Investigation on Dissolving Pulp. XIV. Some Behavior of Wood Pulp and Cotton Linters in Phosphoric Acid

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In a previous paper[1], the author investigated the solubility of various kinds of cellulose into phosphoric acid to know the details of mechanism of the phosphoric-acid swelling which was observed in Heide's test for cellulose reactivity[2], and pointed out the influence of other factors than the degree of polymerization as shown by a Ekenstam[3] on the solubility of various kinds of cellulose into phosphoric acid.

In this paper, the dissolved part of cellulose (sulfite pulp, prehydrolyzed sulfate pulp and cotton linters) in phosphoric acid of various concentrations was studied with regard to the average degree of polymerization, and the rates of hydrolysis in 70% phosphoric acid at 20°C. The rates of hydrolysis of the insoluble residues, swelled to various degrees were also determined.

Experimental

1) Solubility of Cellulose into Phosphoric Acid and Average Degree of Polymerization of Dissolved Part.—First cellulose samples were pretreated with 73.3% phosphoric acid for 10 min. at 20°C, then the proper amount of 82, 86 or 90% phosphoric acid was added drop by drop to get the required concentration under costant stirring, at the constant temperature, 20°C. After 20 minutes, 58% phosphoric acid was added to dilute the solution to 70% Ten minutes after the dilution, the solution was centrifuged and the supernatants were filtered through a glass filter (1G-3). The filtrate was diluted properly and its viscosity was determined in Ostwald's viscometer. The change of viscosity with time in 70% phosphoric acid at 20°C was plotted and the extrapolated value of viscosity to time 0 was determined graphically. Intrinsic viscosity $[\eta]$ was determined by the usual method to plot η_r against various concentrations of the solute. The solubility of cellulose was determined by the oxidation with potassium bichromate and iodometry.

2) The Average Degree of Polymerization of Insoluble Residue.—Insoluble residue in 1 was poured into a large quantity of ice-cold water, washed repeatedly with distilled water, and dried. The cellulose residue was dissolved into cupro-ammonium solution and its viscosity was determined to know the average degree of polymerization. The sample was also dissolved into 85% or 90% phosphoric acid after pretreatment with 73.3% phosphoric acid. After complete dissolution—it takes about 30~60 min.—, to the solution was added 58% phosphoric acid until the concentration of the solution became 70% and the intrinsic viscosity in 70% phosphoric acid was determined by the extrapolation of the viscosity curves to the zero time. The constant K_m of cellulose in 70% phosphoric acid was calculated from the $[\eta]$ and the K_m constant (5×10^{-4}) in cupro-ammonium solution, and $[\eta]$ in the phosphoric acid solution. The value in 70% phosphoric acid thus obtained is about 13×10^{-4}. But this value is not exact and serves only to know the relative change of DP.

1) T. Koshizawa, *J. Soc. Textile and Cellulose Ind., Japan* (*Sen-i Gakkaishi*), in press (Part XII of this paper).
2) K. Heid, *Faserforsch. u. Textil Techn.*, **3**, 486 (1952).
3) Alf af Ekenstam, *Svensk papperstidn*, **45**, 81 (1942).

Results and Discussion

(1) Average Degree of Polymerization of Dissolved Part.—The solubility curves of sulfite pulp, prehydrolyzed sulphate pulp, and cotton linters were shown in Fig. 1. The average degrees of polymerization of cellulose dissolved into the acid of various concentrations were shown in

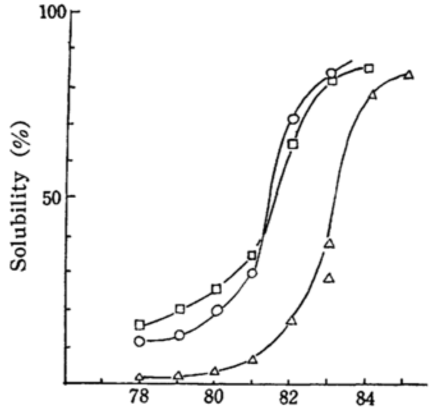

Fig. 1. Solubility of cellulose into phosphoric acid.
△: Cotton linters, ○: Sulfite pulp, □: Prehydrolyzed sulfate pulp

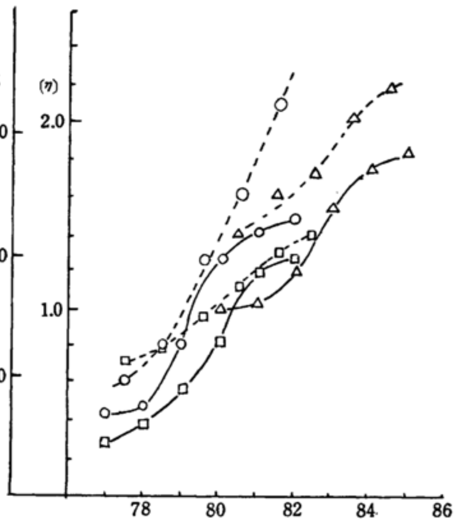

Fig. 2. [η] and $\overline{DP}$ of dissolved part.
△: Cotton linters, ○: Sulfite pulp,
□: prehydrolyzed sulfate pulp.
——: [η] and $\overline{DP}$ of dissolved part,
----: [η] and $\overline{DP}$ of dissolved part corresponding to 1% increase in phosphoric acid concn.

Fig. 2. The degree of polymerization was calculated from [η] using the K_m 13×10^{-4}. Although the K_m constant derived from the comparison of [η] in cupro-ammonium solution and [η] in phosphoric acid solution might not be an exact value, it would be sufficient to discuss the relative difference, as in the present case. The dotted lines in Fig. 2 are the average degree of polymerization of the dissolved part corresponding to the increase in the concentration of phosphoric acid by 1%. The values were calculated from the curves in Fig. 1 and unbroken lines in Fig. 2. In the calculation the assumption that the viscosity shows the weight average of degree of polymerization was taken. The degree of polymerization of newly dissolved part corresponding to the increase in phosphoric acid concentration by a% is calculated from the following relationship,

$$P_{c+a}\times W_{c+a}=P_c\times W_c+P_a\times W_a$$

or $$P_a=(P_{c+a}\times W_{c+a}-P_c\times W_c)/W_a$$

where W_c, W_{c+a} and W_a are weight % of dissolved parts in c%, $c+a$% and a% phosphoric acid, and P_c, P_{c+a} and P_a are their average DP, respectively. Although the above stated assumption might not be strictly valid as we have to consider the distribution of molecular weight or other factors, the curves show us the approximate trends. As seen in the dotted lines in Fig. 2 the average DP of newly dissolved pulp which correspond to the increase in the concentration of phosphoric acid, clearly differ according to the kind of cellulose sample. Namely the increase in concentration of phosphoric acid accompanies a marked increase in the DP of dissolved part in sulfite pulp, while it accompanies a slight increase in the DP in the case of prehydrolyzed sulfate pulp and cotton linters. So the abrupt increase in solubility at a certain concentration of phosphoric acid as shown in Fig. 1 cannot be ascribed solely to the factor of DP as stated by af Ekenstam[3] and suggests the influence of a fine structure such as lateral order upon the solubility of cellulose into phosphoric acid. Needless to say the increase in DP proportional to the increase in concentration of the acid shows the effect of DP, and a relatively large increase in DP with the increase in acid concentration in the case of sulfite pulp may be caused by the wide spread of distribution of DP. The existence of molecules with small DP among large molecules gives much influence upon the solubility or swellability and the fact may be correlated to the lowering of swellability or the hornification caused by cold alkali treatment.

(2) Decrease in Degree of Polymerization in Dissolved and Insoluble Part. —The change of 1/DP of the dissolved part with the time of hydrolysis is shown

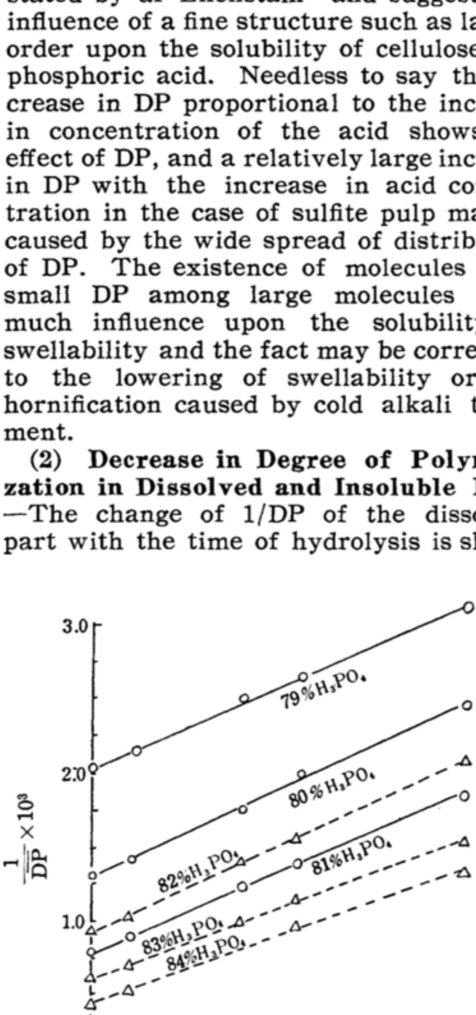

Fig. 3. Degradation of dissolved part in 70% H_3PO_4 at 20°C.
△: Cotton linters, ○: Sulfite pulp.

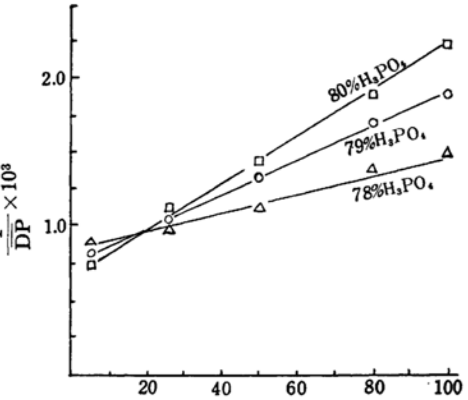

Fig. 4-1. Degradation of insoluble residue in 70% H_3PO_4 at 20°C. (Sulfite pulp)

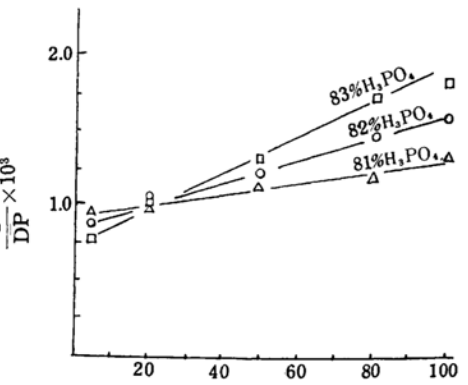

Fig. 4-2. Degradation of insoluble residue in 70% H_3PO_4 at 20°C. (Cotton linters)

in Fig. 3 in which the DP is calculated from $[\eta]$ in 70% phosphoric acid, assuming the constant, K_m 13×10^{-4}. Figs. 4-1, and 4-2 shows that of insoluble residues. The rate constant for the hydrolysis can be derived from the following equation

$$K=1/t\frac{(1-1/DP_0)}{(1-1/DP_t)}$$

where DP_0 and DP_t are the average DP of the cellulose at zero time and time t, respectively. Expansion of the right side of the equation to an infinite series and neglect of all of the terms other than the first gives the following equation,

$$K=1/t(1/DP_t-1/DP_0)$$

Many investigations[4,5] found the validity of this equation in the initial stage of hydrolysis. The tangents of the curves in Figs. 3 and 4 correspond to the rate

TABLE I

RATE CONSTANT OF HYDROLYSIS OF DISSOLVED PART IN 70% PHOSPHORIC ACID AT 20°C

	Cotton linters	
Concn. of H_3PO_4	82%	$K=3.8\times10^{-7}$ min^{-1}
	83%	$K=3.0\times10^{-7}$ min^{-1}
	84%	$K=3.2\times10^{-7}$ min^{-1}
	Sulfite pulp	
Concn. of H_3PO_4	79%	$K=4.0\times10^{-7}$ min^{-1}
	80%	$K=4.0\times10^{-7}$ min^{-1}
	81%	$K=4.0\times10^{-7}$ min^{-1}

TABLE II

RATE CONSTANT OF HYDROLYSIS OF INSOLUBLE RESIDUE IN 70% PHOSPHORIC ACID AT 20°C

	Cotton linters	
Concn. of H_3PO_4	81%	$K=0.56\times10^{-7}$ min^{-1}
	82%	$K=1.3\times10^{-7}$ min^{-1}
	83%	$K=1.7\times10^{-7}$ min^{-1}
	Sulfite pulp	
Concn. of H_3PO_4	78%	$K=0.85\times10^{-7}$ min^{-1}
	79%	$K=1.5\times10^{-7}$ min^{-1}
	80%	$K=2.5\times10^{-7}$ min^{-1}

constants of hydrolysis which are given in Tables I and II. The rate constant of hydrolysis of dissolved part does not vary in either case of linters or sulfite pulp. On the other hand that of insoluble residue changes with the concentration of phosphoric acid before the dilution to 70%. Namely the rate of hydrolysis depends on the degree of swelling in the solution. Thus we may conclude that the rate of inhomogeneous degradation of cellulose is greatly influenced by the state of molecular orientation. This fact also makes easy the test on swellability of cellulose in phosphoric acid which is proposed by Heide[1)] or the test modified by us[1)] to determine the transparency or turbidity of the cellulose suspension in phosphoric acid because, on the one hand, the swelled part dissolves into the solution with the lapse of time because of the greater rate of hydrolysis, and, on the other hand, the insoluble residue such as the constricted part in balloon-like swelling remains unchanged, even after a long time because of the lower rate of hydrolysis.

Summary

The average DP of cellulose dissolved into phosphoric acid of various concentrations has been determined by viscometry. The relations of average DP of dissolved

4) O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).
5) Alf af Ekenstam, *Ber.*, **69B**, 549 (1936).

part to the concentration of phosphoric acid are not the same in the three samples — dissolving sulfite pulp, prehydrolyzed sulfate pulp and cotton linters. The fact may be ascribed to the factors such as lateral order other than the degree of polymerization.

The rate of hydrolysis of cellulose in 70% phosphoric acid at 20°C was also determined as to both cases of dissolved part and insoluble residue. The rate of hydrolysis of the dissolved part is almost independent of the kind of cellulose, while that of the insoluble residue greatly depends on the degree of swelling in the solution.

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