The Heterogeneous Character of the Dilute Acid Hydrolysis of Crystalline Cellulose. II. Hydrolysis in Sulfuric Acid

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SYNOPSIS

Nine prehydrolyzed cellulose samples, including native, mercerized, and regenerated celluloses were hydrolyzed in 2% sulfuric acid at 150, 160, and 170°C. The first-order rate constants and the weight average degrees of polymerization (by size exclusion chromatography) were determined for each sample. The results indicate that Sharples' end-attack model [*Trans. Faraday Soc.*, **53**, 1003 (1957)] is consistent with kinetic data for cellulose II samples, but is not appropriate for characterizing the reactions of cellulose I samples.

INTRODUCTION

Cellulose, a linear polymer of 1,4 linked β-D-glucose, is the most abundant resource obtainable from biomass. The product of cellulose hydrolysis is glucose, an important chemical intermediate for fermentation to ethanol and other chemicals; therefore, saccharification of cellulose is of interest to researchers concerned with the development of alternative sources of liquid fuels. Because technical and economic considerations indicate that the dilute acid hydrolysis of cellulosic materials has the greatest potential for commercialization, much recent research has focused on the dilute acid hydrolysis process. Cellulose is not soluble in dilute acids. Thus the dilute acid hydrolysis of cellulose is a heterogeneous reaction. A better understanding of the heterogeneous character of this reaction would provide useful information for determining strategies to improve the yield of glucose.

X-ray diffraction studies show that cellulose contains both amorphous and crystalline regions.[1-3] Furthermore, studies of the kinetics of these reactions indicate that the hydrolysis of cellulose occurs much faster in the amorphous region than in the crystalline region. Although the dilute acid hydrolysis of crystalline cellulose is a heterogeneous reaction, for both cellulose I and cellulose II, the rates at which solid samples of cellulose lose weight may be modeled as pseudohomogeneous, first-order reactions. Researchers have studied these heterogeneous hydrolysis reactions under a variety of conditions (temperatures, acid strengths, types of acid employed, etc.).[4-13] The fact that the cellulose substrate behaves similarly under widely different conditions indicates that the gross morphology of the cellulose plays a unique role in the reaction kinetics under the conditions investigated.

Several facts concerning the dilute acid hydrolysis of cellulose remain unclear, even though this reaction has been studied for well over 80 years. First, it is not clear why celluloses with the same crystalline morphology but obtained from different sources should hydrolyze at widely differing rates since they are nominally of the same chemical composition. Second, it is not clear why the hydrolysis of cellulosics should obey pseudo-first-order kinetics, given the fact that the reaction is heterogeneous. In order to model the production of glucose from different celluloses without having to study the hydrolysis of each substrate independently, it would be desirable to develop a simple model for the dilute acid hydrolysis of crystalline cellulose that explains the observed first-order rate expression and provides a framework for correlating kinetic data for a variety of cellulosic materials.

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Sharples[8,9] has proposed a model for the dilute acid hydrolysis of crystalline cellulose which can, if proven correct, explain the observed first-order kinetics. However, in testing his model Sharples employed a limited number of cellulosic substrates and carried out the hydrolysis reactions under only one set of reaction conditions (1*N* HCl, 90°C). Other researchers[14-19] have reported data which are apparently inconsistent with Sharples' model.

In a previous investigation,[20] we reexamined Sharples' model using a variety of cellulosics but employing a single reaction condition (constant boiling HCl, 107°C). The hydrolysis of cellulose II samples obeyed the constraints of Sharples' model. However, data for samples characterized by the cellulose I morphology were not consistent with his model. Indeed, Sharples had originally pointed out that his data might indicate this possibility.

The present paper extends our reexamination of Sharples' model to a wider range of reaction conditions (a different acid, different temperatures) in order to determine whether our previous observations are also valid under these conditions. In the results reported here, we investigate the hydrolysis of cellulose with 2% sulfuric acid at higher temperatures (150, 160, and 170°C) than those employed by either Sharples or our own research group.

Sharples' Model[8,9]

In order to provide a basis for discussion of the results obtained in the present work, a review of Sharples' model for the hydrolysis of crystallites of cellulose is presented. Three basic assumptions are involved in the development of this model:

a. Attack can occur on any single pair of opposed faces.
b. The distances between these faces are exponentially distributed.
c. The rate at which the crystal loses weight is proportional to the area attacked.

Let x represent the dimension which is decreasing with time and which is exponentially distributed, and let a be the distribution constant. The number distribution at time $t = 0$, n_0, is then given by

$$n_0 = a_0 \exp(-bx_0) \tag{1}$$

where b is a constant.

Sharples also assumed that all the cellulose crystallites have constant cross-sectional area θ and that the hydrolysis of the crystallites occurs only through scission of the bonds at the ends of the cellulose chains. Under these conditions,

$$-\frac{dw}{dt} = 2B\theta \tag{2}$$

where w is the total weight of the sample and B is an intrinsic rate constant. Integration of eq. (2) between times zero and t gives

$$w_0 - w_t = 2B\theta t \tag{3}$$

where it is assumed that θ does not change with time. Since the weight of the crystalline region is $\rho\theta x_t$, where ρ is the density of the solid, eq. (3) can be written as

$$x_0 - x_t = 2Bt/\rho \tag{4}$$

Thus, in a time t, each crystallite decreases in length by $2Bt/\rho$ until the solubility limit S is reached. This solubility limit represents the degree of polymerization below which the cellulose becomes soluble. Numerically it is equal to the number of glucose monomers constituting the cellulose oligomer at the solubility limit.

The number distribution of x at time t, n_t, is given as

$$n_t = a_t \exp(-bx_t) \tag{5}$$

Since $a_t = a_0 \exp(-2bBt/\rho)$, then

$$n_t = a_0 \exp(-2bBt/\rho) \exp(-bx_t) \tag{6}$$

The total weight of crystallites at time t is given by

$$w_t = \sum_{x_t=S}^{\infty} (n_t \rho \theta x_t)$$

$$= a_0 \rho \theta \exp(-2bBt/\rho) \int_s^{\infty} x_t \exp(-bx_t)\, dx_t \tag{7}$$

and

$$w_0 = \sum_{x_0=S}^{\infty} (n_0 \rho \theta x_0)$$

$$= a_0 \rho \theta \int_s^{\infty} x_0 \exp(-bx_0)\, dx_0 \tag{8}$$

Thus

$$w_t/w_0 = \exp(-2bBt/\rho) \tag{9}$$

or

$$\ln(w_t/w_0) = -2bBt/\rho \qquad (10)$$

Note that eq. (10) can be used to explain the observed first-order weight loss kinetics. The derivation of this equation is not limited by whether the attack occurs laterally or longitudinally. However, Sharples reported that end attack degradation was the preferred model. This preference was established on the basis of the width and length distributions of cellulose crystallites reported by Immergut and Ranby.[15]

To explain the fact that the chain length of the crystallite materials remains almost constant throughout the reaction, Sharples used eq. (6) as a basis for deriving the following relations for the number and weight average crystallite lengths:

$$x_N = S + 1/b \qquad (11)$$

$$x_W = S + 1/b + \frac{1}{b^2(S + 1/b)} \qquad (12)$$

where S again is the solubility limit.

Note that x_N and x_W are approximately equivalent to DP_N and DP_W, the number and weight average degrees of polymerization, respectively. Consequently, these equations indicate that DP_N and DP_W depend only on b and S. Since S and b are constant for a given material, these equations indicate that the chain length remains constant.

From eq. (10), it is apparent that the rate constant for the first-order weight loss process can be expressed as

$$k = 2bB/\rho \qquad (13)$$

Replacing x_W in eq. (12) by DP_W, Sharples derived the following relationship between the rate constant k and DP_W:

$$\frac{1}{k} = \left(\frac{\rho}{4B}\right)\left(\frac{2}{b}\right) \cong \left(\frac{\rho}{4B}\right)\left[DP_W - \frac{2S^2}{(DP_W + 2S)}\right] \qquad (14)$$

Since $2/b$ is related to the degree of polymerization of crystalline cellulose, the end-attack model attributes differences in the rates of hydrolysis of celluloses derived from various sources to differences in their degrees of polymerization. Figure 1 shows a plot of data obtained by Sharples in support of his model.

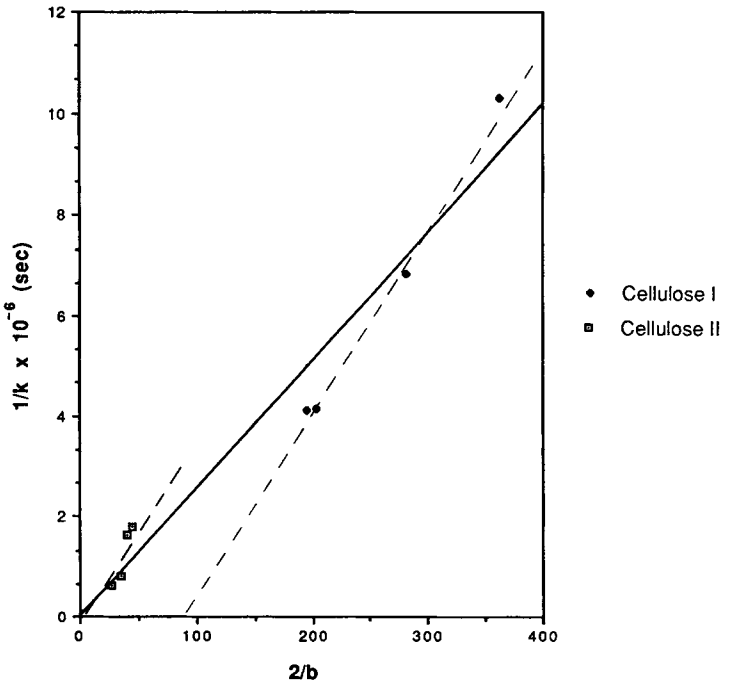

Figure 1 Plot of $1/k$ vs. $2/b$ from Sharples' data (1N HCl, 90°C).[9] Dashed lines indicate that Sharples' data can be separated into cellulose I and cellulose II subsets.

EXPERIMENTAL

Materials

The cellulosic samples used in this study include bleached cotton, bleached ramie, unbleached linen, α-cellulose, mercerized cotton, mercerized ramie, mercerized linen, mercerized α-cellulose, and rayon. The first four samples are commercial, native celluloses. They are characterized by a cellulose I structure. The mercerized celluloses were obtained by treating native celluloses with alkali solution. Rayon is an example of a regenerated cellulose. Both mercerized and regenerated celluloses possess the cellulose II structure.

Preparation of the mercerized samples involved soaking 5 g of air-dried native cellulose in 300 mL of 18% sodium hydroxide solution for 48 h at room temperature, a procedure suggested by Takai et al.[18] After it had been soaked, the cellulose was washed onto a coarse-porosity glass filter with distilled water and 1% acetic acid. Then the sample was thoroughly washed with distilled water and with acetone. Finally, the washed sample was dried *in vacuo* at 60°C overnight.

Methods

Prehydrolysis

Approximately 10 g of each cellulosic sample was subjected to preliminary hydrolysis in 300 mL of aqueous constant boiling 20.2% HCl (108.5°C at 1 atm) for 2 min to remove the readily hydrolyzed amorphous fraction. The residual crystalline hydrocelluloses were freed from acid by washing with distilled water and acetone onto a medium-porosity glass filter. Each prehydrolyzed sample was dried *in vacuo* at 60°C overnight.

Batch Hydrolysis

Approximately 100 mg of a cellulosic sample was placed in a tared 20 cm × 5 mm o.d. Pyrex glass tube which had been sealed at one end. The sample in the glass tube reactor was dried *in vacuo* at 60°C overnight. The weight of the dry cellulosic sample was then determined. The glass tube was sealed with a rubber septum and evacuated. Dilute acid was injected into the glass tube to give a liquid-to-solid ratio of approximately 10 : 1. Finally the glass tube was brought to atmospheric pressure with nitrogen gas and sealed.

The hydrolysis reaction was performed by placing the glass tube reactor into a molten salt bath equipped with a controller which maintained the desired temperature to ±0.25°C. The reaction time was taken as the time from immersion of the reactor in the salt bath to quenching the reaction by transferring the reactor to an adjacent ice-water bath. The contents of the glass tube reactor were washed with distilled water onto a tared coarse-porosity glass filter. The sample was then washed with acetone, dried *in vacuo* at 60°C overnight, and weighed. HPLC analysis[21] was used to determine the sugar content of all starting materials and hydrolyzed residues.

Size-Exclusion Chromatography Analysis

The molecular weight distributions and average degrees of polymerization of all the hydrolyzed celluloses were determined by SEC. Because cellulose does not dissolve in most of the solvents typically used in SEC, derivatization of cellulose prior to the analysis is necessary. In the present study, carbanilation was carried out to render the hydrolysis residues soluble in tetrahydrofuran (THF). Carbanilation of cellulose provides almost complete substitution without degradation.[22-25]

The method and reaction conditions used for carbanilation were those recommended by Schroeder and Haigh[26] except that cellulose tricarbanilate (CTC) was recovered by evaporating the reaction mixture with a nitrogen gas stream to assure complete recovery of the CTC samples.[27] For mercerized cotton, mercerized α-cellulose and rayon, Wood et al.[20] indicated that, after 48 h of reaction time, the carbanilation reaction is still not complete. An alternate procedure was used in which the samples are first soaked in water overnight and then solvent exchanged with pyridine prior to carrying out the carbanilation. After pretreatment of these cellulose samples, they all reacted completely to form CTC within 48 h.

The methods and equipment used in the present study for the size-exclusion-chromatography analysis are the same as those used in the work of Wood et al.[20,27] The output from the data analysis includes the number, weight, viscosity, and z average molecular weights and the number, weight and cumulative number distributions of the molecular weights. However, only the weight average molecular weights were used in the present study.

RESULTS AND DISCUSSION

Kinetic Studies of the Acid Hydrolysis of Cellulose

Prehydrolyzed cellulose samples were subjected to batch hydrolysis for varying lengths of time in 2% sulfuric acid. Kinetic studies were carried out at 150,

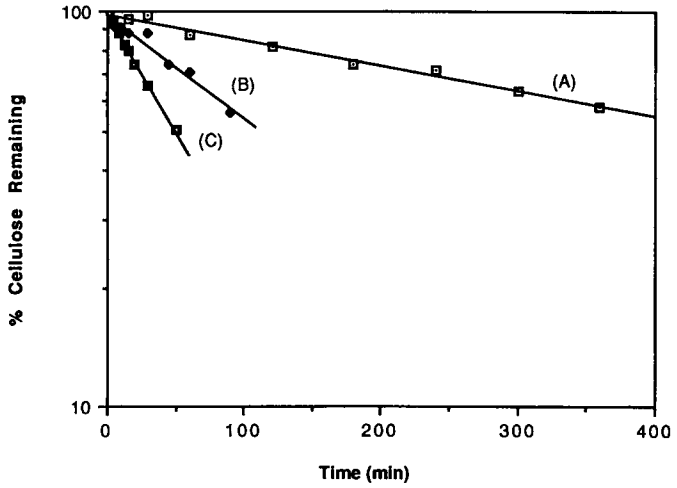

Figure 2 Semilog plots of weight loss data for the cellulose component of cotton hydrolyzed in 2% H_2SO_4 at (A) 150, (B) 160, and (C) 170°C.

160, and 170°C. For each of the hydrolyzed samples, both the total weight loss and the cellulose weight loss (based on sugar analyses[21]) were determined. Representative semilog plots of the cellulose weight loss data for a cotton sample at each reaction temperature are shown in Figure 2.

For all the samples, the weight loss of the cellulose component appears to obey pseudo-first-order kinetics. The first-order rate constants of each prehydrolyzed sample as determined from linear regression analyses are presented in Table I. From the rate constant data shown in Table I, it is obvious that mercerization of cotton and ramie increases the rate of hydrolysis of these samples. However, for linen and α-cellulose samples, mercerization has the opposite effect. These results are consistent with literature reports.[4,20] Between 150 and 170°C, a 10°C increase in temperature causes the rate constant to increase by a factor of 3.1. The corresponding value reported by Foster and Wardrop[6] is 2.8. The data indicate that the rate of hydrolysis of α-cellulose is 1.9–3.0 times that for cotton cellulose. This observation is consistent with data reported by Martin and Pacsu[28] and by Marchessault and Ranby.[29]

The starting material for each specific cellulose substrate is prepared in the same fashion. The starting materials are samples subjected to prehydrolysis in 20.2% aqueous hydrochloric acid at its

Table I Kinetic and Relevant Data for Cellulosic Samples Hydrolyzed at Different Temperatures

			Rate Constant (min^{-1})					
			150°C		160°C		170°C	
Species	DP_w[a]	2/b	k	B/ρ	k	B/ρ	k	B/ρ
Cotton	162 ± 11	161.1	0.00146	0.0588	0.00592	0.238	0.01358	0.547
Ramie	182 ± 4	181.2	0.00146	0.0661	0.00446	0.202	0.01157	0.524
Linen	159 ± 12	158.1	0.00208	0.0882	0.00799	0.316	0.02085	0.824
α-Cellulose	99 ± 1	97.6	0.00441	0.1076	0.01107	0.270	0.03676	0.897
Merc. cotton	80 ± 3	78.3	0.00209	0.0409	0.00667	0.131	0.01698	0.332
Merc. ramie	95 ± 4	93.6	0.00164	0.0384	0.00517	0.121	0.01423	0.333
Merc. linen	102 ± 4	100.7	0.00151	0.038	0.00584	0.147	0.01913	0.482
Merc. α-cellulose	45 ± 1	42.4	0.00325	0.0345	0.01003	0.106	0.03141	0.333
Rayon	17 ± 1	12.4	0.01781	0.0552	0.0448	0.139	0.2116	0.656

[a] Average values from three different reaction temperatures.

constant boiling temperature (108.5°C at 1 atm) for 2 min. By extrapolating the straight lines on the semilog plots of percent cellulose remaining versus time, the crystallinities of the starting materials can be obtained. None of the prehydrolyzed celluloses was completely crystalline. Since the amorphous fraction of cellulose hydrolyzes at a much higher rate than does the crystalline fraction, these facts can account for the uncertainties in the determination of the first order rate constants.

The average activation energies calculated from the rate constants for each substrate at different temperatures using the Arrhenius equation was 42.0 ± 3.1 kcal/mol. The average activation energy for cellulose I samples was 40.7 ± 2.0 kcal/mol, and that for cellulose II samples was 43.0 ± 3.6 kcal/mol. Activation energies reported in the literature for cellulose hydrolysis under different reaction conditions are summarized in Table II. From these values, it is clear that the activation energies for the hydrolysis of crystalline cellulose are dependent on the reaction conditions.[10] The values of activation energy reported by Nelson[10] and Philipp et al.[5] are close since they used similar reaction conditions. Similarly, the activation energies obtained by Daruwalla and Narsian[11] and Marx-Figini[13] are comparable because they used similar reaction temperatures, although different degradation reagents were employed in their hydrolysis procedures. The values of the activation energy obtained in this study are comparable to those obtained in the studies of Saeman,[4] Bhandari et al.,[12] and Foster and Wardrop,[6] who used reaction conditions similar to those used in our work.

SEC Analysis

Because size exclusion chromatography is not an absolute method for determining molecular weights and molecular weight distributions, calibration is necessary. The universal calibration technique[30] employing polystyrene standards was used in this study. Dawkin[31] has suggested the use of a third order polynomial fit of the calibration curve since it has a typical S shape. The polystyrene standards utilized in this study elute at retention volumes ranging from 15 to 26 mL. This range of retention volumes lies on the linear portion of the S-shaped calibration curve (Fig. 3). Therefore, the calibration curve used in this study is correlated by a first-order polynomial. The CTC samples of interest also elute within this range of elution volumes.

Mark–Houwink coefficients reported in the literature for polystyrene in THF are quite consistent. The values ($K = 0.0112$, $\alpha = 0.72$) provided by Kolinsky and Janca[32] were used in this study. For CTC in THF, the values of Mark–Houwink coefficients reported in the literature differ.[23–25,33,34] The values ($K = 0.0053$, $\alpha = 0.84$) reported by Danhelka and Kossler[25] were used in the present case because their data encompassed the widest range of molecular weights. In both cases, the coefficients are based on the same units for intrinsic viscosity (mL/g).

A typical SEC chromatogram is shown in Figure 4. The first peak in the chromatogram may be attributed to the CTC sample. The second peak results from the byproducts of the carbanilation reaction. It contains diphenyl urea and urethan. The chromatogram has been baseline corrected by subtract-

Table II Activation Energies Reported in the Literature

Author	Hydrolysis Reagent	Concentration	Temperature (°C)	Substrate	Activation Energy (kcal/mol)
Saeman[4]	H_2SO_4	0.4–1.6%	170–190	Douglas fir	42.9
Bhandari et al.[12]	H_2SO_4	0.49–1.47%	155–240	Corn stover	45.3
Foster and Wardrop[6]	H_2SO_4	2%	150–170	Holocellulose	38
Philipp et al.[5]	HCl	6*N*	~ 100	Cotton linter and Fortisan rayon	35
Nelson[10]	HCl	6*N*	80–100	Cotton linter, viscose rayon, mercerized cotton and decrystallized cotton	31.4–35.1
Daruwalla and Narsian[11]	HCl and H_2SO_4	1*N* and 0.1*N*	30–70	Cotton and regenerated cellulose	27–28
Marx-Figini[13]	$KHSO_4$	0.5 *M*	40–60	Cotton	24

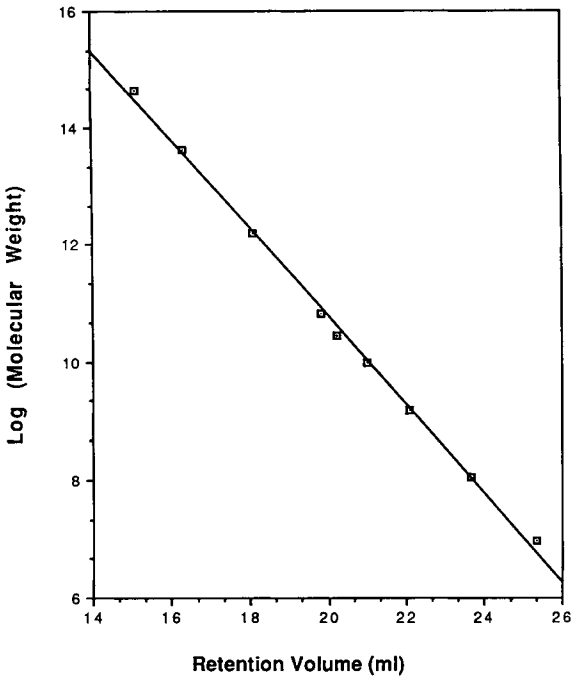

Figure 3 Polystyrene standard calibration curve for SEC system.

ing the baseline from the entire chromatogram. Although the molecular weight of the monomeric unit of CTC (519) is much higher than that of the monomeric unit of cellulose (162), as long as the process of derivatization does not cause degradation of the cellulose, the resultant SEC chromatograms are representative of the cellulose precursor.

The molecular weight data from SEC analysis and values of 2/b and B/ρ calculated from eq. (14) for cellulose samples hydrolyzed in 2% sulfuric acid at 150, 160, and 170°C are listed in Table I. The solubility limit S was taken to be 9.[8] In Sharples' work, the DP_W values used to prepare the plot of $1/k$ versus $2/b$ (Fig. 1) were based on prehydrolyzed samples. The percentages of the weight remaining after prehydrolysis ranged from 62 to 97%. Since celluloses derived from different sources are characterized by different rates of hydrolysis, it is not reasonable to choose the DP_W values corresponding to the same hydrolysis time for all the samples. Millett et al.[7] indicated that values for the degree of polymerization at the half-life of the resistant fraction of cellulose are more characteristic of each material. Therefore, DP_W values at the half-life were used in preparing our plots of $1/k$ versus $2/b$ (Figs. 5 and 6). However, it is hard to prepare the samples at exactly their half-lives. DP_W values closest to the

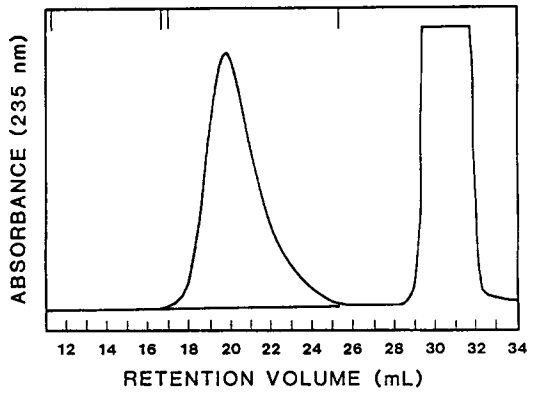

Figure 4 Typical chromatogram of cellulose tricarbanilate from SEC analysis.

50% weight loss condition were used in preparing the plots for cellulose I and cellulose II samples, respectively.

Using these same procedures, Wood et al.[20] found that the differential number distributions for cellulose samples appear to be exponential (as required by Sharples' model) down to a DP of approximately 50. Below this DP there is an excess of low molecular weight material over that predicted by an exponential distribution. One explanation for the excess, low-

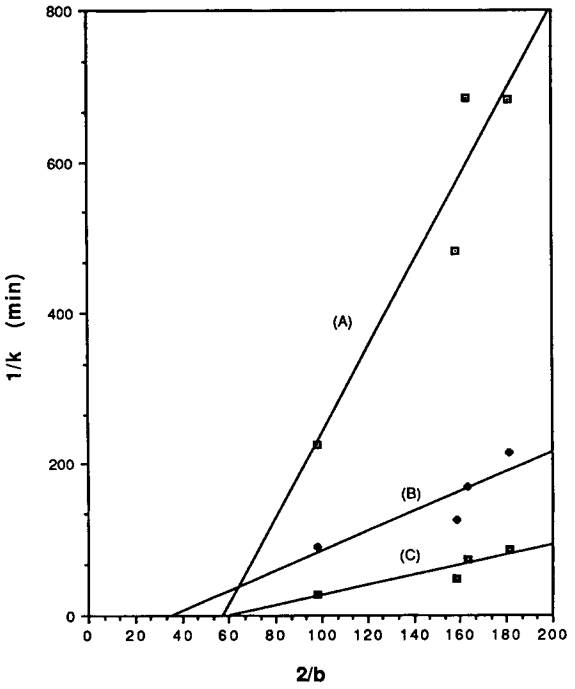

Figure 5 Plots of $1/k$ vs. $2/b$ for cellulose I samples hydrolyzed in 2% H_2SO_4 at (A) 150, (B) 160, and (C) 170°C.

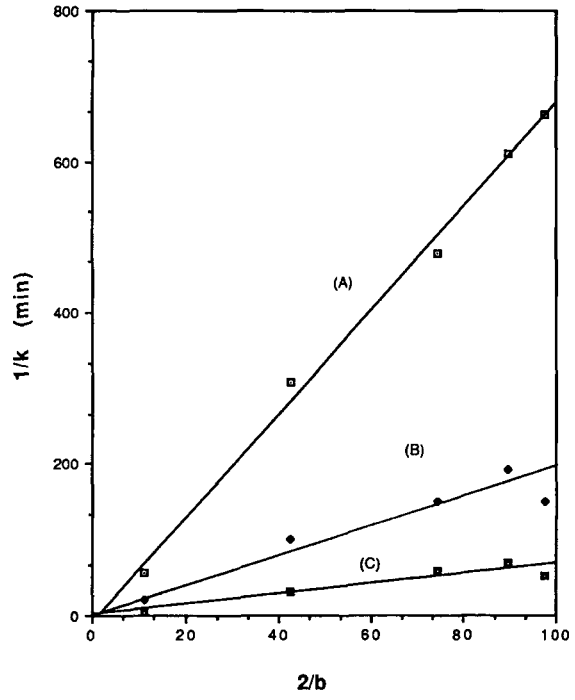

Figure 6 Plots of $1/k$ vs. $2/b$ for cellulose II samples hydrolyzed in 2% H_2SO_4 at (A) 150, (B) 160, and (C) 170°C.

molecular-weight material is that the universal calibration technique is invalid for low molecular weight CTC.[25,33] Since almost all the hydrolyzed rayon had a DP less than 50, the DP values for rayon samples are very uncertain. Marx-Figini[13] and Immergut and Ranby[15] also reported that the molecular weight distribution for crystalline cellulose was approximately exponential.

Examination of plots based on the data (Figs. 5 and 6) indicates that for all three temperatures an apparent linear relationship exists between $1/k$ and $2/b$. Only in the case of the cellulose II samples do the plots go through the origin as required by Sharples' model. Cellulose I and cellulose II polymorphs have different chain configurations and hydrogen bonding patterns as determined by X-ray crystallography. Thus, it is not unexpected that the data from the cellulose I samples and the cellulose II samples exhibit differing linear relationships. However, it would appear that Sharples' model is applicable to the dilute acid hydrolysis of cellulose II, but not to the hydrolysis of cellulose I. These data are consistent with the data we reported previously for cellulose hydrolysis in constant boiling HCl[20] and with our plots of Millett's data,[7] which were also

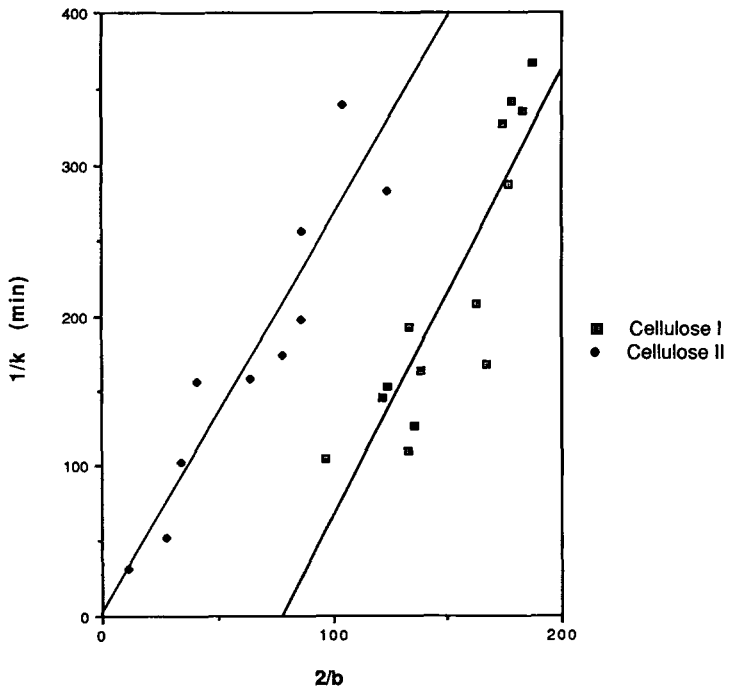

Figure 7 Plots of $1/k$ vs. $2/b$ from data of Wood et al.[20] and Millett et al.[7] (constant boiling HCl, 107°C).

obtained with constant boiling HCl (Fig. 7). When Sharples' data are reexamined carefully, we find that individual straight lines can be drawn through his data points for the cellulose I and cellulose II samples, respectively (Fig. 1). Thus, Sharples' original data are also consistent with our results.

The greatest uncertainty in the derivation of eq. (14) probably arises from the assumption that the mean lengths of the crystalline particles are identical with the mean lengths corresponding to the DP_W of the component chain molecules.[9] The two lengths are only exactly equivalent when all the particles from a given sample contain identical numbers of chain molecules. Since cellulose II samples usually have sharper molecular weight distributions than cellulose I samples, the assumption of equivalence of the average crystallite length and chain length is probably more accurate for cellulose II samples than it is for cellulose I samples. This factor could be one of the reasons that data for cellulose II samples obey Sharples' model while data for cellulose I samples do not.

One possibility which may complicate the measurement of the kinetic data for hydrolysis of cellulose II samples is the transition of the cellulose II structure to a cellulose IV structure at high temperatures in aqueous solution.[35] Raman spectroscopy or solid state NMR could, in principle, be used to determine the extent of this conversion during hydrolysis. However, no data of this type are currently available. Another possible explanation for the observed results could involve hornification of the mercerized celluloses during the drying process in the mercerization protocol. However, hornification was not observed for the mercerized samples in this study.

VanderHart and Atalla[36] have indicated that the molecular conformation in the cellulose I polymorph contains two distinct stable crystalline lattices with different hydrogen bonding patterns. The two forms are designated as cellulose Iα and cellulose Iβ. The Iβ form is more susceptible to hydrolysis than is the Iα form. The relative composition of each form within a given cellulosic sample is dependent on the source. Usually in celluloses derived from higher plants the Iβ form dominates whereas in celluloses derived from algal sources the Iα form dominates. Since the Iα and Iβ forms of cellulose do not hydrolyze at the same rate, variations in the proportions of these two crystalline structures may also partially explain why the hydrolyses of cellulose I samples are not well described by Sharples' model. In order to sort out the relative contributions of each morphological form to the kinetics of cellulose hydrolysis, it will be necessary to determine the ratio of cellulose Iα to cellulose Iβ in each of the cellulose samples. Current research efforts are proceeding in this direction.

CONCLUSION

Results obtained in this study and those reported in the literature indicate that the hydrolysis behavior of cellulose II samples are consistent with the end-attack model of Sharples. Differences in the rates of hydrolysis of cellulose II samples result from differences in the degree of polymerization of these samples. For cellulose I samples, mercerization of cotton and ramie increases their rates of hydrolysis while mercerization of linen and α-cellulose has the opposite effect. The intrinsic rate constants calculated from the end-attack model for hydrolysis at the ends of the crystallites are apparently greater for linen and α-cellulose than they are for cotton and ramie. This may be one of the reasons that Sharples' model does not apply to cellulose I samples since not all the cellulose I samples have the same intrinsic rate constant. Some researchers have reported that two crystalline lattices with different hydrogen bonding patterns are present in the cellulose I structure. Since these two cellulose I crystalline lattices do not hydrolyze at the same rate and their relative ratios are dependent on the source of cellulose, different intrinsic rates of hydrolysis for cellulose I samples may be due to variations in the contents of the two lattices.

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