood cellulose is subjected to another alkaline and oxidative history for the dissolution in these solvents. Recently, various non-aqueous solvent systems for cellulose have been found, and viscosity measurements of cellulose solutions using these solvent systems were reported from viewpoints of molecular chain characteristics in solution^{2–4)}. However, among these solvent systems, paraformaldehyde-DMSO (dimethylsulfoxide) system²⁾ and lithium chloride-DMAc (N, N-dimethylacetamide) system³⁾ require the thermal pretreatments at the temperature

higher than 80°C in DMSO and 160°C in DMAc, respectively, for dissolution of cellulose. NO-X systems such as N₂O₄, NOCl etc have the oxidative and acidic influence inevitably on cellulose molecules^{5,6)}. Thus these heating or oxidative treatments for dissolution cause another degradative history of cellulose. Kamide and Saito reported the viscometric studies of cellulose in 6% aqueous lithium hydroxide solution⁷⁾, but wood pulp is insoluble directly in this solvent.

Since gel permeation chromatographic (GPC) studies of cellulose provide information not only on molecular weights but on molecular distribution patterns, the GPC analyses of cellulose derivatives were applied to pulping studies in order to trace molecular weight and molecular weight distribution patterns of cellulose during pulping and thermal treatments^{8–11)}. Phenylisocyanation of cellulose is generally performed to block all hydroxyl groups of cellulose for the preparation of cellulose derivatives soluble in organic solvents such as tetrahydrofuran. The optimum reaction conditions were examined to obtain the completely substituted cellulose with less degradations^{8,9)}. However, the condition (heating at 80°C for 2 days⁸⁾) is severe for cellulose, and is somehow a com-

promise point.

During our studies of cellulose using SO_2 -amine-DMSO system, which is one of non-aqueous solvent systems for cellulose, it has been found that this cellulose solvent system has some unique properties, compared with other cellulose solvents. Most of native and mercerized celluloses are dissolved rapidly in this system¹²⁾, and regenerated celluloses prepared from SO_2 -diethylamine-DMSO solutions have almost identical molecular weight to that of original ones¹³⁾.

SO_2 -amine systems for cellulose solvents were first found by Hata and Yokota¹⁴⁾, and they reported the viscosity characteristics of cellulose solutions in diethylamine- SO_2 and triethylamine- SO_2 , where liquid SO_2 was used as the main solvent¹⁵⁾. Yamazaki and Nakao reported that DMSO or other many organic solvents can be used for cellulose solvent systems by the addition of relatively small amounts of SO_2 and amine¹⁶⁾.

In this paper, therefore, viscosities of cellulose/ SO_2 -amine-DMSO solution were measured to examine the applicability of this solvent system for evaluation of molecular weight of cellulose in wood pulp.

2. EXPERIMENTAL

2.1 Samples and reagents

Commercial cellulose powder, pulp for filter paper, linter cellulose, cotton and bleached kraft pulp prepared from hardwood (LBKP) and softwood (NBKP) were used as samples.

Pure grade reagents and solvents were used without further purification.

2.2 Preparation of cellulose/ SO_2 -amine-DMSO solution

A SO_2 /DMSO solution with the concentration of ca. 0.3–0.5 g/ml was prepared according to the previous paper¹⁷⁾, and the accurate concentration of SO_2 was determined by the titration method with alkali.

A dry cellulose sample weighed accurately was put into a volumetric flask, whose moist air was evacuated beforehand by drying the flask or spraying some dry gas, such as nitrogen or dichlorodifluoromethane, into the inside. First, a 1–2 weight % cellulose solution was prepared in the flask in order to prepare a clear solution rapidly. After complete dissolution, further DMSO was added to adjust the concentration required for viscosity measurement. Namely DMSO, whose amount was calculated to prepare the ca. 1–2 weight % cellulose solution,

was added to cellulose in the flask, and the flask was maintained at room temperature for one night for sufficient penetration of DMSO into the sample. Then the accurate amount of the SO_2 /DMSO prepared previously and amine were added in this sequence to the suspension of cellulose/DMSO in the flask. The moles of SO_2 and amine were both adjusted to 1.5 times as much as that of the hydroxyl group of cellulose. After complete dissolution, DMSO was further added to the volumetric flask to adjust the concentration of the solution for the viscosity measurement.

2.3 Preparation of cellulose/Cuen solution

Cellulose in 0.5 mole Cuen was prepared according to the conventional method¹⁾. Limiting viscosity numbers $[\eta]$ were obtained from specific viscosities η_{sp} and the concentration of cellulose C by the following formula (1)¹⁸⁾, and degrees of polymerization (DPv) of cellulose in Cuen were calculated from the limiting viscosity numbers by the following four formulae (2)–(5) reported so far^{9, 19–21)}.

$$[\eta] = \eta_{sp}/C / (1 + 0.28 \times \eta_{sp}) \quad \text{Ref. 18} \quad (1)$$

$$[\eta] = 0.909 \times \text{DP}^{0.85} \quad \text{Ref. 9} \quad (2)$$

$$[\eta] = 0.0974 \times \text{DP}^{0.9} \quad \text{Ref. 19} \quad (3)$$

$$[\eta] = 0.571 \times \text{DP}^1 \quad \text{Ref. 20} \quad (4)$$

$$[\eta] = 1.333 \times \text{DP}^{0.905} \quad \text{Ref. 21} \quad (5)$$

2.4 General analyses

The viscosity of the cellulose solution was measured using a capillary type viscometer (Cannon-Fenske) at 25°C.

UV spectra were obtained with a Shimadzu UV-200 spectrometer.

3. RESULTS AND DISCUSSION

3.1 Solubility of cellulose in SO_2 -amine-DMSO

As described in the previous papers, almost all native and mercerized cellulose samples are soluble in SO_2 -diethylamine(DEA)-DMSO^{12, 13)}, in which all hydroxyl groups of cellulose form a special complex with diethyl-

Fig. 1 Dissolution state of cellulose in SO_2 -amine-dimethylsulfoxide systems.

amine and SO₂, as shown in Fig. 1²²⁾. In contrast, almost all regenerated celluloses are not dissolved completely in this system, irrespective of the crystallinity of the regenerated celluloses¹²⁾. This insolubility of regenerated cellulose is clearly one shortcoming of SO₂-DEA-DMSO for viscosity measurements of cellulosic materials such as regenerated films and fiber. However, the rapid dissolution without degradation is most significant for the characterization of cellulose in wood pulp, especially in terms of pulping chemistry.

Cellulose samples used in this work and their DP_v obtained by the Cuen method are shown in Table 1. DP_v values were calculated according to four equations proposed so far^{9,19-21)}. The equations (2) and (3) were obtained from light scattering analyses, and DP_v values calculated from these equations are close to DP_w.

Since the cellulose/SO₂-DEA-DMSO solution is transparent when the moles of SO₂ are less than those of DEA, the dissolution of cellulose can be judged visually with ease, compared with, for instance, the Cuen solution having a dark blue color. The time required for complete

dissolution in SO₂-DEA-DMSO after the addition of SO₂ and DEA into cellulose/DMSO is also shown in this Table. Sufficient penetration of DMSO into cellulose samples accelerates the dissolution of cellulose in this system, and SO₂-DEA-DMSO is found to dissolve most rapidly among other aqueous and non-aqueous cellulose solvents.

Yamazaki and Nakao reported that triethylamine, piperidine or iso-amylamine can also be used as amine with SO₂ in DMSO for dissolution of cellulose¹⁶⁾. However, these amine-SO₂-DMSO systems required longer time for complete dissolution than SO₂-DEA-DMSO, and thus the SO₂-DEA-DMSO system was used as the cellulose solvent for viscosity measurements.

Two regenerated cellulose samples with very low molecular weight were completely dissolved in SO₂-DEA-DMSO.

As shown in Fig. 1, since the hydroxyl groups of cellulose form the complex with SO₂ and DEA in the solution, the complete dissolution of cellulose in this system requires the moles of SO₂ and DEA equivalent to or more

Table 1 Cellulose samples used for viscosity measurements in SO₂-diethylamine-dimethylsulfoxide and time required for complete dissolution in this system.

Mark Sample	Degree of polymerization				Time required for complete dissolution in SO ₂ -DEA-DMSO ⁵⁾
	DP _v ¹⁾	DP _v ²⁾	DP _v ³⁾	DP _v ⁴⁾	
a regenerated cellulose	8	7	9	5	ca. 5 sec
b regenerated cellulose	27	21	26	15	ca. 5 sec
c cellulose powder	298	201	202	138	ca. 10 sec
d filter paper pulp	1506	929	799	632	ca. 1 min
e LBKP ⁶⁾	2276	1371	1136	932	ca. 2 min
f linter cellulose	2711	1619	1317	1098	ca. 5 min
g NBKP ⁷⁾	3369	1986	1585	1347	ca. 10 min
h cotton cellulose	3635	2135	1691	1447	ca. 20 min

1-4) DP_v values of cellulose in cupriethylenediamine hydroxide were obtained from

- 1) ; $[\eta] = 0.909 \times DP^{0.85}$, 2) ; $[\eta] = 0.974 \times DP^{0.9}$,
3) ; $[\eta] = 0.571 \times DP^1$ and 4) ; $[\eta] = 1.333 \times DP^{0.905}$

5) Time required for complete dissolution of cellulose in SO₂-diethylamine-dimethylsulfoxide after the addition of SO₂ and diethylamine.

6) Bleached kraft pulp prepared from hardwood.

7) Bleached kraft pulp prepared from softwood.

than those of the hydroxyl groups of cellulose. Thus the dilution of the cellulose/SO₂-DEA-DMSO with further DMSO does not bring about the regeneration of cellulose but still keeps the solution state. This phenomenon is different from Cuen, aqueous LiOH, LiCl-DMAc or many other cellulose solvent systems. The concentration of reagents (cupriethylenediamine hydroxide, LiOH, LiCl etc) in the solvents (water, DMAc etc) affects the solubility of cellulose.

3.2 Stability of cellulose solution

Hata and Yokota reported that, when liquid SO₂ is used as the main solvent, the viscosities of the cellulose solutions decrease with increase in aging time of cellulose solutions¹⁵⁾. During our studies, the coloration of the solution to brown and/or the occurrence of regenerated cellulose gels were often observed in solution within a few days after preparation of the cellulose solution. The rapid dissolution of cellulose in this system may cause, in turn, the instability of the cellulose solution because of the high reactivity of the SO₂-amine complex to, for instance, moisture slightly present in a vessel.

The stability of cellulose in SO₂-DEA-DMSO having different molar ratios of SO₂ and DEA was examined, and the results are shown in Table 2. In this experiment, microcrystalline cellulose powder was used as the cellu-

lose samples and the amount of SO₂ was kept to 1.5 times as much as that of the hydroxyl groups of cellulose in all samples. As shown in Fig. 1, the hydroxyl of cellulose, SO₂ and DEA form the complex at the molar ratio of 1 : 1 : 1 in DMSO. Table 2 shows that free SO₂ or free DEA causes the instability of the cellulose solutions. UV spectra of SO₂-DEA-DMSO also supported that, when the molar ratio of SO₂ and DEA is 1:1, the solution has most stable UV absorbance to aging time.

The aging effects of cellulose solutions have been studied also by measuring the relative viscosity as a function of time (Fig. 2). Viscosities of 0.002 g/ml solutions

Fig. 2 Effects of aging time on viscosity of cellulose solution at 25°C.

d; Filter pulp kept free from oxygen in a vessel, d'; filter pulp exposed to atmospheric air, f; linter cellulose kept free from oxygen in a vessel and f'; linter cellulose exposed to atmospheric air.

of linter and filter paper pulp measured at 25°C decreased with increasing the aging time, especially when the solutions were exposed to atmospheric air. Furthermore, regenerated cellulose gels appeared after 12–24 hours for the solutions exposed to atmospheric air or after 2–6 days for those kept free from oxygen in vessels. The appearance of cellulose gels is related to the molar ratio of SO₂ and DEA, as described above, moisture in cellulose samples, humidity in air and so on. Especially the presence of moisture in cellulose samples or in air often prevents the complete dissolution of cellulose.

Table 2 Stability of cellulose/SO₂-diethylamine-dimethylsulfoxide solutions at 25°C¹⁾.

Aging days	Molar ratio of DEA/SO ₂ ²⁾				
	4/6	5/6	6/6	7/6	8/6
0	△ ³⁾	○ ⁴⁾	○	○	○
1	× ⁵⁾	○	○	○	○
2	××	○	○	○	+ ⁶⁾
3	××	++	○	+	++
4	××××	×++	+	++	++
5	××××	×++	++	++	++

1) Cellulose powder was used as the cellulose sample, and the concentration was 0.002 g/ml.

2) The amount of SO₂ was fixed as 1.5 times as much as that of hydroxyl of cellulose, and the amount of DEA was varied.

3) △ : Incomplete dissolution.

4) ○ : Complete dissolution.

5) × : Appearance of fine regenerated cellulose powder.

6) + : Appearance of regenerated cellulose gels.

The results indicate that the solution of cellulose in SO₂-DEA-DMSO is not so stable for long time, and the viscosities have to be measured soon after the dissolution of cellulose.

3.3 Viscosity characteristics

For viscosity measurements, the concentrations of cellulose in SO₂-DEA-DMSO were adjusted 0.004–0.002 g/ml, and the molar ratio of SO₂ and DEA was fixed to equivalent with each other. When SO₂ and DEA were added directly to the cellulose soaked in DMSO, whose amount was adjusted to the required concentration, it took longer time for complete dissolution because the concentrations of SO₂ and DEA are too low to react with all hydroxyl groups of cellulose soon after the addition. Thus ca. 1 % cellulose solution was prepared first, and then it was diluted with DMSO to the concentration necessary for viscosity measurements, as described in the Experimental part.

The Huggins plots are shown in Fig. 3 for cellulose samples in SO₂-DEA-DMSO at 25°C. Limiting viscosity numbers were obtained from the intercepts of the lines, which were drawn by the least-squares method (Table 3).

Several relationships between limiting viscosity numbers, specific or relative viscosities and concentrations have been proposed as shown below.

$$\text{Huggins}^{23):} \quad \eta_{sp}/C = [\eta] + k_H' \times [\eta]^2 \times C \quad (6)$$

$$\text{Mead-Fuoss}^{24):} \quad \ln \eta_{rel}/C = [\eta]^2 \times C \quad (7)$$

$$\text{Martin}^{25):} \quad \ln(\eta_{sp}/C) = \ln[\eta] + k \times [\eta] \times C \quad (8)$$

$$\text{Baker}^{26):} \quad [\eta] = a \times (\eta_{rel}^{1/a} - 1) / C \quad (9)$$

$$\text{Schulz-Blashke}^{18):} \quad [\eta] = \eta_{sp}/C / (1 + a \times \eta_{sp}) \quad (10)$$

Where, C is the concentration of cellulose, $[\eta]$ is the

limiting viscosity number, η_{rel} is the relative viscosity, and k_H' , β , k, a and α are constants.

The constants for SO₂-DEA-DMSO calculated from the limiting viscosity numbers, concentrations and specific or relative viscosities of cellulose samples examples examined so far were listed in Table 3, and these values were not identical to each other. Especially, the constants for the two low molecular weight celluloses were far from those of other cellulose samples. Fig. 4 shows the relationship between the slopes in Fig. 3 and limiting viscosity numbers. Cellulose powder, filter paper pulp, LBKP, linter and NBKP had a linear relationship, although those of low molecular weight celluloses and

Fig. 3 Relations between η_{sp}/C and concentrations of cellulose samples in SO₂-diethylamine-dimethylsulfoxide.

Alphabets correspond to cellulose samples in Table 1.

Table 3 Limiting viscosity numbers $[\eta]$ of cellulose samples obtained from intercepts in Fig. 3, and constants for calculation of limiting viscosity numbers¹⁾

	a	b	c	d	e	f	g	h	c-h ²⁾
$[\eta]$	14	26	162	728	1275	1678	1956	2154	
Constant ³⁾									
k_H'	34	20	0.241	0.490	0.403	0.304	0.275	0.322	0.348
β	-33	-19	0.270	0.092	0.115	0.129	0.145	0.129	0.139
k	27	16	0.187	0.378	0.317	0.233	0.210	0.236	0.267
a	—	—	1.226	5.040	3.790	2.284	2.125	2.386	3.689
α	22	13	0.136	0.300	0.253	0.172	0.165	0.181	0.207

1) Alphabets correspond to cellulose samples in Table 1.

2) Average constant for cellulose samples c, d, e, f, g and h.

3) Refer to calculation formulae (6) – (10) in this paper.

cotton were deviated from the line. However, since cellulose in wood pulp generally has molecular weight within this range, this linear relation is applicable to the calculation of the limiting viscosity number of wood cellulose in SO₂-DEA-DMSO, although this relationship has been obtained from Fig. 4 without any theoretical reasons. Thus the relationship between η_{sp} , C and $[\eta]$ for wood cellulose in SO₂-DEA-DMSO was obtained as the following formula from the data of cellulose powder, filter paper pulp, LBKP, linter and NBKP.

$$[\eta] = \frac{\eta_{sp}/C + 1.22 \times 10^5 \times C}{1 + 5.94 \times 10^2 \times C} \quad (11)$$

Coefficients of variation (%) between measured $[\eta]$ and calculated $[\eta]$ were shown in Table 4. The Huggins method provided the lowest value of coefficient of variation for cellulose samples c, d, e, f, g and h, compared with other methods. However, for cellulose samples c, d, e, f and g, which have standard molecular weight of cellulose in wood pulp, the limiting viscosity numbers calculated using the above equation (11) showed the best fitness to those measured in Fig. 3.

Although the parameters K_m and a in the Mark-Houwink-Sakurada equation for the cellulose/SO₂-DEA-DMSO solutions should be obtained by the light scattering analyses and the viscometric measurements, DP_v values of cellulose samples obtained by the Cuen method,

Fig. 4 Relations between $[\eta]$ and slopes in Fig. 3.

Alphabets correspond to cellulose samples in Table 1.

Table 4 Coefficients of variation (%) between measured and calculated limiting viscosity numbers.

	1 ¹⁾	2 ²⁾	3 ³⁾	4 ⁴⁾	5 ⁵⁾	6 ⁶⁾
Average in each cellulose sample ⁷⁾						
c Powder	9.52	9.28	10.21	9.79	10.55	15.83
d Filter	16.11	16.06	17.69	16.03	19.65	11.29
e LBKP	5.52	8.36	5.78	4.88	7.09	5.05
f Linter	4.82	3.48	7.89	7.26	11.93	3.49
g NBKP	6.68	5.60	10.04	9.20	14.56	3.41
h Cotton	4.30	6.10	8.57	6.73	15.07	12.87
Average in various samples						
c, d, e, f, g, h	7.83	8.15	10.03	8.98	13.14	8.66
c, d, e, f, g	8.53	8.56	10.32	9.43	12.76	7.82

- 1-6) Calculation methods for limiting viscosity number, 1); Huggins, 2); Mead-Fuoss, 3); Martin, 4); Baker, 5); Schulz-Blaschke and 6); equation (11) in this paper.

Refer to formulae (6) - (10).

- 7) Average coefficient of variation (ACV) between measured $[\eta]$ and calculated $[\eta]$ of each cellulose sample.

$$ACV (\%) = \frac{\sum |([\eta]_{mea} - [\eta]_{cal})| / ([\eta]_{mea} \times 100)}{N}$$

Where, $[\eta]_{mea}$ is the measured limiting viscosity number, $[\eta]_{cal}$ is the limiting viscosity number calculated using the average constant for each formula in Table 3, and N is the sample number of one cellulose sample.

Fig. 5 Log-log plots of DP_v obtained from the Cuen method and $[\eta]$ of cellulose samples in SO_2 -diethylamine-dimethylsulfoxide.

DP_v values of cellulose in Cuen were obtained from

1; $[\eta] = 0.909 \times DP^{0.85}$, 2; $[\eta] = 0.974 \times DP^{0.9}$,
3; $[\eta] = 0.571 \times DP^1$ and 4; $[\eta] = 1.333 \times DP^{0.905}$

which is accepted well for evaluation of DP_v of wood pulp, were used in this work. Fig. 5 shows the log-log plots of $[\eta]$ measured for cellulose in SO_2 -DEA-DMSO versus DP_v obtained from the four equations of the Cuen method. The plots of cellulose powder, filter paper pulp, LBKP, linter, NBKP and cotton are almost on the lines, whereas those of the low molecular weight regenerated cellulose do not. These straight lines suggested that the

Table 5 K_m and a values of the Mark-Houwink-Sakurada equation¹⁾ for cellulose/ SO_2 -diethylamine-dimethylsulfoxide solution.²⁾

	K_m	a	$r^{3)}$
Mark-Houwink-Sakurada equation for cellulose/Cuen			
1; $[\eta] = 0.909 \times DP^{0.85}$	0.411	1.04	0.997
2; $[\eta] = 0.974 \times DP^{0.9}$	0.353	1.10	0.997
3; $[\eta] = 0.571 \times DP^1$	0.231	1.23	0.997
4; $[\eta] = 1.333 \times DP^{0.905}$	0.657	1.11	0.997

1) $[\eta] = K_m DP^a$

2) Obtained from the data of cellulose powder, filter pulp, LBKP, linter, NBKP and cotton by the least-squares method.

3) Coefficient of correlation for the above six cellulose samples to each straight line in Fig. 5, which corresponds to the K_m and a values in this Table.

Mark-Houwink-Sakurada equations are well established for the molecular weight range of the above six cellulose samples. The parameters K_m and a were evaluated for six cellulose samples by using the least-squares method, and are listed in Table 5. The a values for cellulose/ SO_2 -DEA-DMSO are higher than those for the corresponding cellulose/Cuen method. As shown in Fig. 1, cellulose forms the complex with SO_2 and DEA at almost all hydroxyl groups, and thus cellulose chains should expand due to steric and/or ionic repulsion of the SO_2 -DEA complexes associated with hydroxyl groups of cellulose.

Thus the viscometric measurements of cellulose in SO_2 -DEA-DMSO were found to be applicable for evaluation of molecular weight of cellulose in wood pulp, but the instability of the cellulose solution to aging should be considered.

REFERENCES

- 1) TAPPI Standard Methods T230 om-82, 1982.
- 2) H. A. Swenson, *Appl. Polym., Symp.* **28**, 945 (1976).
- 3) C. L. McCormick, P. A. Callais and B. H. Hutchinson Jr., *Macromolecules*, **18**, 2394 (1985).
- 4) M. Terbojevich, A. Cosani, G. Conio, A. Ciferi and E. Bianichi, *Macromolecules*, **18**, 640 (1985).
- 5) M. Pasteka and D. Mislovicova, *J. Polym. Sci., A-1*, **8**, 107 (1974).
- 6) A. Vankateswaran and L. P. Clermont, *J. Appl. Polym. Sci.*, **18**, 133 (1974).
- 7) K. Kamide and M. Saito, *Polym. J.*, **18**, 569 (1986).
- 8) R. L. Schroeder and F. C. Haigh, *Tappi*, **62**, 103 (1979).
- 9) S. R. Evans and A. F. A. Wallis, *Proceedings of The 4th International Symposium on Wood and Pulping Chemistry, Paris, April 27-30, 1987*, Vol. 1, p. 201.
- 10) J. J. Cael D. J. Cietek and F. J. Kolpak, *Appl. Polym. Symp.*, **37**, 509 (1983).
- 11) Y. H. Suleman and R. A. Youg, *Cellulose Chem. Technol.*, **22**, 3 (1988).
- 12) A. Isogai, A. Ishizu, J. Nakano and R. H. Atalla, *ACS Symp. Ser.*, No. 340, Washington D. C., 1987, p. 292.
- 13) A. Isogai and R. H. Atalla, *J. Polym. Sci., Polym. Phys. Ed., under contribution*.
- 14) K. Hata and K. Yokota, *Sen-i Gakkaishi*, **22**, 96 (1966).
- 15) K. Hata and K. Yokota, *Sen-i Gakkaishi*, **26**, 571

- (1970).
- 16) S. Yamazaki and O. Nakao, *Sen-i Gakkaishi*, **30**, T234 (1974).
- 17) A. Isogai, A. Ishizu, J. Nakano, S. Eda and K. Kato, *Carbohydr. Res.*, **138**, 99 (1984).
- 18) G. V. Schulz and S. Blashke, *J. Prakt. Chem.*, **158**, 130 (1941).
- 19) M. Marx, *Makromol. Chem.*, **16**, 157 (1955).
- 20) D. K. Smith, R. F. Bampton and W. J. Alexander, *Ind. Eng. Chem., Process Design Develop.*, **2**, 57 (1963).
- 21) H. Sihtola, B. Kyrklund, L. Laamanen and I. Paenius, *Paperi ja puu*, **45**, 225 (1963).
- 22) A. Isogai, A. Ishizu and J. Nakano, *J. Appl. Polym. Sci.*, **33**, 1283 (1987).
- 23) M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2712 (1942).
- 24) D. F. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **64**, 277 (1942).
- 25) A. F. Martin, *Ind. Eng. Chem.*, **45**, 2497 (1953).
- 26) W. E. Davis and J. H. Elliot, *J. Colloid Sci.*, **4**, 313 (1949).

セルロース/SO₂-アミン-ジメチルスルホキシド溶液の粘度測定

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無水亜硫酸-アミン-ジメチルスルホキシド系セルロース溶液の安定性および粘度測定から木材セルロースの重合度測定への適用性を検討した。

コットン, 漂白木材パルプ, 低重合度再生セルロースなど8種のセルロース試料を用いたところ, 他のセルロース溶剤に比較して迅速に溶解し, かつ透明な溶液が得られるが, 長期間安定ではない。Huggins プロットからそれぞれのセルロース試料の固有粘度を求め, 一点法による固有粘度計算式を提案した。また, 用いたセルロース試料の銅エチレンジアミン溶液から得られた重合度に

対応するように, 無水亜硫酸-ジエチルアミン-ジメチルスルホキシド溶液での粘度式の係数を決定した。1.04-1.23という高い a 値から, セルロースはこの溶剤中でかなり剛直な状態で溶解しているものと考えられる。

本セルロース溶液は長期間安定ではないが, 通常の測定条件であればセルロースを分解しないので, 酸化処理, 熱処理, 化学処理などを受けた木材パルプ中のセルロースの重合度測定に適用できるものと考えられる。