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A Study of the Alcoholysis of Cellulose

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A STUDY OF THE ALCOHOLYSIS

OF CELLULOSE

A thesis submitted by

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INTRODUCTION

Cellulose is a straight-chain high polymer and its fine or submicroscopic structure is typical of such polymers. The fine structure of such polymers is described very well by Howsmon (1):

> Most high polymers, under proper conditions, will crystallize to form imperfectly ordered solids which exhibit a complex polyphase structure. Certain regions within a given sample possess a high degree of internal geometrical order and are commonly called "crystallites". These regions have many properties found in crystals of low molecular weight compounds; they diffract x-rays to produce regular fiber diagrams and they exhibit birefringence. Unlike crystals of low molecular weight materials, however, these regions do not have well defined plane boundaries or sharp edges. Their size and/or degree of perfection seem to vary widely from sample to sample or even in different parts of a given sample and almost without exception they are rodlike or ribbonlike. These "crystallites" seem almost comparable to the grains of a polycrystalline metal.
>
> High polymers do not consist entirely of such crystalline domains, but always contain a certain number of disordered, entangle chain molecules which give rise to "amorphous" or "disordered" regions. Like the crystalline regions, these disordered portions may also vary in size and/or degree of imperfection or randomness in different polymers or within a given polymer sample.

The density of the crystallites is high enough so that the interior cannot be penetrated by other molecules unless the crystalline structure is modified. This is not true of the amorphous portions which are available to molecules. A measure of the availability of portions of cellulose to other molecules or atoms is defined as the accessibility of the cellulose. The rate at which the cellulose reacts when it is available is not measured in determining accessibility. Under the

definition just given, cellulose is completely accessible only in a truly homogeneous reaction. Completely inaccessible cellulose does not exist, since the grossfiber surfaces are always accessible. The intermediate cases include all heterogeneous reactions in which the cellulose is only partly accesible.

In nonswelling heterogeneous reactions, the crystallites are not considered to be accessible. The remainder of the cellulose varies in accessibility because it varies in the degree of imperfection. Such variations create portions of cellulose which are accessible to a small molecule such as water but are not accessible to a larger molecule. Other regions might be accessible to molecules of greatly differing sizes. The dependence of accessibility on the size of the penetrating molecule has been indicated in past investigations. Previous techniques were generally not direct nor complete and it seemed, therefore, that the development of an additional technique particularly designed to study the variation of accessibility with molecular size would be valuable.

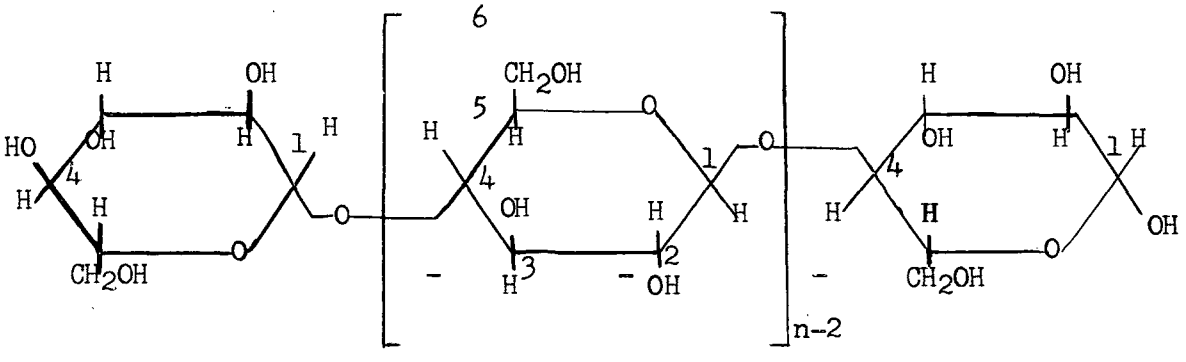
A promising approach for studying the variation of accessibility appeared to be that of alcoholytic degradation. Alcoholysis was considered to be an acid-catalyzed reaction in which the 1-4 links in the cellulose molecule were split by the alcohol. If such a mechanism were correct, then alcoholysis using a series of homologous alcohols could be used to determine the variation of the accessibility of the cellulose with the size of the alcohols. The reactions would be carried out in as nearly anhydrous a medium as feasible to minimize hydrolytic side reactions.

HISTORICAL REVIEW

CHEMICAL AND PHYSICAL CHARACTERISTICS OF CELLULOSE

The reactions of cellulose must be considered a result of both its chemical and physical properties. In most cases the effects cannot be separated. In order to develop a background for the understanding of alcoholysis reactions, certain of these chemical and physical properties will be discussed. More complete summaries of the properties of cellulose may be found in Hägglund (2), Wise and Jahn (3), and Ott and Spurlin (4).

Cellulose is a polyanhydroglucose. The individual glucose molecules are linked by 1-4 glycosidic bonds to form long-chain molecules as shown in the sketch.



Terminal Unit A Terminal Unit B

The average degree of polymerization (the number of glucose units per molecule) of native cellulose has been found to be at least 5000 (5). As in all natural substances the degree of polymerization (D.P.) of individual molecules varies considerably around the average.

Cellulose takes part in those reactions typical of glucose, but modified somewhat by the fact that cellulose is a large molecule. Three hydroxyl groups are available on each glucose unit. The sixth carbon atom contains a primary hydroxyl group; the second and third carbon atoms contain secondary hydroxyl groups. On each cellulose molecule, one terminal glucose unit (A on the sketch of the cellulose molecule) has an additional secondary hydroxyl group on the fourth carbon atom. The other terminal glucose unit (B on the sketch of the cellulose molecule) has a reactive aldehydic group, normally present as the hemiacetal. The cellulose molecule just described is somewhat idealized since actual samples contain small amounts of other reactive groups. For example, carboxyl groups may be formed by oxidation of the terminal hemiacetal groups or the primary hydroxyl groups.

The use of x-ray diffraction techniques indicated that cellulose was at least partially crystalline in nature. The amount of crystalline material varies according to the source of the cellulose. The values found by x-ray diffraction vary from 70% for cotton to 40% for rayons (6). The crystalline regions are not continuous but are separated by regions of less order. The average length of undegraded cellulose molecules is such that they extend through several regions of crystallinity and connect the crystalline regions. The physical structure of cellulose can be considered to combine a somewhat flexible structure (the noncrystalline portions) with regions of connection or rigidity (the crystalline portions).

EVIDENCE OF THE EFFECTS OF MOLECULAR SIZE IN HETEROGENEOUS REACTIONS

In 1943, Davis, Barry, Peterson, and King (7) studied the swelling of cellulose. They found that methyl, ethyl, and propylamine would swell cellulose directly. After preswelling with either liquid ammonia or ethylamine, straight-chain amines as large as heptylamine could swell cellulose. X-ray diffraction measurements showed that the crystal lattice was expanded by the amines. It appeared that the general fiber system was not accessible to the larger amines without an initial expansion by an amine of low molecular weight.

Assaf, Haas, and Purves (8) studied the variation of the accessible portion of cellulose with the molecular weight of the solvent used to carry a reacting molecule into the cellulose. Thallous ethylate, the reacting molecule, formed a thallium alcoholate compound with the accessible cellulose (see Equation 1). The alcoholate was then decomposed with methyl iodide replacing the thallium atom with a methyl group (see Equation 2) and the methoxyl content of the cellulose gave a measure of the accessibility of the cellulose to the solvent used. Complete methylation (45.59%) was considered to represent complete accessibility. Three series of solvents were used: normal ethers, alcohols, and hydrocarbons. The results were plotted as the percentage of methoxyl introduced versus molecular volume of the solvent (molecular weight divided by density) as shown in Figure 1.

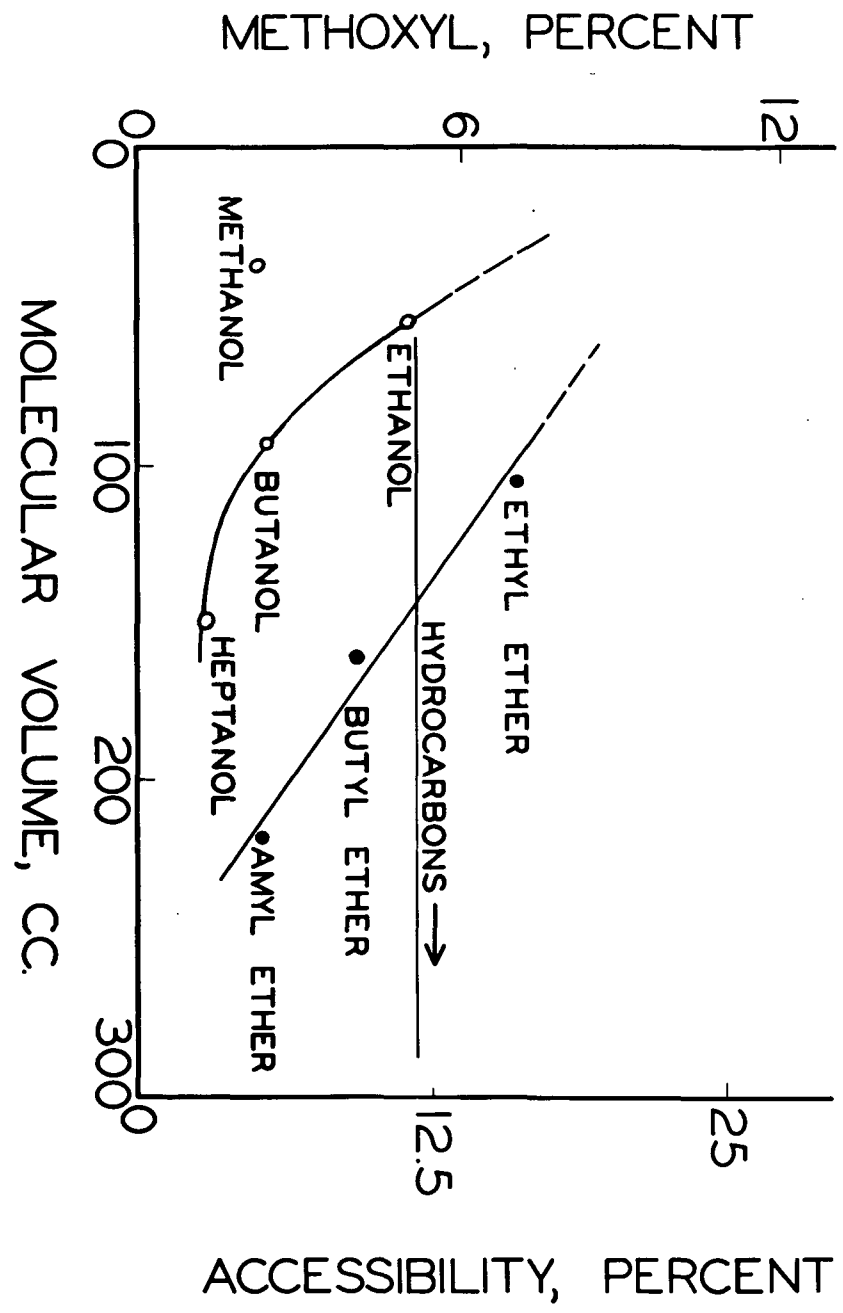


Figure 1

Superficial Methylation of a Uniform, Swollen Cellulose by Thallous Ethylate Dissolved in Various Organic Liquids, After Assaf, Haas, and Purves (8)

$$CellOH + TlOEt \longrightarrow CellOTl + EtOH \qquad (1)$$

$$CellOTl + MeI \longrightarrow CellOMe + TlI \qquad (2)$$

The relation between the methoxyl content and molecular volume was not a straight line when alcohols were used but the curves for ethers and alcohols extrapolated to the same value of methoxyl content at zero molecular volume. The authors used the values obtained by extrapolation of the curves to measure the accessibility of cellulose samples to a "nonswelling solvent of zero molecular volume." By this definition percentages of accessible cellulose were: 0.4% in ramie, 0.25% in cotton linters, and 9 to 22% in various samples of swollen linters. The values are lower than those found using other techniques for measuring accessibility.

The present writer calculated the molecular volume of thallous ethylate using the density determined by Sugden (9). The value found was 71 cc. which is larger than the molecular volumes calculated for both methanol and ethanol (10). When the molecular volume of the solvent is less than that of the thallous ethylate, there is some question whether the extent of accessibility is determined by the solvent or the reactant. Nevertheless, the work of Assaf and co-workers shows a definite relation between the molecular volume (or size) of the solvent molecules and the accessibility of the cellulose to the molecules. The data further indicate that the relation is dependent on both the molecular weight and the nature of the molecule.

Walseth (11, 12) found that enzyme-catalyzed hydrolysis was characterized by a smaller drop in the average D.P. of the residue and

a greater weight loss compared to an acid-catalyzed hydrolysis of the same cellulose. The study was made on unmodified linters and on the same linters made more reactive by swelling in cold concentrated phosphoric acid. The results are given in Table I.

TABLE I

A COMPARISON OF ENZYMATIC AND ACID HYDROLYSIS OF COTTON LINTERS

Sample	Treatment	Reaction Time, hr.	Weight Loss, %	D.P. of Residue
Cotton linters	None	--	--	1385
	H_2O Blank[a]	24	--	1140
	Enzyme	144	6.7	1105
	Acid[b]	48	6.3	105
Medium reactivity linters[c]	None	--	--	1310
	H_2O Blank[a]	24	--	1120
	Enzyme	144	37.6	1080
	Acid[b]	48	8.3	80
High reactivity linters[d]	None	--	--	1215
	H_2O Blank[a]	24	--	740
	Enzyme	144	79.3	295[e]
	Acid[b]	48	13.9	40

[a] pH = 6.0

[b] 0.25 N H_2SO_4 at boiling point

[c] Cotton linters swollen by 85% phosphoric acid, 2 to 3°C., 10 min.

[d] Cotton linters swollen by 85% phosphoric acid, 2 to 3°C., 2 hours.

[e] D.P. determined after only 82 hours degradation.

Walseth believed that enzyme hydrolysis attacked only a small portion of the noncrystalline cellulose but broke the portion attacked into soluble fragments. He contrasted this behavior to that in acid-catalyzed hydrolysis in which the hydrolysis proceeded throughout the entire noncrystalline region producing insoluble, low molecular weight fragments. Blum and Stahl (13), using a different enzyme, also found that the average D.P. of the residue was lowered only slightly in enzyme-catalyzed hydrolysis. They found, however, that the soluble losses were low. It is possible that the enzyme which they used was unable to convert larger carbohydrates to soluble fragments. The molecular weights of the enzymes used were unknown in both studies. Enzymes are protein molecules of considerable size, however, and it appears that much of the cellulose was inaccessible to such a large molecule (11).

Hartler and Samuelson (14) studied the hydrolysis of wood cellulose using sulfuric and lignosulfonic acids as the catalysts. The effective acidities of the two acids were made equal by using concentrations of each which gave the same rate of cane sugar inversion. Degradation of the cellulose, measured by the viscosity of the residues, was more rapid when using sulfuric acid than when lignosulfonic acid was used. At the same degree of degradation, the losses were lower when sulfuric acid was used as the catalyst. The authors suggested that, during the early stages of the degradation, the larger molecular size of the lignosulfonic acid catalyst caused the differences observed. The lignosulfonic acid was not stable and low molecular weight acids were built up during the hydrolyses so that the limiting viscosity represented the effect of a low molecular weight catalyst.

Weaver, Mackenzie, and Shirley (15) studied the alkylation of cotton cellulose by the lower straight-chain esters of p-toluenesulfonic acid. Using 15.5 N sodium hydroxide at 100 to 120°C., a maximum of 2.7 methoxyl groups per glucose unit was introduced in two hours, only 1.0 ethoxyl group per glucose unit was introduced in seven hours, and only 0.4 propoxyl group per glucose unit could be introduced even after 15 hours. No reaction occurred with any of the higher esters. The differences in the rates of reaction were attributed to differences in reactivities of the various esters. On the other hand, the decrease in the maximum amount of alkylation attained as the size of the alkyl group increased indicated a partial influence of molecular size on the course of the reaction.

An analysis of the various studies reported in the literature is handicapped by a lack of data concerning the effective size of the various reacting molecules in comparison with the available spaces in cellulose. A comparison should be made on the basis of the spheres of influence of the molecules with respect to the cellulose-solvent-reactant system. Without such data, however, two other approaches may be made. The physical size of the reactants may be compared with the known size of the openings within the cellulose fibers, or the effects of the various series of reagents may be compared on the basis of molecular volumes.

The size of the spaces within and around the microfibrils in a cellulose fiber have been measured by precipitating colloidal gold and silver within the spaces. Frey-Wyssling (16) using x-rays de-

termined the size of the gold and silver particles to be 50 to 135-A. long and about 10-A. wide. He stated that two capillary systems were present; those within the microfibrils and around the micelles (about 10-A. wide) and those between the microfibrils (about 100-A. wide). Using x-rays, Wardrop (17) found the particle size of the precipitated gold to be 73 to 122-A. Direct measurements using electronmicrographs indicated that the particles were somewhat smaller.

Sizes of some of the molecules mentioned in this review were determined by the present writer using Fisher-Hirschfeld-Taylor atomic models. The sizes used in these models are the collision diameters of the molecules at low velocities. The dimensions found are given in Table II.

If only collision diameters are considered, then any capillary (about 100-A. wide) between the microfibrils should be accessible to the molecules listed in Table II. The spaces (about 10-A. wide) within the microfibrils are of the same order of magnitude as n-butanol, n-butylamine, and diethyl ether. As these molecules have some flexibility, the effective sizes may be somewhat smaller. The relation between size and experimentally determined accessibility is good for n-butanol [see Assaf, Haas, and Purves (8)] and butylamine [see Davis, Barry, Peterson, and King (7)]. Cellulose is apparently more accessible to ethyl ether (8) than it should be judging from the molecular size. This may be a result of the difference in functional groups on three compounds.

TABLE II

MOLECULAR SIZES USING FISHER-HIRSCHFELD-TAYLOR ATOMIC MODELS

Molecule	Extended Length, A.	Width, A.	Flexible
Methanol	5	4	No
Ethanol	6.5	4	No
Propanol	8	5	No
n-Butanol	9	5	Yes
sec-Butanol	8	6	Yes
tert-Butanol	6.5	6	No
n-Heptanol	10.5	5	Yes
n-Octanol	24	5	Yes
Methylamine	5.5	4.5	No
Ethylamine	6	4.5	No
Propylamine	7.5	5	No
Isopropylamine	6.5	6	No
n-Butylamine	8	5	Yes
Diethyl ether	9	4.5	Yes
Diamyl ether	17.5	6.5	Yes
Diisoamyl ether	14	6.5	Yes
Dibutyl ether	14.5	5	Yes
Hydronium ion (H_3O^+)	4	2.5	No
Ammonia (NH_3)	4	4	No

The molecular volumes of some of the compounds discussed in this review have been calculated (10, 18, 19) and are listed in Table III.

TABLE III

MOLECULAR VOLUMES OF SOME COMPOUNDS

Compound	Molecular Volume, cc.
Methanol	40
Ethanol	59
n-Butanol	92
n-Hexanol	125
n-Heptanol	140
n-Octanol	160
Methylamine	41
Ethylamine	66
Propylamine	82
Isopropylamine	85
Butylamine	99
Amyl ether	140
Thallous ethylate	71
Methyl p-toluenesulfonate	160
Ethyl p-toluenesulfonate	220

The relation between molecular volume and accessibility is not as good as that found between size and accessibility and seems more dependent on the functional groups on the molecules. Comparing amines, propylamine swells cellulose directly while butylamine and isopropylamine do not. The effect of branching should be noticed. Cellulose is more accessible to n-amyl ether than to n-heptanol although the molecular volume of the alcohol is much smaller. The alkylation studies of Weaver, Mackenzie, and Shirley (15) indicated that swollen cellulose reacted with methyl p-toluenesulfonate to a greater extent than would ethyl p-toluenesulfonate. Part of the difference was attributed to differences in reactivity. From the limited data presented in the review, it appears that unswollen cellulose is accessible to compounds having molecular volumes of 80 cc. or less. After swelling, cellulose is accessible to compounds with a molecular volume of as high as 160 cc. On this basis, unswollen cellulose should be accessible to methanol, ethanol and propanol, but not to higher alcohols.

ALCOHOLYSES

Irvine and Hirst (20) in 1922, and Heuser and Aiyer (21) in 1924, used heterogeneous methanolyses to produce methyl glucosides from cellulose triacetate. The catalyst was hydrogen chloride (0.75%) and the temperature was 125°C. The yield of mixed glucosides was very nearly quantitative in spite of the severe conditions.

Reeves and co-workers studied the heterogeneous alcoholysis of cellulose in some detail. In 1946, Reeves, Schwartz and Giddens (22)

compared the heterogeneous degradation of cellulose at 20°C. using 0.5 N hydrogen chloride in methanol, ethanol, water, and ten per cent water in methanol. The fluidity and copper number of the residue are shown as a function of the time of treatment in Figures 2 and 3. The authors stated that under the same conditions of temperature and acid concentration, methanolysis and ethanolysis degraded cellulose much more rapidly than did hydrolysis. The addition of water to methanol decreased the rate of degradation markedly. They stated that methanolyzed cellulose differs from hydrolyzed cellulose in being nonreducing, as indicated by the copper number determination, in stability to hot aqueous alkali, and in containing acid-labile alcohol residues. They found under more severe conditions that the same limiting fluidity would be reached in both methanolysis and hydrolysis. The methanolyzed samples had higher methoxyl contents (0.58% for a methanolyzed native cellulose compared to a normal value of 0.25% before methanolysis) which could be decreased by refluxing for 24 hours in 0.5 N hydrochloric acid. The authors believed that the glucose-glucose links in the original cellulose were split by the acid-catalyzed alcohol with the simultaneous introduction of an alcohol residue on the cellulose molecule. Reeves, Mazzeno, and Hoffpauir (23) measured the amount of the cellulose solubilized in methanolysis at 30°C. at various concentrations of catalyst. The results are given in Table IV.

Reeves (24) in a patent reported the alcoholysis of cotton with several other alcohols at 120°C. The results are listed in Table V.

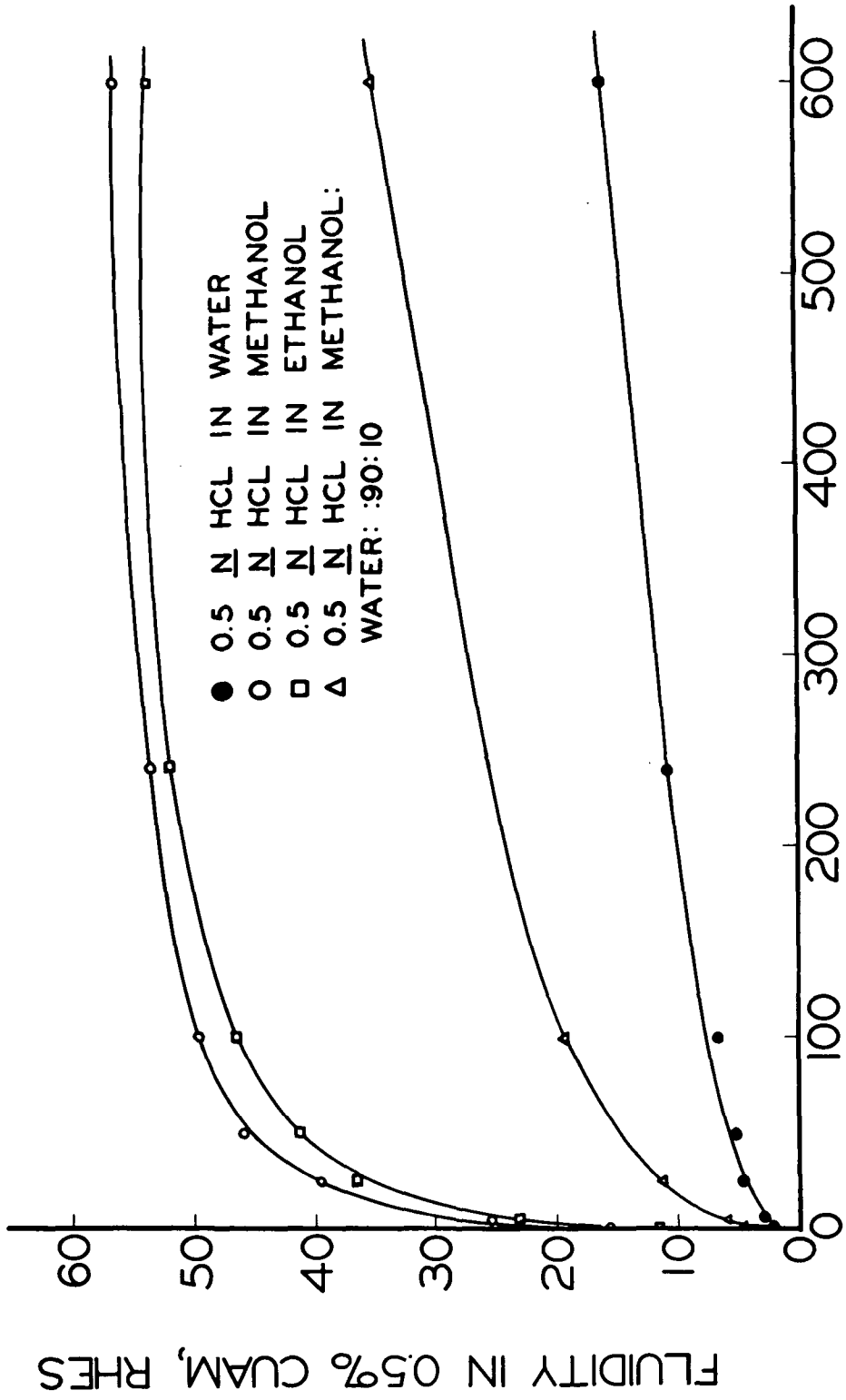


Figure 2

Variation of Fluidity With Time of Degradation at 20°C., After Reeves (22)

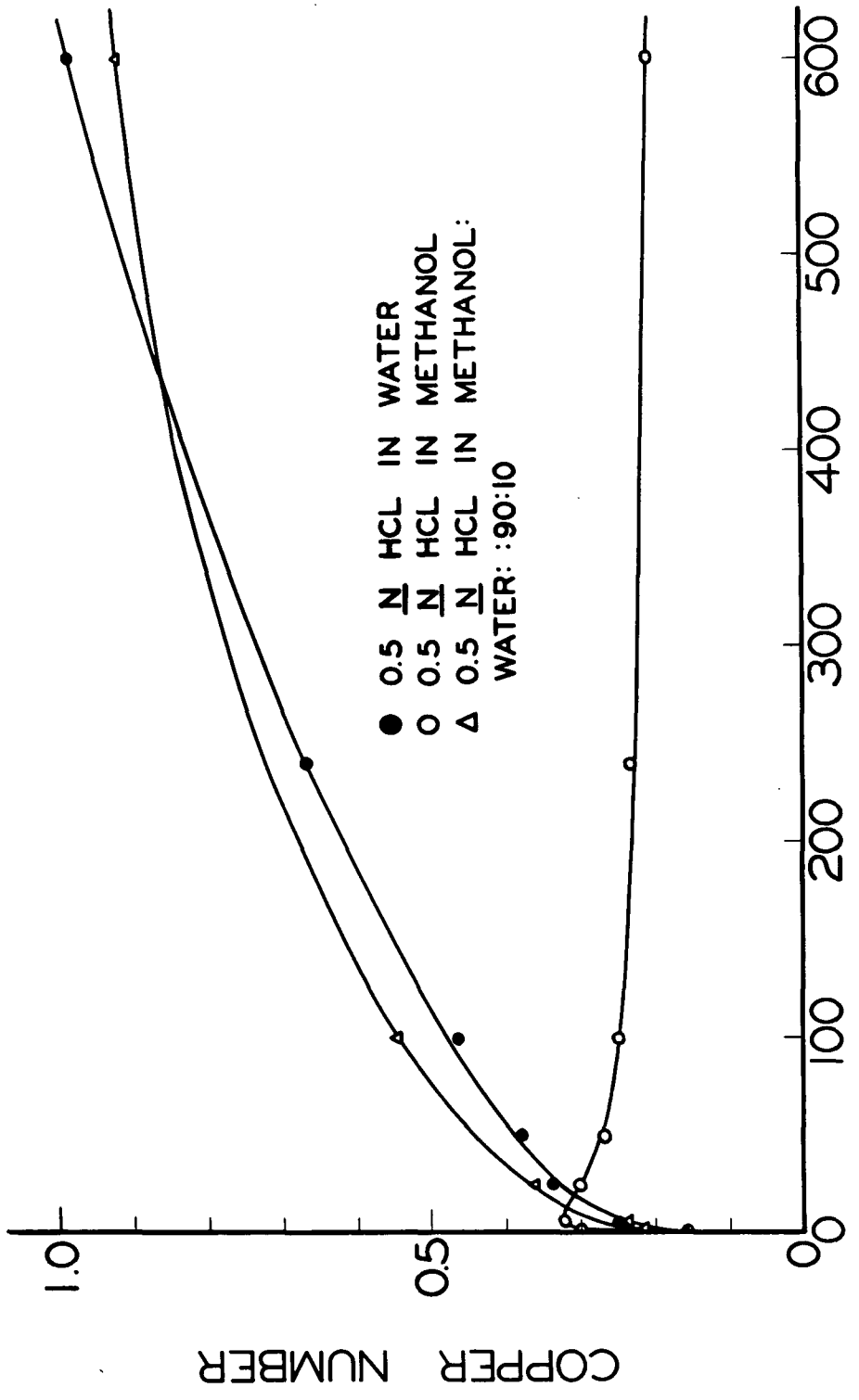


Figure 3

Variation of Copper Number With Time of Degradation at 20°C., After Reeves (22)

TABLE IV

CELLULOSE SOLUBILIZED DURING METHANOLYSIS[a]

Conditions: 30°C., HCl as catalyst

Catalyst Concn., N	Time, hr.	Soluble Losses, %
	Part I	
0.01	240	0.006
0.05	240	0.202
0.185[b]	240	0.372
0.44 [b]	240	0.816
	Part II	
0.50	1	0.087
0.50	2	0.087
0.50	5	0.101
0.50	25	0.247
0.50	97	0.757
0.50	240	1.12
0.50	450	1.84
0.50	810	2.81
0.50	1200	2.71
0.50	2010	4.26

[a] A portion of the data of Reeves, Mazzeno, and Hoffpauir (23).

[b] Concentration varied and this is an average value.

TABLE V

ALCOHOLYSIS OF COTTON WITH HIGHER ALCOHOLS

Temperature: 120°C.

Alcohol	Concentration of HCl, N	Time, min.	Fluidity in Caum, Rhes.	Loss of Weight, %
n-Propanol	0.11	30	17.9	6.0
	0.22	30	19.2	9.0
	0.44	60	23.0	18.0
n-Butanol	0.11	30	17.9	2.0
	0.44	60	18.9	16.0
	0.44	240	23.9	16.5
n-Pentanol	0.44	60	22.2	19.0

In every instance the residue was discolored. He also stated that either sulfuric or p-toluenesulfonic acid could be used as the catalyst. The recommended limit of catalyst concentration was 2 normal.

Mehta and Pacsu (26), and Pacsu (27) studied the heterogeneous methanolysis of cotton and rayon at 0°C. using 9.42 N hydrogen chloride as a catalyst. The results were similar to those found by Reeves and co-workers. The limiting D.P. for the cotton was found to be 250.

Blair (28) studied the alcoholysis of several cotton samples using 2-methoxyethanol and p-toluenesulfonic acid. The temperature range covered 90 to 110°C. and the concentration of catalyst varied from 0.15 to 1.0 N.

In 1954, Sharkov, Korol'kov, and Krupnova (29) reported the methanolysis and ethanolysis of cotton using sulfuric acid as the catalyst. The original work was in Russian and only the abstract was available in English. The rate of degradation was found to increase with: an increase in the alcohol concentration in the acid-alcohol-water system, the addition of a nonpolar solvent (benzene, toluene, or carbon tetrachloride) to the solvent system, and an increase in the available surface (mercerization). Two important statements were made in the abstract: "The nature of cleavage is analogous to that observed in hydrolysis," and "The adsorbed aqueous layer on the surface of the fiber, under the above conditions, does not appear to dilute the H_2SO_4 content of the reaction mixture."

CHEMICAL AND PHYSICAL PROPERTIES OF ALCOHOLS

Reactions With Hydrogen Chloride

Reeves, Hoffpauir, and Demint (30) studied the formation of water at 0°C. in methanol acidified with hydrogen chloride. The changes in water and hydrogen chloride concentration are given in Table VI.

TABLE VI

REACTION OF HYDROGEN CHLORIDE WITH METHANOL

Reeves, Hoffpauir, and Demint (30)
Temperature, 0°C.

Concentration of HCl, N			Concentration of Water[a] g./l.		
Initial	7 days	45 days	Initial	7 days	45 days
4.11	4.06	3.81	0.250	0.250	0.300
10.41	10.19	9.12	0.278	0.406	1.617
12.05	11.78	--[b]	0.250	0.500	1.750[b]

[a] Methanol contained 0.116 g./l. of water before acidification
[b] Inaccurate because of bubbles

The initial concentrations of hydrogen chloride were much higher than those used in actual methanolyses by Reeves and his co-workers. There is no further information in the literature concerning the formation of water from reactions between alcohols and hydrogen chloride.

Association of Alcohol Molecules in the Liquid State

A complicating factor in the analysis of any accessibility data concerning alcohols is the question of whether the alcohols are penetrating the cellulose as individual molecules or as associated

groups of large size. Lagemann (32) estimated the possible association of alcohols using the velocity of sound in the liquids and the critical temperatures and pressures. He found methanol to be associated and similar to water in many physical properties. Ethanol was intermediate in its properties between associated and nonassociated liquids. Parshad (33) estimated association using values for compressibility and expansion coefficients. He found methanol to be associated in much the same way as water. The associated molecules were not fixed but were in equilibrium with nonassociated molecules.

REACTIONS OF NEUTRAL ALCOHOLS WITH CELLULOSE

Chemical Degradation of Cellulose by Neutral Alcohols

There is no direct evidence concerning the degradation of cellulose by neutral alcohols at room temperatures. An estimate of the effects can be made from the following data. Kleinert (31) heated cotton in mixtures of ethanol and water at 180°C. for four hours. Cotton heated in ethanol-rich mixtures showed a higher residual weight and lower copper number than did the cotton samples heated in water-rich mixtures. The alpha-cellulose content of the cotton heated in ethanol was 97.6% compared to 56.6% for cotton samples heated in water. At high temperatures, it appears that ethanol is less destructive to cellulose than is water. It seems reasonable to assume that neutral alcohols should have no more effect on cellulose at room temperatures than does water. Further, Blum and Stahl (13) found that neutral water at 40°C. did not lower the D.P.

of cotton samples. Therefore, neutral alcohols at room temperatures should not affect the properties of cellulose to any measurable degree.

Swelling of Cellulose by Alcohols

Kress and Bialkowsky (34) found that methanol and ethanol would swell cotton to a lesser degree than would water. Butyl and amyl alcohols did not swell cotton appreciably.

Sorption of Alcohol Vapors by Cellulose

Richter, Herdles, and Wahtera (35) and Sheppard and Newsome (36) studied the sorption of alcohol vapors by cellulose at high relative vapor pressures. For cellulose samples which would sorb 20 to 25% by weight of water, the sorption of alcohol vapors was: methanol, 10 to 12%; ethanol, 8 to 11%; n-propanol, about 5%; and n-butanol, 1.2 to 1.8%. It was also observed by Sheppard and Newsome that the pickup of nonaqueous vapors was increased if the cellulose sample was first dried from a nonaqueous liquid.

HETEROGENEOUS HYDROLYSES

In view of the similarities between alcoholyses and hydrolyses observed by previous investigators, there will be a limited discussion of heterogeneous acid-catalyzed hydrolyses. Some of the terminology and concepts used in discussing hydrolyses will be used in the present work on alcoholyses.

In 1943, Davidson (37) measured the loss of weight and the fluidities of the residues of cotton linters degraded under four different conditions: (a) 10 N hydrochloric acid at 20°C., (b) 6 N hydrochloric acid at 20°C., (c) 10 N sulfuric acid at 20°C., and (d) 0.5 N sulfuric acid at 100°C. He found that the hydrochloric acid was much stronger in its effects than was the sulfuric acid. Six normal hydrochloric acid degraded cotton at a faster rate (measured by either fluidity or weight loss) than did 10 N. sulfuric acid. The results from the use of 0.5 N sulfuric acid at 100°C. were comparable to those from 10 N hydrochloric acid at 20°C.

Battista and Coppick (38) studied the hydrolysis of several cotton samples using 5 N hydrochloric acid at 18°C. The samples used were: cotton linters, the same linters prehydrolyzed for four hours at 6°C. using 2 N sulfuric acid, the regenerated cellulose obtained from a cuprammonium solution of the linters, and regenerated cellulose obtained from a cuprammonium solution of the prehydrolized linters. The degradation was followed by determining the D.P.'s of the residues (see Table VII). The authors suggested that prehydrolysis removed the easily accessible portion and that further hydrolysis could only attack the resistant portion very slowly. After regeneration, the amount of easily accessible cellulose was increased.

TABLE VII

HETEROGENEOUS HYDROLYSIS OF CELLULOSE[a]

5 N HCl: 18°C.

Time, hr.	Degree of Polymerization			
	Cotton Linters	Regenerated[b] Linters	Pre-Hydrolyzed[c] Cotton Linters	Regenerated[b,c] Pre-Hyd. Linters
0	835	824	335	345
2	780	---	330	---
4	745	---	328	---
8	602	278	340	260
24	477	---	321	190
48	392	150	309	---
120	334	112	300	135
240	328	102	291	100
480	304	92	288	84

[a] Taken from a portion of the data of Battista and Coppick (38).
[b] Regenerated by precipitation from cuprammonium hydroxide.
[c] Pre-hydrolyzed 4 hours at 60°C., 2 N sulfuric acid.

Philipp, Nelson, and Ziifle (39) studied hydrolysis using strong hydrochloric acid at high temperatures. The determined reaction constants for the accessible and crystalline portions of the cellulose by assuming that the reactions were first order. The results are shown in Table VIII. At 100°C., they found that hydrolysis in both the accessible and inaccessible regions was faster for a Fortisan rayon sample than for a cotton linter sample.

Meller (40, 41), using 8% hydrochloric acid at 80 to 100°C., found that the degradation of the difficultly accessible portion was zero order.

TABLE VIII

REACTION CONSTANTS FOR HETEROGENEOUS HYDROLYSIS[a]

	Cotton Linters			Fortisan Rayon			
Temperature, °C.	100	100	95	100	100	100	95
HCl Concentration, N	4	6	6	2.5	4	6	4
k_c[b], sec.$^{-1}$	5.33×10^{-6}	18.0×10^{-6}	9.4×10^{-6}	5.15×10^{-6}	16.9×10^{-6}	61.2×10^{-6}	8.7×10^{-6}
k_a[c], sec.$^{-1}$	$102. \times 10^{-6}$	$312. \times 10^{-6}$	$186. \times 10^{-6}$	$110. \times 10^{-6}$	$349. \times 10^{-6}$	--	$178. \times 10^{-6}$

[a] Recalculated from a portion of the data of Philipp, Nelson, and Ziifle (39).
[b] Reaction constant for the crystalline portion.
[c] Reaction constant for the accessible portion.

Howsmon (42) and Hermans and Weidinger (43) studied the variations in crystallinity of the undissolved cellulose during heterogeneous hydrolysis. Howsmon, using 5 N hydrochloric acid at 50°C., found that the crystallinity (measured by heavy water exchange and moisture regain) increased rapidly before the loss of weight was sufficient to allow for the solubilization and removal of the noncrystalline portions. He suggested that recrystallization of the amorphous regions was occuring during the hydrolysis. Hermans and Weidinger (43), using 2.5 N sulfuric acid at the boiling point, studied the crystallinity of the residues (determined by moisture regain and x-ray diffraction). They found that recrystallization occurred during the hydrolysis of viscose rayon but not during the hydrolysis of ramie fibers.

Battista (44) studied the degradation of cellulose under several conditions of acidity and temperature. Figures 4 and 5 show the variation of D.P. of the residue with time of treatment. When the temperature was held at 40°C., the D.P. appeared to be decreasing to a leveling-off value. The present writer plotted 2/D.P. versus the time in seconds following Sharples' (52) suggestion and the results are shown in Figures 6 through 9. At 50°C., the plots were straight after an initial transition period. At higher temperatures, the transition period increased. The raw cotton and bleached cotton linters showed definite indications of some very reactive links as judged from the initial steep increase in the value of 2/D.P.

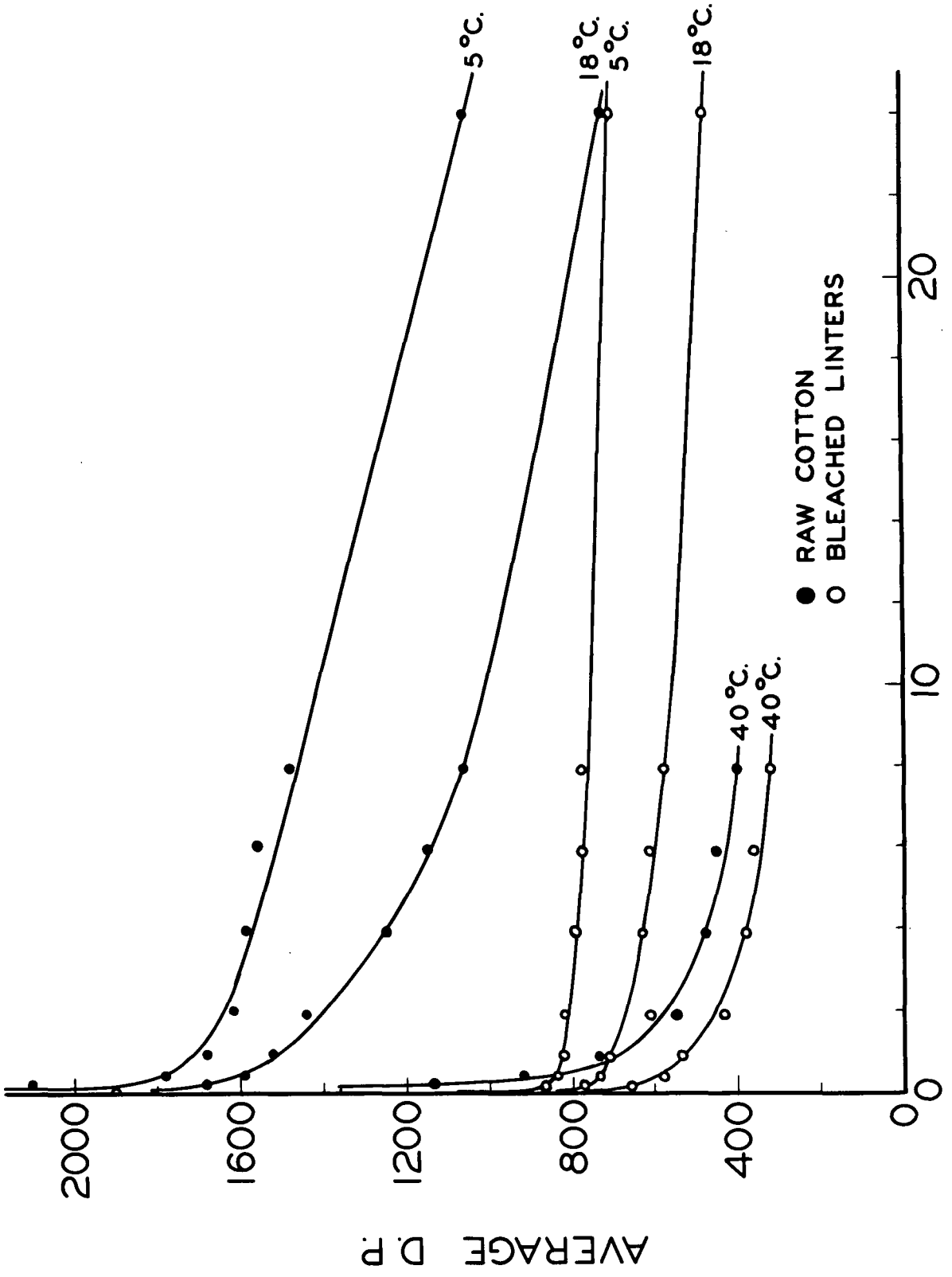


Figure 4

D.P. Versus Time for Cellulose Samples Hydrolyzed in 5 N HCl at Various Temperatures, After Battista (44)

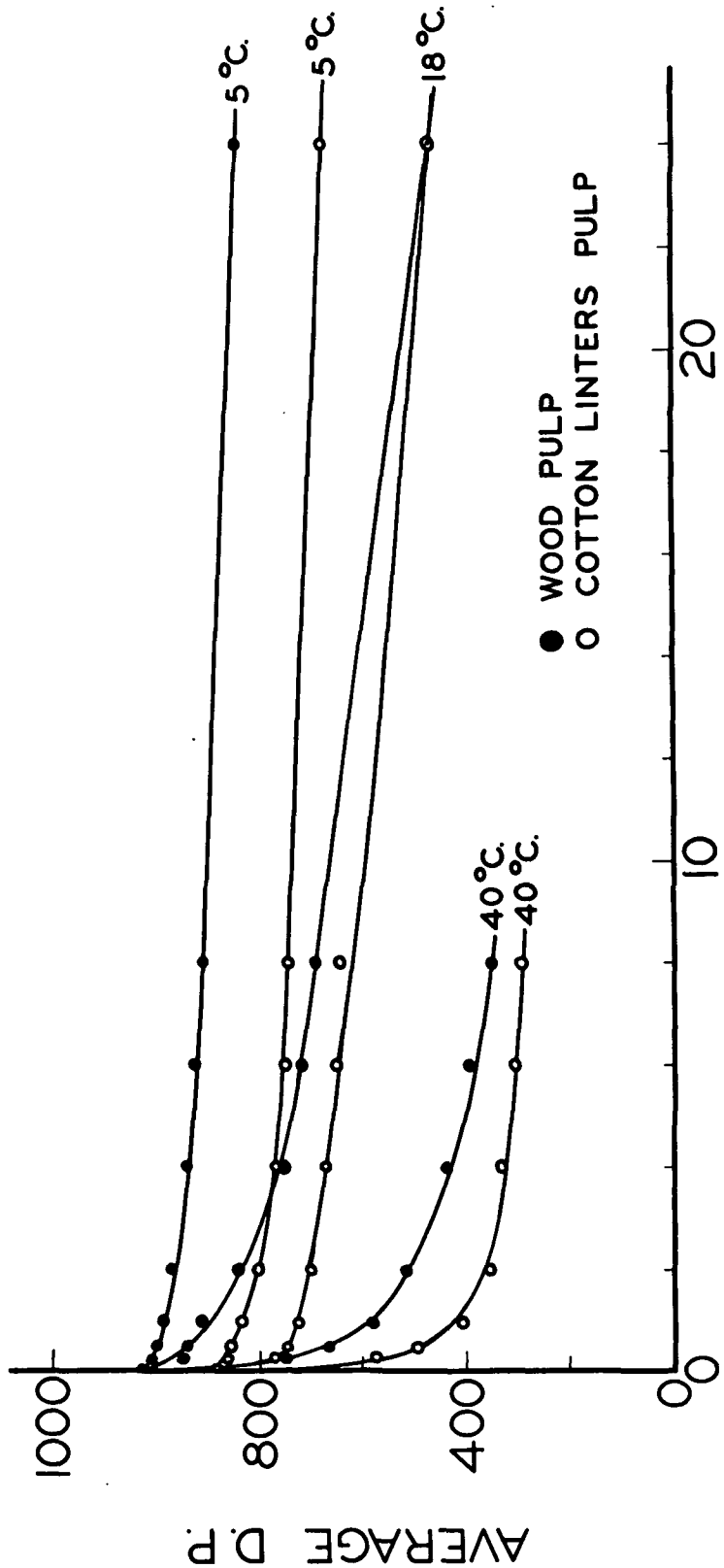


Figure 5

D.P. Versus Time for Cellulose Samples Hydrolyzed in 5 N HCl at Various Temperatures, After Battista (44)

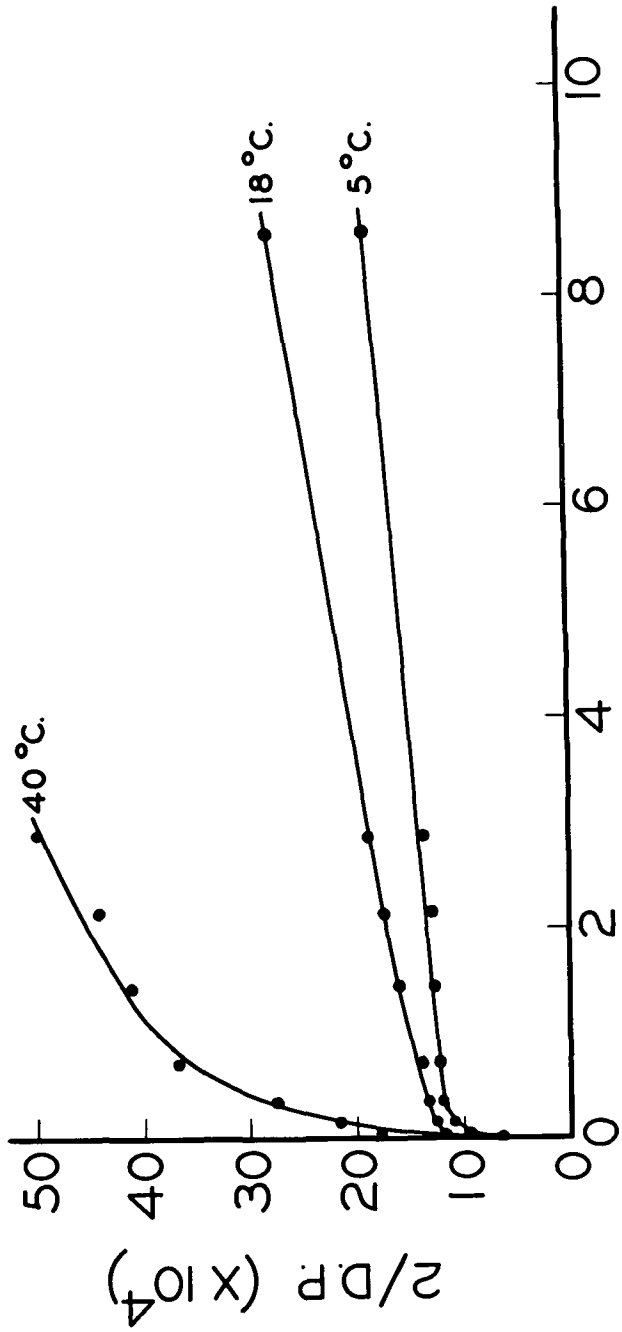


Figure 6

2/D.P. Versus Time of Treatment in 5 N HCl, Raw Cotton

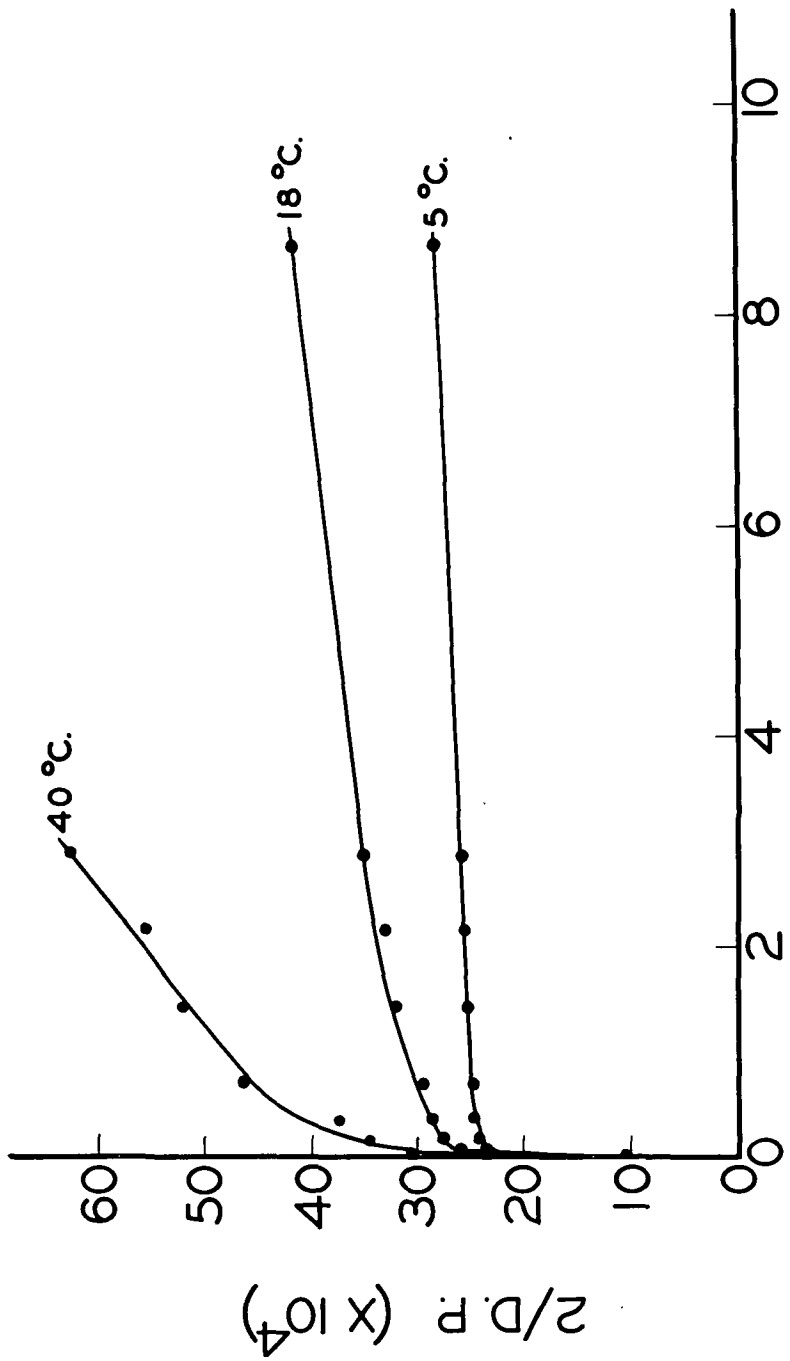


Figure 7

2/D.P. Versus Time of Treatment in 5 N HCl, Bleached Linters

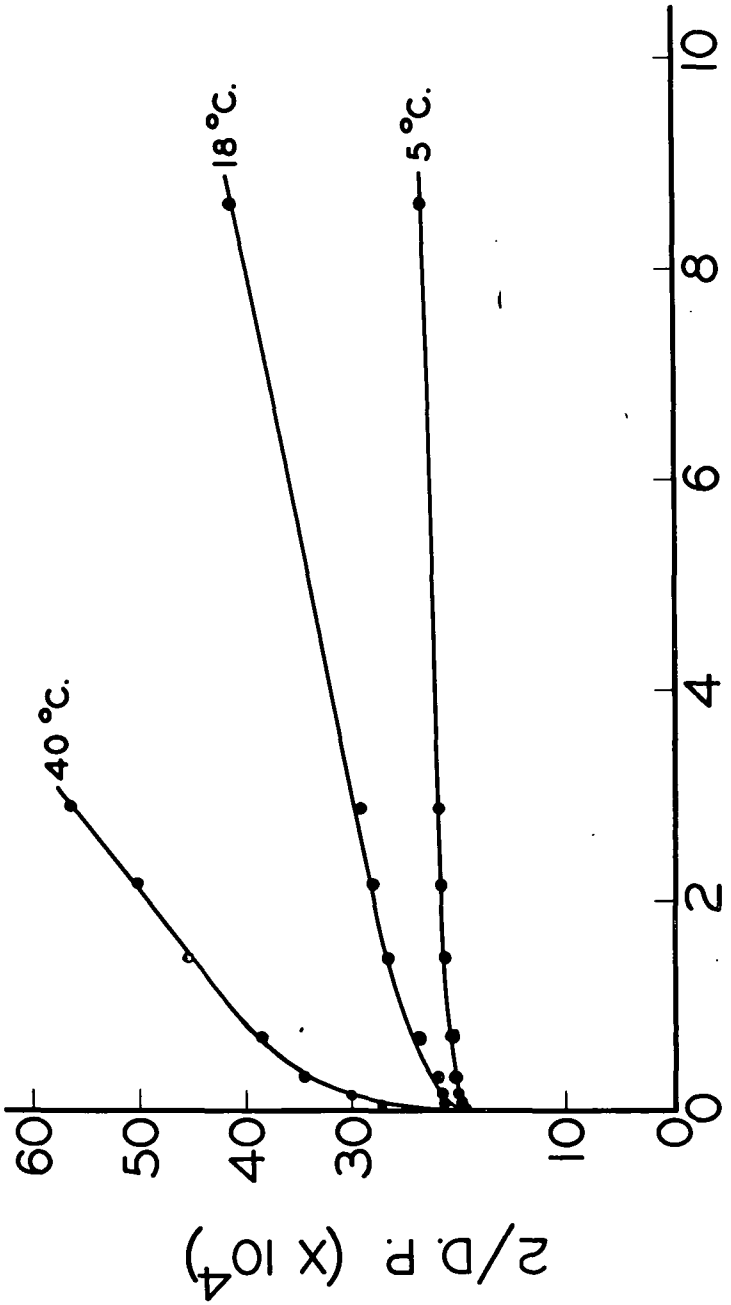


Figure 8

2/D.P. Versus Time of Treatment in 5 N HCl, Wood Pulp

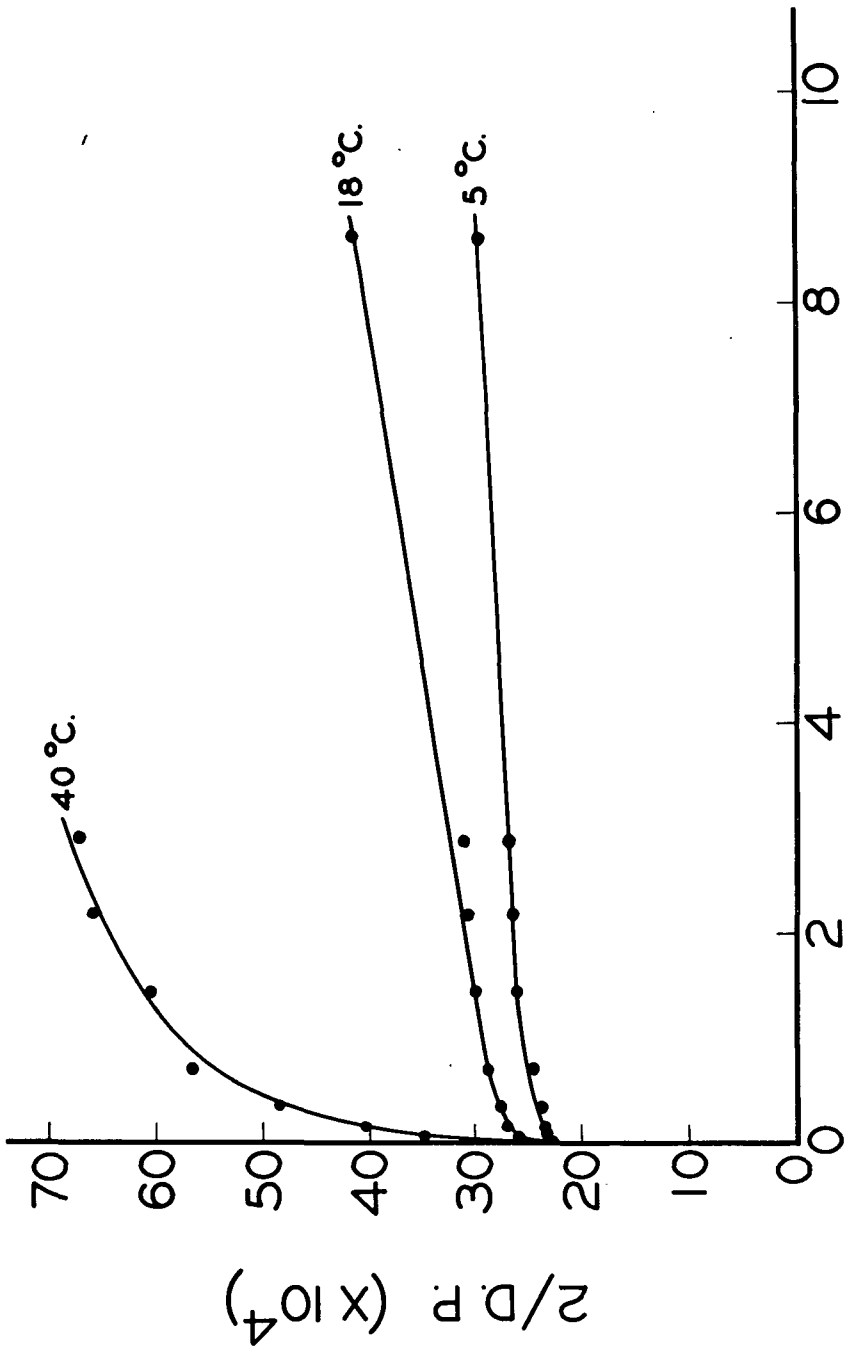


Figure 9

2/D.P. Versus Time of Treatment in 5 N HCl,
Cotton Linters Pulp

Bauer and Pacsu (45) studied the effects of 1.0 N hydrochloric acid at 60°C. on mercerized cotton. They plotted 1/D.P. versus time and found that the reaction constant was 55 x 10^{-8} sec.$^{-1}$ initially and decrease gradually to 8.0 x 10^{-8} sec.$^{-1}$ when the D.P. of the residue was about 220. The present writer's plot of 2/D.P. versus time also showed a transition zone with no sharp break. The slope of the straight line portion of the graph was 0.93 x 10^{-8} sec.$^{-1}$.

Roseveare (46) studied the degradation of cellulose at 96°C. using 2.5 N sulfuric acid. In order to eliminate the build up of degradation products during the reaction, the acid was allowed to run through the cellulose which was held in a fritted glass crucible. The rate of degradation was followed by measuring the percentage of material lost. The author found the reaction constant for cotton linters and rayons to be about 1.80 and 2.19 x 10^{-1} hr.$^{-1}$, respectively.

Nelson and Tripp (47) studied the degradation of cotton linters and rayon at 100 and 80°C. in 2.5, 1.0, 0.1, and 0.01 N hydrochloric acid. Each type of cellulose was found to reach a leveling-off D.P. after sufficient time, no matter what conditions were used. The authors also found that the rate of degradation decreased tenfold on decreasing the temperature 20°C. The rate of degradation increased exponentially with an increase in the acid concentration. The soluble losses were all less than four per cent until after the leveling-off D.P. was reached. The moisture regain decreased for all the samples during the rapid drop in viscosity, then was constant.

Rånby and Ribi (48), and Rånby (49) hydrolyzed cotton samples, and then dispersed the residue ultrasonically. Electronmicrographs of the colloidal suspensions which resulted showed that the cellulose had broken down into fragments 500 to 600 A. long and 50 to 100 A. wide. The length corresponded to the average D.P. of the residue, and the authors suggested that the fragments represented the original crystallites of the cellulose. Further work was done by Morehead (50) and is shown in Table IX.

TABLE IX

COMPARISON OF LIMIT D.P. AND CRYSTALLITE LENGTH AFTER MOREHEAD (50)

Fiber	Limit D.P.	Crystallite Length Calculated from D.P., A.	Average Observed Crystallite Length, A.
Cotton	280	1442	1460
Wood	297	1535	1450
Ramie	251	1293	1200
Fortisan	65	335	334
Rayon	50-60	254-309	240

Millett, Moore, and Saeman (51) followed the degradation of cellulose samples to almost complete solution by percolating the condensed vapors of constant boiling hydrochloric acid over the samples. They found that after an initial rapid loss of weight of less than five per cent, the loss of weight was first order to complete solution. When they plotted the average D.P. of the residue against the percentage of residue the average D.P. did not level off.

Sharples (52, 53) degraded several samples of cellulose using 0.1 N sulfuric acid at 96°C. He determined the average D.P. of the residues and plotted 2/D.P. versus time. All the samples showed a fast initial reaction with a reaction constant of 1.8×10^{-4} sec.$^{-1}$. Then there was an immediate sharp break in the curve followed by a straight line portion of the graph which gradually became concave downward. The slope of the straight line was 0.17×10^{-8} sec.$^{-1}$. Sharples found that the fast initial reaction could be decreased by eliminating all oxygen in the preparation of samples.

It is, of course, dangerous to compare the results of various workers who have used different methods of analysis and have worked with different cellulose samples. There is, however, a certain pattern which can be seen in the heterogeneous hydrolyses discussed. The reaction constants actually reported by various workers or calculated by the present writer using the original data are given in Table X. The constants are divided in two main groups representing "mild" hydrolysis with a reaction constant of less than 2×10^{-8} sec.$^{-1}$ and "drastic" hydrolysis with a reaction constant greater than 10^{-6} sec.$^{-1}$. The decrease in the average D.P. of the residue is slower in a mild hydrolysis and the leveling-off D.P. is not reached in less than ten hours. The work of Nelson and Tripp (47) indicates that in time, the same leveling-off D.P. is reached in all hydrolyses of a given sample but the rapidity of the drop in a drastic hydrolysis makes samples taken at early times poor in reproducibility. A second difference between mild and drastic hydrolysis may be noted when the

work of Battista is replotted as 2/D.P. versus time (see Figures 6 through 9). Hydrolysis at 5 and 18°C. gives straight line plots after the initial rapid reaction. At 40°C., the reaction constant is out of the "mild" range and the plots are curved, hiding the straight line portion.

TABLE X

REACTION CONSTANTS FOR HETEROGENEOUS HYDROLYSIS OF COTTON LINTERS CALCULATED FOR FIRST ORDER REACTION

Acid Used	Temperature, °C.	Acid Concn., N	Reaction Constant $sec.^{-1}$	Source
HCl	100	6.0	3.12×10^{-5}	(39)[a]
HCl	100	4.0	1.02×10^{-5}	(39)[a]
HCl	100	2.2	1.64×10^{-4}	(40)[a]
H_2SO_4	96	2.5	0.50×10^{-4}	(46)[a]
HCl	95	6.0	1.86×10^{-5}	(39)[a]
HCl	90	2.2	0.55×10^{-4}	(40)[a]
HCl	80	2.2	0.19×10^{-4}	(40)[a]
HCl	100	0.1	0.48×10^{-8}	(47)[a]
HCl	100	0.01	1.13×10^{-8}	(47)[a]
HCl	80	0.1	1.06×10^{-8}	(47)[a]
HCl	80	0.01	0.15×10^{-8}	(47)[a]
HCl	60	1.0	0.93×10^{-8}	(45)[a]
H_2SO_4	50	0.1	0.17×10^{-8}	(52)[b]
HCl	18	5.0	1.32×10^{-8}	(44)[a]
HCl	18	5.0	1.91×10^{-8}	(38)[a]
HCl	5	5.0	0.47×10^{-8}	(44)[a]
HCl	40	5.0	7.45×10^{-8}	(44)[a]

[a] Recalculated from published data
[b] Taken from published graphs

STATEMENT OF THE PROBLEM

It is proposed to study the alcoholysis of cellulose. In this work, the term, "alcoholysis" will be used in the same sense as it was used by Reeves and co-workers (23), that is, the splitting of 1-4 links in cellulose by acid-catalyzed alcohol with the simultaneous introduction of an alcohol residue in the cellulose molecule. The term "acid degradation" will be used in a general sense to include all degradations of cellulose by acidified liquid. The mechanism is specifically not implied.

Three catalysts have been used in alcoholyses: hydrogen chloride, sulfuric acid, and p-toluenesulfonic acid. Hydrogen chloride was selected for this work because of its low molecular weight and its availability as a dry gas. There was no information concerning the reactivity of the alcohols toward hydrogen chloride under the conditions used. A decision was made to use straight-chain primary alcohols because: primary alcohols are less reactive and the straight-chain primary alcohols are less reactive than either branched-chain or aromatic primary alcohols.

An examination of the data reported in the section on the Evidence of the Effects of Molecular Size in Heterogeneous Reactions indicated that unswollen cellulose should be accessible to methanol, ethanol, and propanol, partly accessible to butanol, and inaccessible to the higher alcohols. The alcohols used in this study therefore included methanol, butanol, n-hexanol, and n-octanol.

It appears that any data concerning the accessibility of cellulose to methanol must be considered in the light of possible modification of the physical structure of the cellulose by the methanol. All the linters samples were pretreated in the same manner to minimize such effects. The cotton linters were stored moist and the water removed by solvent replacement with methanol just prior to an experiment.

EXPERIMENTAL PROCEDURES

MATERIALS

ORGANIC LIQUIDS

The organic solvents used in the degradation studies were obtained commercially. Methanol and n-butanol were C.P. reagents. The n-octanol was Eastman grade EK 871. The tetrahydrofuran was Eastman grade EK 5308. The n-hexanol could only be obtained as the practical grade, Eastman EK P 825. All reagents were purified by distillation no more than ten days before using.

All alcohols were stored over anhydrous sodium sulfate for at least one week prior to distillation. The methanol and n-butanol were distilled at atmospheric pressure using a jacketed Widmer column. The n-octanol was distilled at a total pressure of 90 mm. mercury in a Vigreux column. The impure n-hexanol was refluxed for 24 hours with sodium methoxide in an excess of methanol, then distilled at a total pressure of 50 mm. mercury. After distillation, the alcohols were stored over anhydrous sodium sulfate until used. The tetrahydrofuran was refluxed over sodium for 24 hours and then distilled through the Vigreux column at atmospheric pressure. The distilled product was stored over sodium. Table XI gives the values which were found for distillation range, density, and water content. The reported values for boiling point and density are also given.

TABLE XI

PROPERTIES OF DISTILLED ORGANIC LIQUIDS USED IN DEGRADATION STUDIES

Liquid	Distillation Temperature,[a] °C.	Density at 20°C.[a], g./ml.	Water Content, mg./ml.	Reported Values (9) Boiling Point, °C.	Reported Values (9) Density at 20°C., g./ml.
Methanol	65.5-66.6[b]	0.791-.793	0.7-0.8	64.5[b]	0.7928
n-Butanol	115.2-118.0[b]	0.809-.810	0.5-0.8	117.7[b]	0.8097
n-Hexanol	86.5-90.5[c]	0.819-.821	0.2-0.6	82.2[c]	0.8191
n-Octanol	132.4-132.9[d]	0.825	0.1-0.2	132.9[d]	0.8248
Tetrahydrofuran	65.8-66.3[b]	0.888	0.2	65-67[b]	0.888

[a] Values given are the highest and lowest values found in several distillations.
[b] At 760 mm. Hg
[c] At 50 mm. Hg
[d] At 90 mm. Hg

Data on the amount of water soluble in the various reagents at 30°C. was not available in the literature. An approximate value for the solubility of water in n-butanol, n-hexanol, and n-octanol was obtained by mixing water and the liquids in stoppered flaskes. The flasks were kept, with occasional shaking, in a bath at 30°C. for one week. At the end of this time, the water content of the nonaqueous layer was determined by Karl Fisher analysis. The values found are given in Table XII.

TABLE XII

SOLUBILITY OF WATER AT 30°C.

Liquid	Water Content, mg./ml.	Water Content, % by weight
n-Butanol	158	20
n-Hexanol	53.7	6.6
n-Octanol	33.2	4.1

ACIDIFIED ORGANIC LIQUIDS

All acidified organic reagents were prepared by bubbling dry hydrogen chloride through approximately 200 ml. of the liquid until the desired concentration of acid was exceeded. The acidified reagent was then diluted to the volume needed, the acid concentration was measured, and a final adjustment of the acidity was made.

COTTON LINTERS

The linters used in this work were bulk cotton linters of D.P. 1200 obtained from the Buckeye Cotton Oil Company. The linters were air dry and were rewet by soaking for 48 hours. The linters were slurried in small batches, centrifuged, and disintegrated in the pulp disintegrator. After disintegration, the pulp was thoroughly mixed, placed in several polyethylene bags and stored at 5 to 10°C. The average ovendry solids content was 46.6%.

Extractable material, ash, copper number, and aldehyde number were determined on linter samples dehydrated by washing with methanol, acetone, and ether, followed by air drying. The values are given in Table XIII.

TABLE XIII

ANALYSIS OF UNDEGRADED COTTON LINTERS

Ash at 600°C.	0.142%
Copper number	0.156
Aldehyde number	0.0093 mmol.CHO/g.
Successive extractions by:	
Ethyl ether	0.193%
95% ethanol	0.034%
Absolute methanol	0.073%
Total extractives	0.300%

The intrinsic viscosity at 30°C. in cupriethylenediamine was found to be 5.08 [using a constant of 190 (55), the average D.P. of

the linters was 966]. The agreement between the value reported by Buckeye and that measured is considered good for a sample of such indefinite age.

ANALYTICAL PROCEDURES

WATER DETERMINATION BY KARL FISHER REAGENT

All Karl Fisher determinations were carried out following the general procedure proposed by McKinney and Hall (56). In this method, an excess of Karl Fisher reagent is added to the unknown and then back-titrated with standard water-in-methanol. The end point is determined electrometrically using the dead stop method.

The Karl Fisher reagent was prepared in two stock solutions: (a) 256 g. of iodine in 4000 cc. of redistilled methanol and (b) about 390 g. of sulfur dioxide in 1600 cc. of C.P. pyridine. The two solutions were stored at 5 to 10°C. until needed, at which time the Karl Fisher reagent was made up from 1000 cc. of the iodine solution and 400 cc. of the sulfur dioside solution. After preparation, the reagent was protected from both light and moisture in the air. Standard water-in-methanol was made up by adding about 5 cc. of water to a liter of C.P. methanol. Methanol, used for dilutions was redistilled before using to lower the water content. The water-in-methanol was standardized against the trihydrate of potassium acetate. About 50 to 100 mg. of the salt was dissolved in 25.0 cc. of dry methanol and the titration was made on the solution in the normal way.

In most cases, it was necessary to dilute liquid samples in a known amount of methanol in order to obtain satisfactory end points. Fiber samples were tested using the method proposed by Mitchell (57) in which the unknown is added to methanol, allowed to stand one hour and then titrated in the standard manner with the fibers still present. This procedure was not completely satisfactory because the fibers tended to mat on the electrodes. An attempt was made to improve the results by titrating aliquot portions of the methanol removed from a fiber-methanol mixture. The results from this technique were too erratic to be of use. It is believed that the method used would be quite satisfactory if the placing of the electrodes in the flasks were modified to allow for better agitation.

A study of the precision and accuracy of the method was made by analyzing samples prepared by adding known amounts of water to methanol. Each sample was diluted with methanol, aliquots of the diluted sample were added to 25.0 ml. of dry methanol, and the titration performed. The results of the triple determinations are given in Table XIV. The precision of duplicate measurements is dependent on: (a) the concentration of water in the unknown compared to the concentration of water present in the methanol blank, and (b) the size of the sample added to the methanol blank. Using a sample size of 1.0 ml., the maximum deviation was 1.2% of the average value found. The maximum difference between the average found value and the known value was about 0.3% of the known value. The precision of

TABLE XIV

ACCURACY OF KARL FISHER DETERMINATION

Measurement of water in methanol

Calculated Water Content, mg./ml.	Dilution of Original Sample	Volume of Diluted Sample Taken,* ml.	Measured Water Content, mg./ml. Individual			Average	% σ
101	10/100	0.4	102	99	95	99	2.9
250	25/100	0.2	246	250	245	247	0.9
499	50/100	0.1	499	507	527	511	2.3
759	75/100	0.05	607	887	742	745	15.4
907	1/25	1.0	904	908	898	903	0.5
991	1/25	99	993	989	989	990	0.2
998	1/25	1.0	1013	992	986	997	1.2

* All samples were diluted further before titrating in 25.0 ml. of dry methanol containing 0.571 mg./ml. of water.

those determinations in which the volume of the final sample was less than 1.0 ml. was not as satisfactory. The solids content of a linters sample was determined by the Karl Fisher reagent and compared to the vacuum dried solids content of the same linters. The values found were 46.8 and 48.4%, respectively. While this was not good, it seemed satisfactory for the estimation of small amounts of water in alcohol-wet samples.

ACIDITY

The acidity of the alcohols after the introduction of hydrogen chloride was determined by adding an aliquot of the alcohol to water and titrating with base using phenolphthalein as an indicator. All the end points were sharp and easily observed. No study was made of the accuracy of the method.

VISCOSITY

The viscosities of all samples were determined at 30°C. in cupriethylenediamine solution following the general procedure outlined by Wetzel, Elliot, and Martin (58). The intrinsic viscosity of each sample was determined from measurements of the viscosity at four different concentrations.

Cupriethylenediamine solution (1.0 M in copper and 2.0 M in ethylenediamine) was obtained from the Ecusta Paper Corporation. Solvent was removed from the storage bottle and tested for copper and ethylenediamine concentration (TAPPI Method T 230 sm-50) before

it was used. In several instances the copper concentration differed by more than 0.5% from the specified concentration and a correction was made in the ratio of solvent and water to adjust the final solvent solution to 0.5 M in copper. Viscosities were determined on the air-dry samples of cellulose.

All samples were dissolved under prepurified nitrogen in the following manner: (a) Airdry cellulose was weighed by difference into 60-ml. serum bottles. (b) An estimate was made of the volume of liquid necessary to give the final concentration needed (0.05 to 0.25 g./100 cc.). (c) Distilled water equal to one-half of the amount of liquid calculated was added and the serum bottle stoppered with a self-sealing stopper. (d) The air present in the sample was removed by alternately evacuating and filling the bottle with prepurified nitrogen using the apparatus described by Browning, Sell, and Abel (59). (e) After the air was flushed from the bottle, 1.0 M cupri-ethylenediamine was added to give a final solution which was 0.5 M in copper. (f) The sealed bottles were shaken for one hour and then placed in the constant temperature bath for at least one hour before a sample was removed by hypodermic syringe. (g) The viscosity was determined at 30°C. in Ostwald-Fenske-Cannon pipettes.

Intrinsic viscosities were determined from the four viscosity measurements on each sample by plotting $\eta sp/c$ versus c. The relation between measured viscosity and intrinsic viscosity is shown in the following equation.

$$\eta_{rel} = \eta/\eta_o$$

$$\eta_{sp} = \eta_{rel} - 1 = (\eta - \eta_o)/\eta_o$$

$$[\eta] = [\eta_{sp}/\underline{c}]_{c \rightarrow o}$$

where

η_o = solvent viscosity, cp.
η = solution viscosity, cp.
η_{rel} = relative viscosity
η_{sp} = specific viscosity
$[\eta]$ = intrinsic viscosity
$\underline{c}$ = concentration of cellulose, g./100 cc.

In the concentration range covered, the plot of $\eta_{sp}/\underline{c}$ versus $\underline{c}$ was a straight line.

Viscosities were measured at 30°C. because of the availability of a bath at that temperature. Four of the samples measured at 30°C. were also measured at 20°C. in order to determine any differences in intrinsic viscosity. The results are given in Table XV. The only sample showing any appreciable variation was undegraded linters. This variation would affect only a few samples of those measured; therefore, no correction was made.

TABLE XV

COMPARATIVE INTRINSIC VISCOSITIES

Sample	Intrinsic Viscosity At 19.5°C	At 29.9°C.
Cotton linters	4.58	5.08
Linters degraded 215 hours at 30°C. in methanol containing 0.05 N HCl	1.94	1.91
Linters degraded 72 hours at 30°C. in n-hexanol containing 0.05 N HCl	1.78	1.67
Linters degraded 210 hours at 30°C. in n-butanol containing 0.05 N HCl	1.42	1.54

COPPER NUMBER

Copper numbers were determined on airdry samples using a modification of TAPPI Method T 215 m-50. The sample size was reduced to about 0.4 g. The normality of the potassium permanganate solution was also decreased to 0.02 N to improve the sensitivity of the titration. A permanganate solution of this strength is not stable for long periods so a solution was made daily by diluting 0.1 N stock solution. The diluted solution was standardized against sodium oxalate. It was found that the reproducibility of duplicate samples was improved by titrating to a definite color and then correcting for the excess permanganate solution required by titrating an equal volume of distilled water to the same color.

ALDEHYDE NUMBER

An estimate of the reactive aldehyde groups in the cellulose samples was made using the method of Martin, Smith, Whistler, and Harris (60). In this method, the aldehyde groups are oxidized selectively to carboxyl groups by iodine in a buffered alkaline solution at low temperatures to minimize side reactions. The slow side reaction which persists even at low temperatures was corrected for by measuring the rate of the side reaction on undegraded linters. No determination of the rate of the slow reaction was made on any of the samples degraded in acidified alcohols. If the rate of the slow reaction did not change because of such treatment, the correction made is accurate. However, to emphasize the fact that it may be safer to use the values obtained as relative values only, they

have been called "aldehyde numbers." Numerically they are equal to one-half the number of milliequivalents of iodine consumed per gram of cellulose.

The reaction mixture consisted of 100 ml. of sodium carbonate-bicarbonate buffer (pH 10.6) and 25.0 ml. of iodine solution (about 0.5 N). The two solutions were cooled separately to 5°C. in a constant temperature bath and mixed. The cellulose sample was added, and after two to five hours the reaction was halted by acidifying the solution; the iodine liberated was titrated with 0.1 N sodium thiosulfate to a starch end point. It was necessary to determine a value for the iodine blank since the recovery of iodine was not quantitative. A correction was made for the side reaction and the results were expressed as millimoles of aldehyde per gram of cellulose, or aldehyde number, by assuming that one-half milliequivalent of iodine was equal to one millimole of aldehyde.

CARBOXYL CONTENT

The carboxyl content was determined following the method used by Elizer (61). An excess of silver-o-nitrophenolate was added to a sample of cellulose (the sample was ground if it had not already disintegrated) and the amount of reaction was determined using ammonium thiocyanate. Only three samples were measured.

TOTAL REDUCING SUGARS

Total reducing sugars were determined by the Somogyi method (62). The determination was standardized against known concentrations of D-glucose.

All values of sugar concentrations were determined on solutions that were 0.5 M in sodium chloride. When determining very low sugar concentrations, both the blanks and the standard sugar solutions were also made 0.5 M in sodium chloride to correct for a small change in rate caused by the presence of salt.

METHANOL TEST

During certain of the preliminary experiments it was necessary to determine the concentration of small amounts of methanol present in other alcohols. While there was no method reported in the literature which could be used directly, it had been reported that small amounts of methanol in alcoholic beverages were measured using the Deniges Permanganate-Fuchsin test (63). In this test, the methanol is oxidized to formaldehyde, which is measured by decolorizing a fuchsin dye. Unknowns are compared to a series of knowns prepared at the same time. The reagents used were those specified by Georgia and Morales (64). A 5-ml. sample is oxidized with 2 ml. of 3% potassium permanganate (acidified with 12.5% phosphoric acid) for ten minutes. The reaction is halted with 2 ml. of 5% oxalic acid (in 30% sulfuric acid). The formaldehyde formed by the oxidation of the methanol is determined after the addition of 5 ml. of Schiff's reagent (0.1% fuchsin dye, 1% sodium sulfite, and hydro-

OVENDRY SOLIDS

The solids contents of all samples were determined by vacuum-oven drying at 80°C. The temperature was increased over the 40°C. usually used in order to assist in the removal of the higher boiling alcohols. Under these conditions, samples were dried to constant weight within four to five hours.

A comparison was made of the solids content of two samples of cotton linters determined by drying to constant weight at 80°C. under vacuum and overnight oven drying at 105°C. (Institute Method 423). The values found are given in Table XVII.

TABLE XVII

COMPARISON OF SOLIDS DETERMINATION

Drying Conditions	Solids, % Sample 1	Sample 2
80°C. under vacuum to constant weight	95.07	49.88
105°C. overnight	95.03	49.84

~~Grot,John and Hess (65) and~~ Russell, Maass, and Campbell (67) found that as much as two per cent of methanol and other alcohols were retained by cellulose on drying alcohol-wet cellulose samples, even at 100°C. under vacuum. Staudinger and Döhle (66) found the same type of behavior but also stated that drying ether-wet samples in a moist atmosphere would remove the organic liquids. All of the samples collected in this work were dried by washing successively with methanol, acetone, and ethyl ether, then removing the ether by drawing air through the sample. This procedure is hereafter called "solvent drying." The

possibility of high solids contents occurring from the entrapment of solvents was tested by determining the solids content of moist linters in two ways: (a) solvent drying followed by vacuum drying at 80°C. and (b) vacuum-oven drying at 80°C. The results were 55.6% for solvent drying plus oven drying and 56.3% for vacuum-oven drying. It does not appear that there is any inclusion of organic liquids in cotton samples air-dried from ether.

EXPERIMENTAL RESULTS AND DISCUSSION

PRELIMINARY EXPERIMENTS

REACTION BETWEEN ALCOHOL AND HYDROGEN CHLORIDE

One possible source of water during alcoholysis is the formation of water from a reaction between the alcohol and hydrogen chloride. Reeves, Hoffpauir, and Demint (30) demonstrated that there was an appreciable formation of water at 0°C. in strongly acidified methanol. The conditions used differed from those to be used in this work both in acidity and temperature and the only alcohol studied was methanol. Additional information more pertinent to this work was obtained by determining the changes in acidity and water content for methanol, n-butanol, n-hexanol, and n-octanol acidified with dry hydrogen chloride. The initial acidity was about 0.5 N and the temperature was held at 30°C. in a constant temperature water bath. The results are given in Figures 10 and 11. Only methanol showed a marked reaction. The other alcohols appeared to be approaching an equilibrium water content.

REACTION BETWEEN TETRAHYDROFURAN AND HYDROGEN CHLORIDE

Somewhat later, a similar study was made using tetrahydrofuran acidified with 0.05 N hydrogen chloride at 30°C. An estimate was also made of the formation of peroxides from the amount of iodine formed by addition of potassium iodide and acid. The results are shown in Table XVIII.

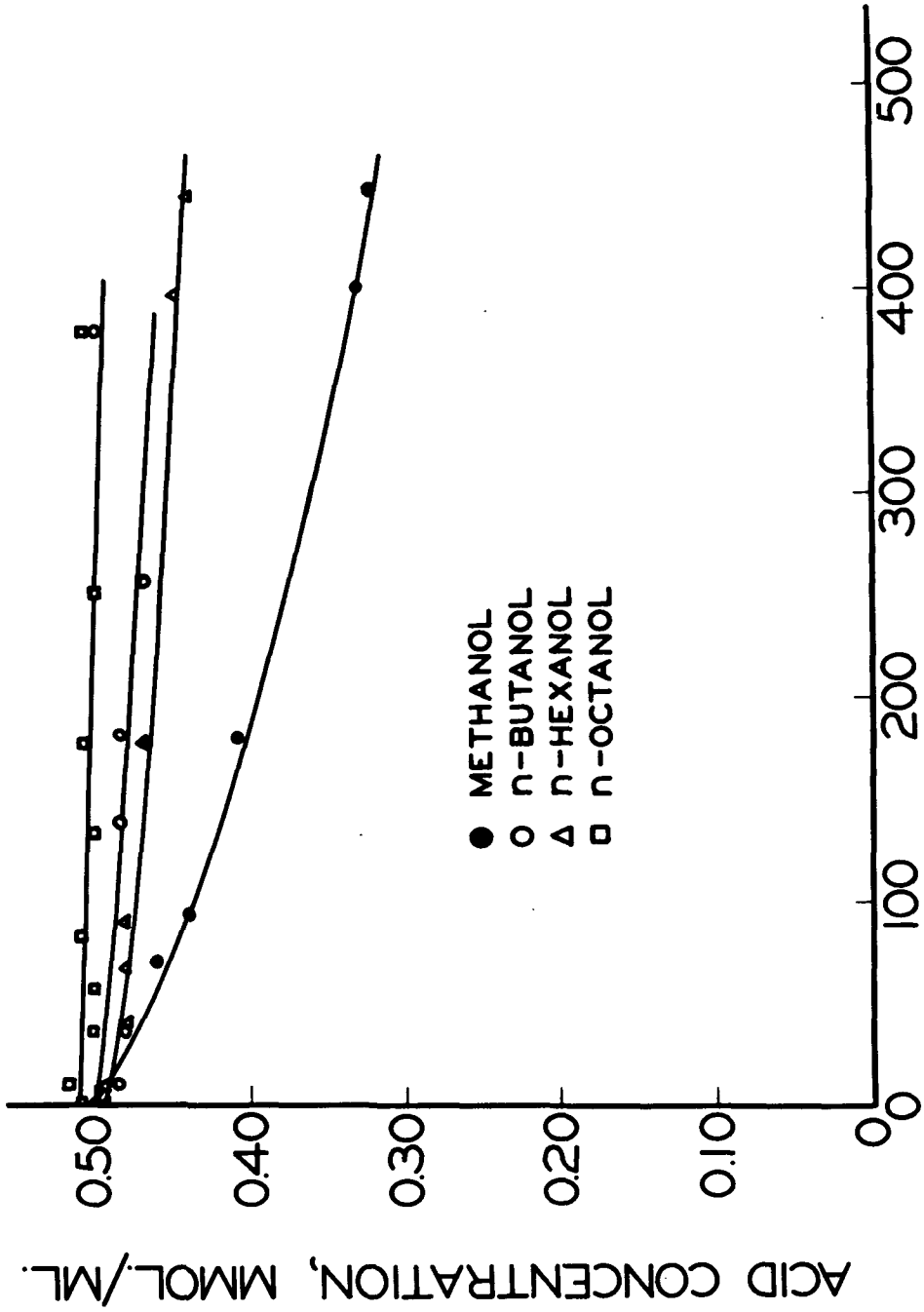


Figure 10

Acidity Changes in Alcohols Acidified With Hydrogen Chloride at 30°C.

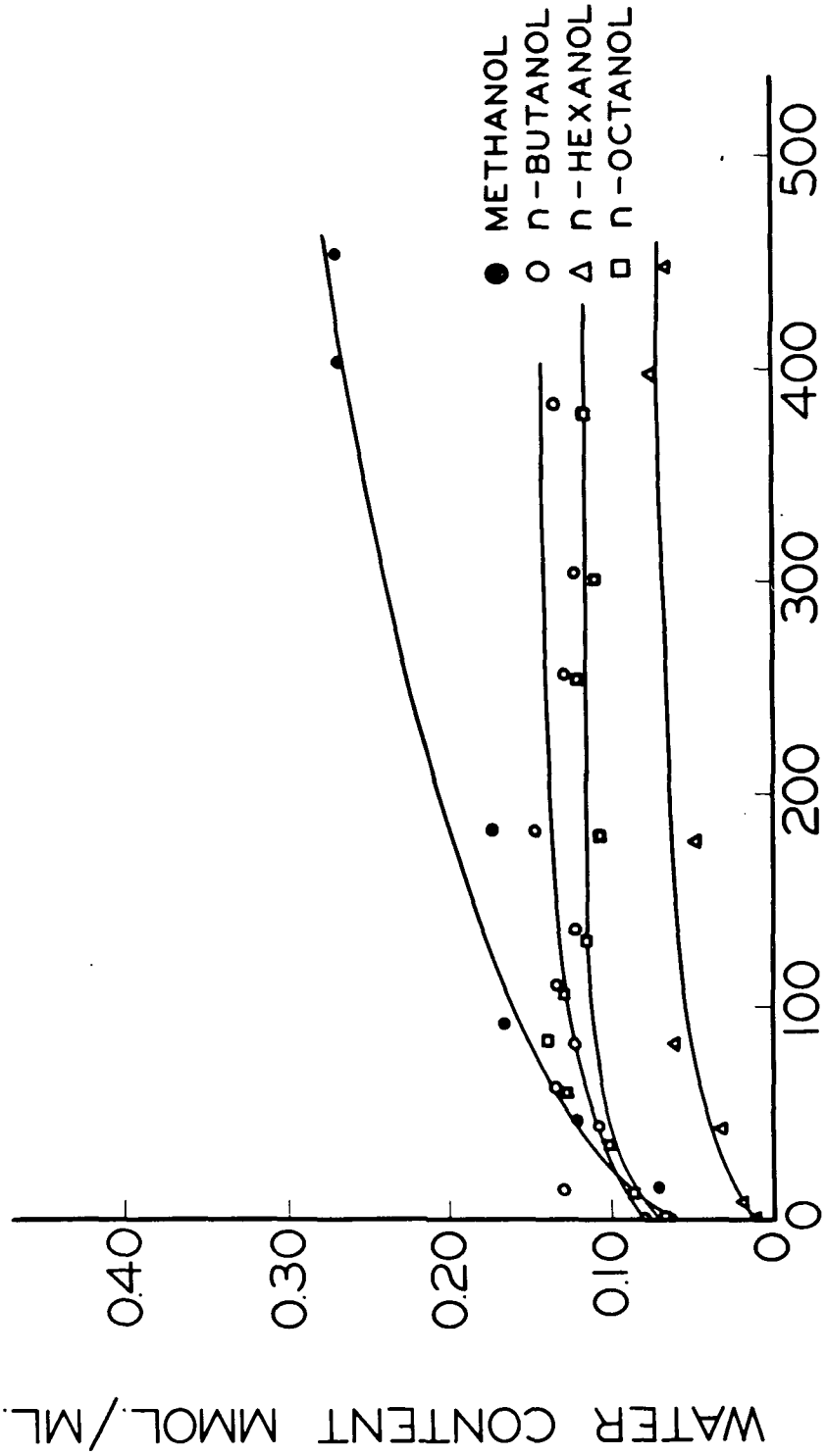


Figure 11

Water Changes in Alcohols Acidified With Hydrogen Chloride at 30°C.

TABLE XVIII

CHANGES IN WATER, ACID, AND PEROXIDE CONCENTRATIONS IN ACIDIFIED TETRAHYDROFURAN

Time, hr.	Concentration of HCl, N	Concentration of Water, mg./ml.	Concentration of Peroxide, mmol. H_2O_2/ml.
0.0	0.0505	0.15	0.0050
0.6	0.0504	0.074	--
47.5	0.0476	0.140	--
142	0.0455	0.25	--
215	0.0435	0.41	0.0108
294	0.0393	--	0.0125
296	--	0.76	--

When the acid degradation studies were made at a later date, the catalyst concentration used was 0.05 N. The approximate amounts of water which could be expected from the reaction between the alcohols and the hydrogen chloride were estimated from the data which had been accumulated. The following assumptions were necessary: (a) The only reaction occurring was the equilibrium reaction, ROH + HCl = RCl + H_2O. (b) The tenfold reduction in acid concentration would not greatly change the equilibrium constants. (c) The water and acid contents measured at the end of the experiments were approaching the equilibrium values. Table XIX gives the calculated equilibrium constants and the equilibrium water contents for the four alcohols.

TABLE XIX

ALCOHOL-ACID REACTION

Equilibrium Constants and Water Contents at Equilibrium

$$ROH + HCl = RCl + H_2O$$

$$K = [RCl][H_2O]/[ROH][HCl] \text{ or } K[ROH] = K' = [H_2O]^2/[HCl]$$

Alcohol	K' at 0.5 N HCl	Water Content at Equilibrium, 0.05 N HCl, mg./ml.
Methanol	0.401	2.54
n-Butanol	0.0341	0.74
n-Hexanol	0.0121	0.44
n-Octanol	0.0248	0.64

Measurable amounts of water are formed in alcohols acidified with hydrogen chloride even when the acid concentration is 0.05 N. The formation of water would proceed even in thoroughly dehydrated alcohols and should reach the same values. For this reason, it was considered unnecessary to attempt to dehydrate the alcohols to any greater extent than was achieved as part of their purification.

REMOVAL OF WATER FROM COTTON LINTERS

Another source of water during alcoholysis was the water present on the cellulose. Therefore, the linters were dehydrated as thoroughly as possible before the addition of the alcohol. Direct drying of water-wet cellulose was not used since it was shown by Grotjahn and Hess (65) and Staudinger and Döhle (66) that drying from water decreased the internal surface and the reactivity of cellulose toward organic liquids. In addition, trials using dry fibers indicated that

air-dried cellulose was not easily wet by the higher alcohols. Dehydrating the cellulose by solvents was chosen since it would eliminate both of the above problems.

The apparatus developed for solvent replacement of water in cellulose is shown in Figure 12. The upper portion is a 500-ml. filter flask with the base cut off. The lower portion is a sintered glass funnel. The edges in contact were ground to give a tight fit at 28 inches of vacuum. A Y tube fastened to the side arm of the flask connects to either a vacuum line or a drying tube. A glass tube fitted with a glass spray-head is inserted through a rubber stopper in the top of the flask.

The general procedure for replacing a liquid on a pad of linters was as follows: (a) A measured volume of the replacing liquid was sucked in through the spray head by applying vacuum to the side arm. (b) After a period of soaking, the pad was drained by applying vacuum to the filter allowing dry air to enter through the drying tube fastened to the side arm. (c) The cycle was repeated as many times as needed to attain maximum dehydration.

A preliminary series of experiments was made in which only the water content of the filtrate was measured. The washing procedure consisted of four soaks, each lasting one hour with 5 minutes of filtration between the washes. About 25 grams of linters were used in each experiment. Three experiments were made in which the volume of

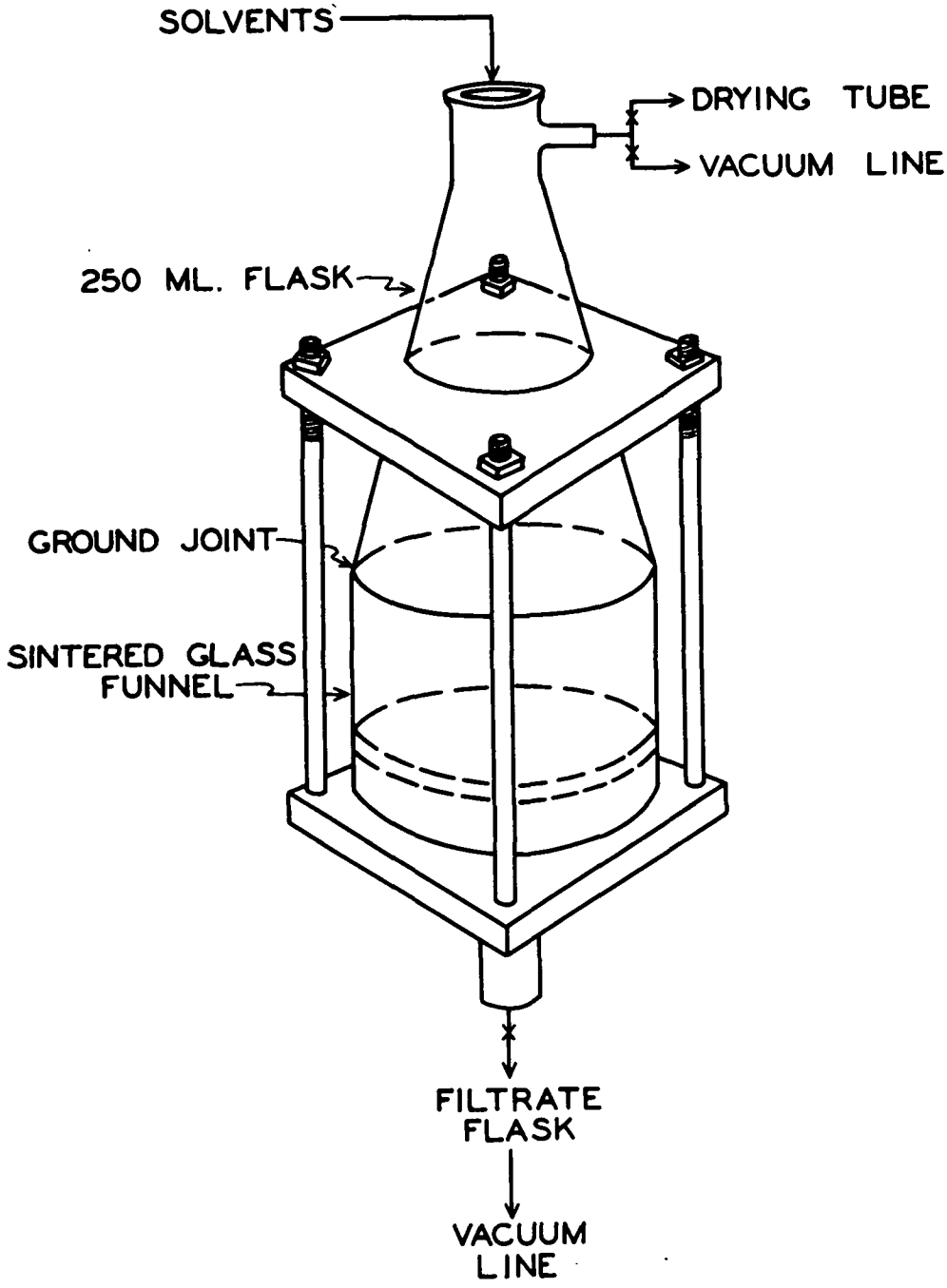


Figure 12

Solvent Replacement Apparatus

methanol used in each soak was 50, 100, and 150 cc., respectively. Another series of experiments was made in which the soaking periods were 15 and 30 minutes, respectively, using 100 ml. of methanol per soak. The water contents of the filtrates obtained after each soak are shown in Figures 13 and 14. Using one hour soaks, four extractions with 100-ml. portions or three extractions with 150-ml. portions are equally as effective in removing water from the linters. A consideration of Figure 14 indicates that the bulk of the water diffuses into the methanol rapidly. The final traces appear to leave the cellulose more slowly.

A comparison of the water-methanol ratio of the liquid wetting the cellulose to the water-methanol ratio of the filtrate was made. The detailed calculations are given in the Appendix. After one extraction with methanol, the water content of the filtrate was 260 mg. per ml. The water-methanol ratio of the liquid remaining on the linters was 90.1 mg. per ml. The water content of the second filtrate was 30.3 mg. per ml. as compared to a water-methanol ratio on the linters of 1.2 mg. per ml. In both instances, the ratio of water to methanol in the filtrate was higher than the ratio of the liquid on the linters. It appears then, that if conditions of dehydration are chosen such that the water content of the final methanol filtrate is about 1.0 mg. per ml., maximum dehydration will have been attained using this technique.

Two attempts were made to remove water from linters using azeotropic vacuum distillation and low temperature sublimation. The linters used were dehydrated using solvent replacement prior to the additional treatment. Vacuum distillations were tried using n-butanol and n-hexanol.

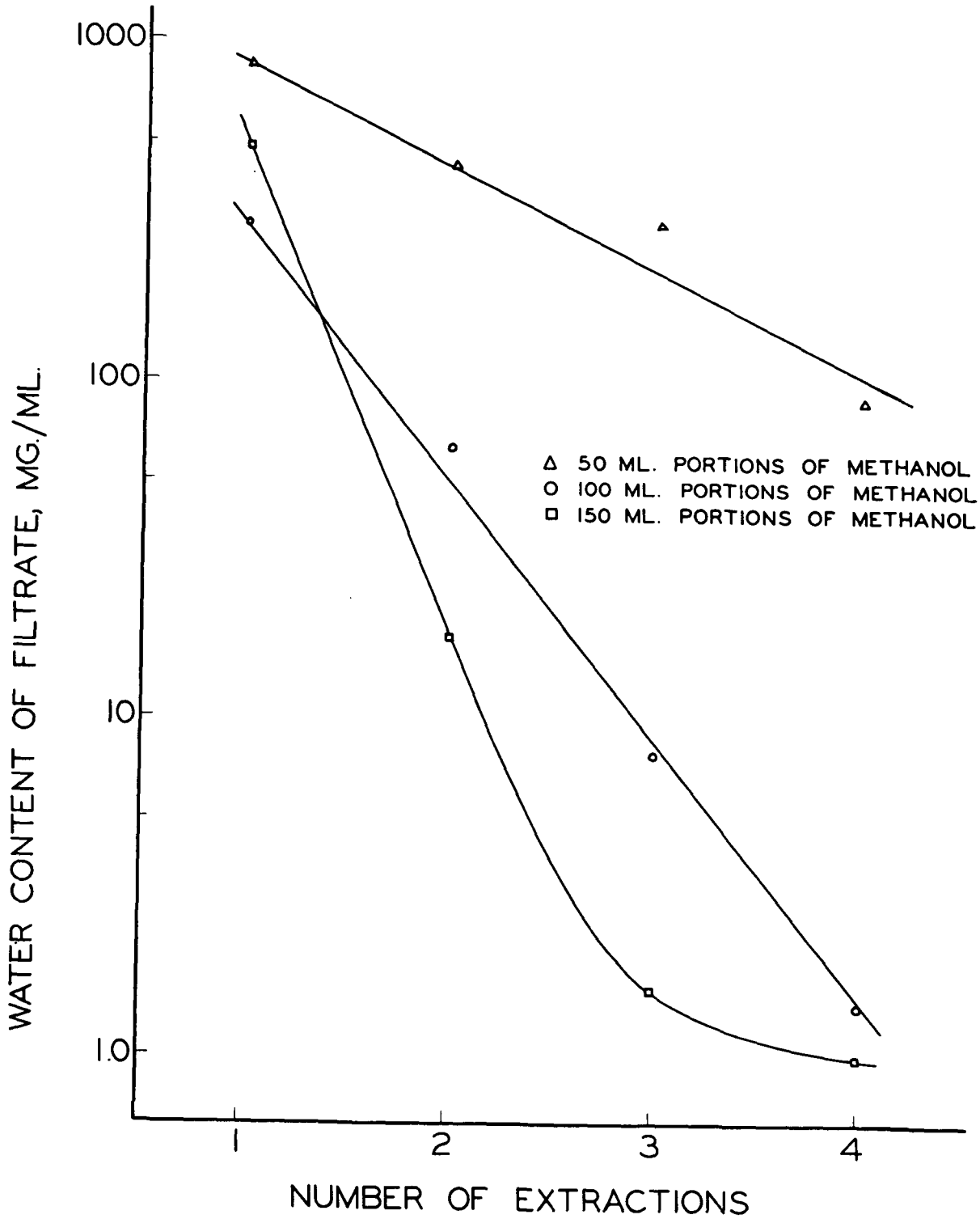


Figure 13

Removal of Water From Cotton Linters by Methanol, Water Content of Filtrates From 25 g. Pad, Each Extraction Soaked One Hour

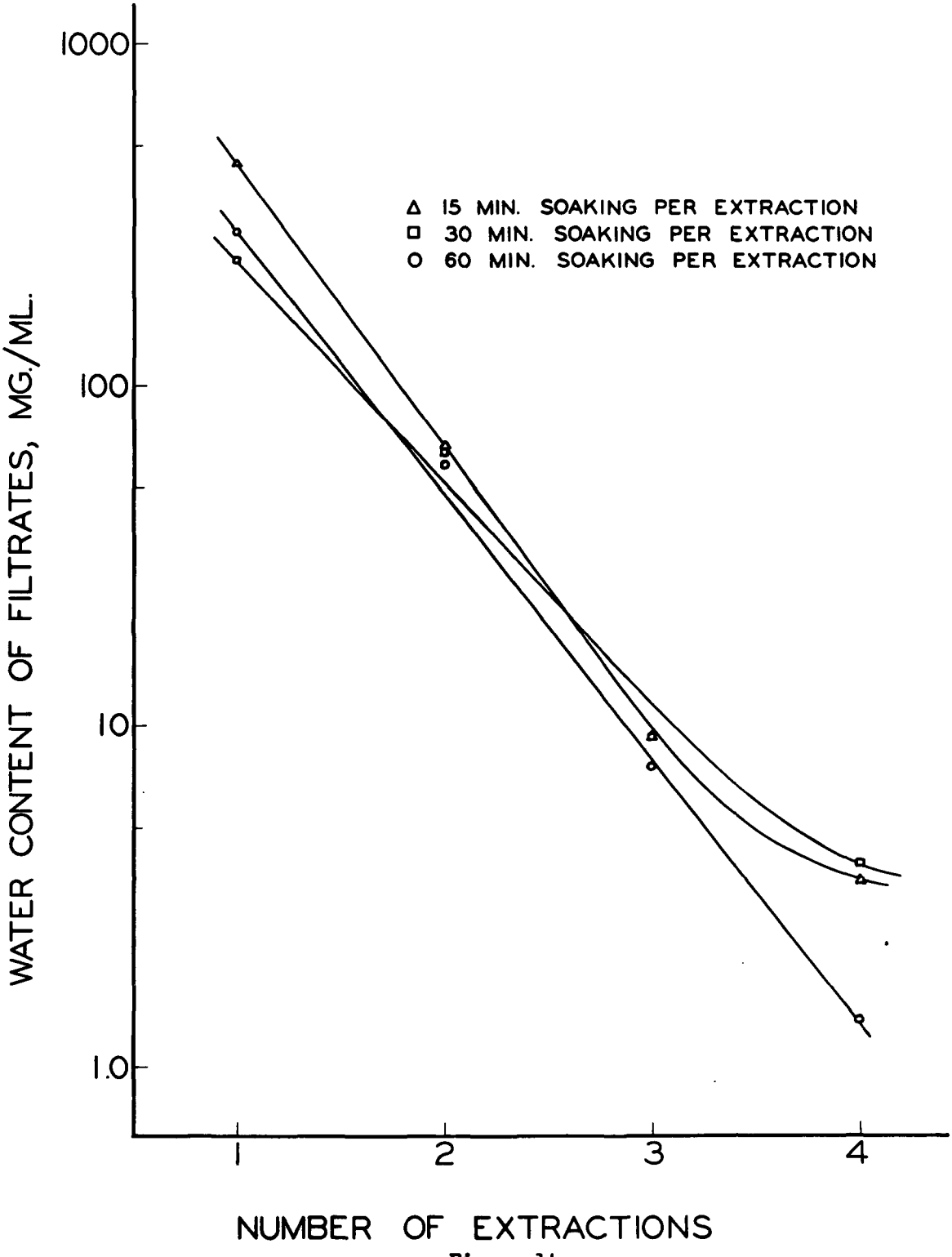


Figure 14

Removal of Water From Cotton Linters by Methanol, Water Content of Filtrates from 25 g. Pad, Each Extraction Used 100 ml. of Methanol

The water contents of the distillates were determined periodically until a minumum value was reached, and then the water content of the linters was measured. Low temperature sublimation of traces of water was attempted by cooling a linter sample wet with tetrahydrofuran in a salt-ice bath, then maintaining a vacuum in the flask overnight and measuring the water content of the linters. Table XX compares the amount of residual water on linters dried by the several methods used. There does not appear to be any advantage gained by other treatments in addition to solvent replacement.

TABLE XX

DRYING OF CELLULOSE

Comparison of Various Methods

Method	Liquid	Water Based on Dry Cellulose, %
Repeated distillation	n-Butanol	0.41
Repeated distillation	n-Hexanol	0.31
Sublimation at -10°C.	Tetrahydrofuran	0.24
Solvent replacement*	Methanol	0.79
Solvent replacement*	n-Butanol	0.40
Solvent replacement*	n-Hexanol	0.40
Solvent replacement*	n-Octanol	0.32
Solvent replacement*	Tetrahydrofuran	0.78

*Linters were dehydrated with 3 extractions using methanol followed by 3 additional extractions with the liquid listed.

The data which were accumulated concerning the amounts of water present in cotton linters and acidified alcohols makes possible some general observations. A typical alcoholytic degradation, using an alcohol other than methanol, consisted of 15 g. of linters (wet with 35 ml. of alcohol) dispersed in 850 ml. of acidified alcohol. The linters contained about 0.4% water (based on the dry weight of the linters) and the alcohol contained about 0.33 mg. per ml. of water. Initially the total water in the system was 340 mg., 60 mg. from the cellulose, and 280 mg. from the alcohol. During the first 100 hours of the experiment additional water was formed from the reaction of alcohol with hydrogen chloride. This added another 160 mg. of water to the system. The amounts of water present, based on the dry weight of the linters, were 2.3% initially and 3.4% after 100 hours. If methanol was the alcohol, the equilibrium water content would be much higher. At 100 hours there would be about 10% by weight of water, two-thirds of which came from the methanol-acid reaction.

An anhydrous system may be defined as one in which insufficient water is present to allow for the hydrolysis of the cellulose. The approximate amount of water needed in these experiments was calculated by assuming that a cellulose sample having a number average D.P. of 800 was hydrolyzed to a product having a number average D.P. of 200. Such D.P.'s correspond roughly to the viscosity average D.P.'s found for the linters used in this work. Three 1-4 links must be cut to lower the average D.P. from 800 to 200 and this requires the addition of three moles of water per mole of 800 D.P. cellulose, producing four moles of

200 D.P. cellulose. On a weight basis, 0.033% of water is needed. This value is about one-seventieth of the amount of water initially present in the reactions carried out in this study. Even if the alcohol and the linters could be absolutely dehydrated prior to an experiment, acidification of the alcohol would initiate the formation of water. While there is no information concerning the rate at which water would be formed in very anhydrous acidified alcohols, a concentration of only 0.05 mg. per ml. of water in the alcohol corresponds to 0.3% by weight of water on the linters (using 15 g. of linters in 850 ml. of alcohol). This value is ten times the minimum value of 0.033% on the cellulose and is only about one-tenth the equilibrium water content of acidified alcohol. Therefore, the alcohol-acid-cellulose system cannot be considered to be anhydrous as defined earlier, nor does it appear possible to either create or maintain an anhydrous system in the presence of acidified alcohols. It also follows that the amount of water present in the system is sufficient to allow hydrolysis of the cellulose to occur.

HYDROLYSIS OF MODEL COMPOUNDS

It was anticipated that the soluble losses would be one per cent or less for most of the alcoholyses. Such small losses could be determined more accurately by measuring the concentration of solids in liquids than by determining the yields gravimetrically on the residues. The soluble losses were determined by hydrolyzing the soluble carbohydrates in solution in the liquors and measuring the reducing power of the hydrolyzates by Somogyi's reagent. This is, in general, the method used by Reeves, Mazzeno, and Hoffpauir (23).

The time required for hydrolysis of the carbohydrates which might be encountered in this work was determined by hydrolyzing aqueous solutions of D-glucose, cellobiose, methyl α- and β-D-glucosides, hexyl β-D-glucosides, and octyl β-D-glucoside. The reducing power was determined by Somogyi's test and expressed as the apparent concentration of glucose for samples removed at intervals throughout the hydrolysis. The results, expressed as percentage of the theoretical yield of glucose on complete hydrolysis, are given in Table XXI and are shown in Figure 15.

TABLE XXI

REDUCING POWER OF CARBOHYDRATES ON HYDROLYSIS

1.0 N HCl at Reflux

	Reducing Power Expressed as Apparent Glucose, Per Cent of Theoretical Yield of Glucose						
Time, hr.	0	2	3	4	6	9	12
Sample							
D-glucose	101	107	---	101	94	---	---
Cellobiose	70	68	---	77	97	---	---
Methyl α-D-glucoside	0	70	---	96	96	---	---
Methyl β-D-glucoside	1	---	102	---	100	98	109
n-Hexyl β-D-glucoside	1	---	149	---	127	118	117
n-Octyl β-D-glucoside	0	---	132	---	135	116	113

It was probable that the major constituents of any solution would be glucose and cellobiose. The relative reducing power of glucose and cellobiose nearly coincided at 6 hours hydrolysis. Therefore all

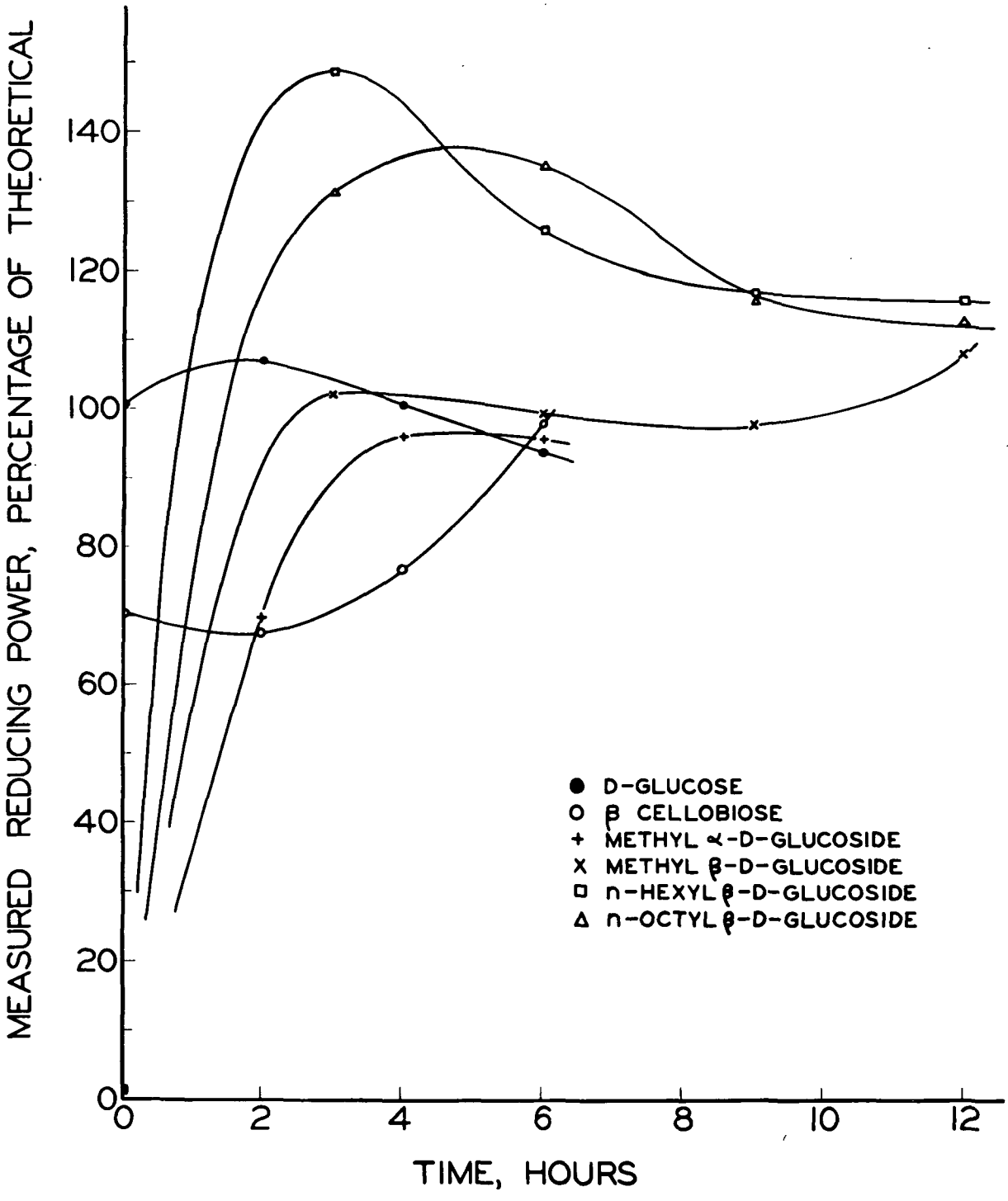


Figure 15

Relative Reducing Power of Model Compounds Versus Time, 1.0 N HCl Under Reflux

samples would be hydrolyzed 6 hours and the reducing power at that time, expressed as glucose, was about 95% of the theoretical concentration.

At least a portion of the carbohydrates measured would be present originally in alcoholic solutions, so a study was made to determine if D-glucose could be recovered quantitatively from alcoholic solutions. The sugar dissolved directly in methanol but it was not possible to dissolve appreciable amounts of sugar in the higher alcohols. The procedure adopted for the other alcohols was to dissolve the sugar in water, dilute the water with methanol, and then add the higher alcohol. The ratio of the three liquids was water: methanol:higher alcohol::10:45:45. The alcoholic solutions were transferred to water using the following methods: (a) An excess of water was added to the methanolic solution and the mixture distilled until the methanol was removed. (b) An excess of water was added to the butanolic solution and the butanol removed as an azeotrope with a portion of the water. (c) Solutions containing hexanol or octanol were extracted with water in a separatory funnel and any alcohol traces removed by distillation of the aqueous layer. All the aqueous samples were acidified, and then hydrolyzed for six hours under reflux. The samples were neutralized with sodium hydroxide and the concentration of glucose was determined (see Table XXII).

TABLE XXII

DETERMINATION OF GLUCOSE IN ALCOHOLIC SOLUTIONS

Original Solvent	Known Concn. of Glucose, mg./ml.	Found Concn. of Glucose, mg./ml.	Found/Known, %
Methanol	0.201	0.190	95
Water:methanol:butanol:: 10:45:45	0.092	0.097	105
Water:methanol:hexanol:: 10:45:45	0.112	0.111	99
Water:methanol:octanol:: 10:45:45	0.094	0.107	113

ACID DEGRADATIONS OF COTTON LINTERS

PROCEDURE AND GENERAL OBSERVATIONS

All degradations were made at 30±0.2°C. in a constant temperature bath. All the studies made on large samples of linters were carried out in two-liter round-bottomed flasks fitted with a glass stirrer running through a mercury seal. The studies made on small samples were carries out in 500-ml. round-bottomed flasks fitted with ground glass stoppers.

The cotton linters were prepared in the following manner: (a) A known weight of moist linters was dispersed in distilled water. (b) The fiber suspension was filtered in the filter which forms the base of the solvent-replacement apparatus (see Figure 12). (c) The pad was washed three times with 100-ml. portions of distilled methanol. (d) Those linters which were to be degraded with some other organic liquid were washed three more times with 100-ml. portions of that

liquid. (e) The dehydrated linters were removed from the filter and placed immediately in the reaction flask. Those linters which were to be degraded with aqueous acid were dispersed in water, filtered, and placed in the reaction flask.

After preparation, the acidified solvents were placed in a stoppered flask and held in the constant temperature bath. The solvent was added to the linters within one hour of its acidification.

The method of treating fiber samples taken during the experiments was developed to insure that the insoluble material did not contain short-chain fragments soluble in water or methanol but insoluble in a higher alcohol. Unless this precaution were taken, apparent differences in losses might actually be caused by differences in solubility. Two procedures were followed. Hydrolyzed samples were filtered using suction, washed with distilled water until the filtrate was neutral, washed successively with methanol, acetone, and ether, and air dried. Samples of linters degraded in organic liquids received the following treatment: (a) The filtered linters were redispersed in methanol and the residual acidity neutralized using sodium hydroxide. (b) Additional water was added to methanol to give a final ratio of methanol to water of five to one. (c) After 24 hours, the sample was again filtered, washed successively with methanol, acetone, and ether, and air dried. All filtrations were made on sintered glass filters and in early studies no attempt was made to measure the losses of fiber trapped within the filter. In later work, the filters were tared before using and the losses were determined.

All the original liquors removed with each filtrate were collected and the volumes determined. A portion of each liquor sample was set aside for the determination of soluble carbohydrates (following the procedure outlined in the section on Hydrolysis of Model Compounds). The methanol-water extractions of all samples were also collected and treated in the same manner.

Table XXIII is a summary of the degradation conditions. The rate of degradation was not known in Series I and it was necessary to take several small samples during the early stages. In later experiments the early samples were larger as it was known approximately when to take the samples.

With the exceptions of 0.05 N hydrolysis (Study W-2) and Series IV, the linters lost their fibrous nature during the first 24 hours of the reaction. The exceptions were probably caused by low acidity in Study W-2 and by lack of agitation in Series IV. There was no change in color of the liquid phase in any of the hydrolyses but all of the alcohols tended to show a slight color after several days. The degradations carried out in tetrahydrofuran also differed in that there was a decrease in pressure within the flask as indicated by a change in the level of the mercury in the stirrer seal. No such change was noticed in any other study. Further, if the flask was flushed with nitrogen after removing a sample, the subsequent pressure drop was eliminated. It appears that oxygen in the atmosphere held within the flask was absorbed by the reaction mixture.

TABLE XXIII

SUMMARY OF DEGRADATION CONDITIONS

Series	Study Number	Liquid	Acidity, N	Initial Weight of Cellulose, g.	Initial Volume of Liquid, cc.	Number of Samples Taken	Approximate Sample Size, g.
I	W-1	Water	2.0	17.7	916	6	0.5-1.0[a]
I	B-1	n-Butanol	0.05	32.6	840	66	0.5-1.0[a]
II	W-2	Water	0.05	15.6	892	4	4-6
II	M-1	Methanol	0.05	14.9	887	4	4-6
II	H-1	n-Hexanol	0.05	24.3	913	4	4-6
II	O-1	n-Octanol	0.05	22.6	909	4	4-6
II	T-1	Tetrahydrofuran	0.05	16.2	899	4	4-6
III[b]	W-3	Water	2.0	14.6	834	4	4-6
III	B-2	n-Butanol	0.05	13.2	857	4	4-6
III	H-2	n-Hexanol	0.05	15.9	862	4	4-6
IV[b,c]	W-4	Water	2.0	5.8	143	1	5-6
IV	B-3	n-Butanol	0.05	5.3	289	1	5-6
IV	M-2	Methanol	0.05	6.9	286	1	5-6

[a] Last sample was much larger (over 10 g.).
[b] Fibers trapped in sintered glass filters were measured.
[c] Mixture was not stirred during the experiment.

PROPERTIES OF DEGRADED LINTERS

Intrinsic Viscosity

Table XXIV gives the values of intrinsic viscosity found for all samples. Figures 16 and 17 show the variation of intrinsic viscosity with time and log time, respectively. The reproducibility between duplicate studies was good as is shown in Figures 24, 25, and 28 in the Appendix. Figure 18 gives the plot of 2/D.P. versus time following Sharples' (52) technique. The reaction constants for the straight line portions of the curves were calculated and are given in Table XXV. The constants found are of the same order of magnitude as those listed in Table X for mild heterogeneous acid hydrolysis.

TABLE XXIV

PROPERTIES OF DEGRADED LINTERS

Sample	Time of Treatment, hr.	Intrinsic Viscosity	Copper Number	Aldehyde Number, mmol.CHO/g.	Appearance
Control	0	5.08	0.16	0.0093	F[h]
W-1-A[a]	0.5	4.29	0.80	--	F
W-1-B	1	4.00	1.05	0.0292	F
W-1-C	4	3.11	1.23	0.0243	F
W-1-D	28	2.52	2.22	0.0266	D[i]
W-1-E	72	1.78	3.07	0.0414	D
W-1-F	216	1.50	4.95	0.0377	D
W-2-A[b]	4	4.55	0.36	0.0100	F
W-2-B	26	4.29	0.39	0.0088	F
W-2-C	80	4.18	0.33	0.0103	F
W-2-D	218	4.09	0.55	0.0151	F
W-3-A[a]	5	3.53	--	--	F
W-3-B	65	1.76	--	--	D
W-3-C	234	--	5.28	--	D
W-3-D	312	1.37	--	--	D
W-4-A[a]	237	1.53	5.27	--	F
M-1-A[c]	4	3.66	0.39	0.0113	F
M-1-B	28	2.63	0.37	0.0108	D
M-1-C	91	1.75	0.38	0.0094	D
M-1-D	283	1.22	0.35	0.0070	D
M-2-A[c]	215	1.88	1.29	--	F
B-1-A[d]	0.5	3.87	0.84	0.0141	F
B-1-B	1	3.55	0.67	0.0271	F
B-1-C	4	3.00	0.61	0.0165	F
B-1-D	24	2.54	0.99	0.0178	D
B-1-E	72	1.89	0.91	0.0225	D
B-1-F	138	1.54	0.80	0.0084	D

[a] Hydrolyzed, 2.0 N HCl at 30°C.
[b] Hydrolyzed, 0.05 N HCl at 30°C.
[c] Degraded using 0.05 N HCl in methanol at 30°C.
[d] Degraded using 0.05 N HCl in n-butanol at 30°C.
[h] Fibrous
[i] Disintegrated

TABLE XXIV (Continued)

PROPERTIES OF DEGRADED LINTERS

Sample	Time of Treatment, hr.	Intrinsic Viscosity	Copper Number	Aldehyde Number, mmol.CHO/g.	Appearance
Control	0	5.08	0.16	0.0093	F[h]
B-2-A[d]	5	3.17	--	--	F
B-2-B	64	1.83	--	--	D[i]
B-2-C	74	--	--	--	D
B-2-D	312	1.34	0.50	--	D
B-3-A[d]	210	1.43	1.51	--	F
H-1-A[e]	3	2.83	0.85	0.0217	F
H-1-B	24	2.03	1.31	0.0206	D
H-1-C	72	1.68	1.72	0.0210	D
H-1-D	262	1.36	1.32	0.0230	D
H-2-A[e]	5	2.82	--	--	F
H-2-B	58	1.65	--	--	D
H-2-C	248	--	0.98	--	D
H-2-D	312	1.31	--	--	D
O-1-A[b]	4	2.79	0.67	0.0209	F
O-1-B	24	1.96	1.46	0.0149	D
O-1-C	72	1.78	1.28	0.0128	D
O-1-D	263	1.41	1.06	0.0170	D
T-1-A[g]	4	2.53	0.73	0.0182	F
T-1-B	28	1.99	1.78	0.0221	D
T-1-C	72	1.53	1.98	0.0278	D
T-1-D	288	1.25	2.94	0.0354	D

[d] Degraded using 0.05 N HCl in n-butanol at 30°C.
[e] Degraded using 0.05 N HCl in n-hexanol at 30°C.
[f] Degraded using 0.05 N HCl in n-octanol at 30°C.
[g] Degraded using 0.05 N HCl in tetrahydrofuran at 30°C.
[h] Fibrous
[i] Disintegrated

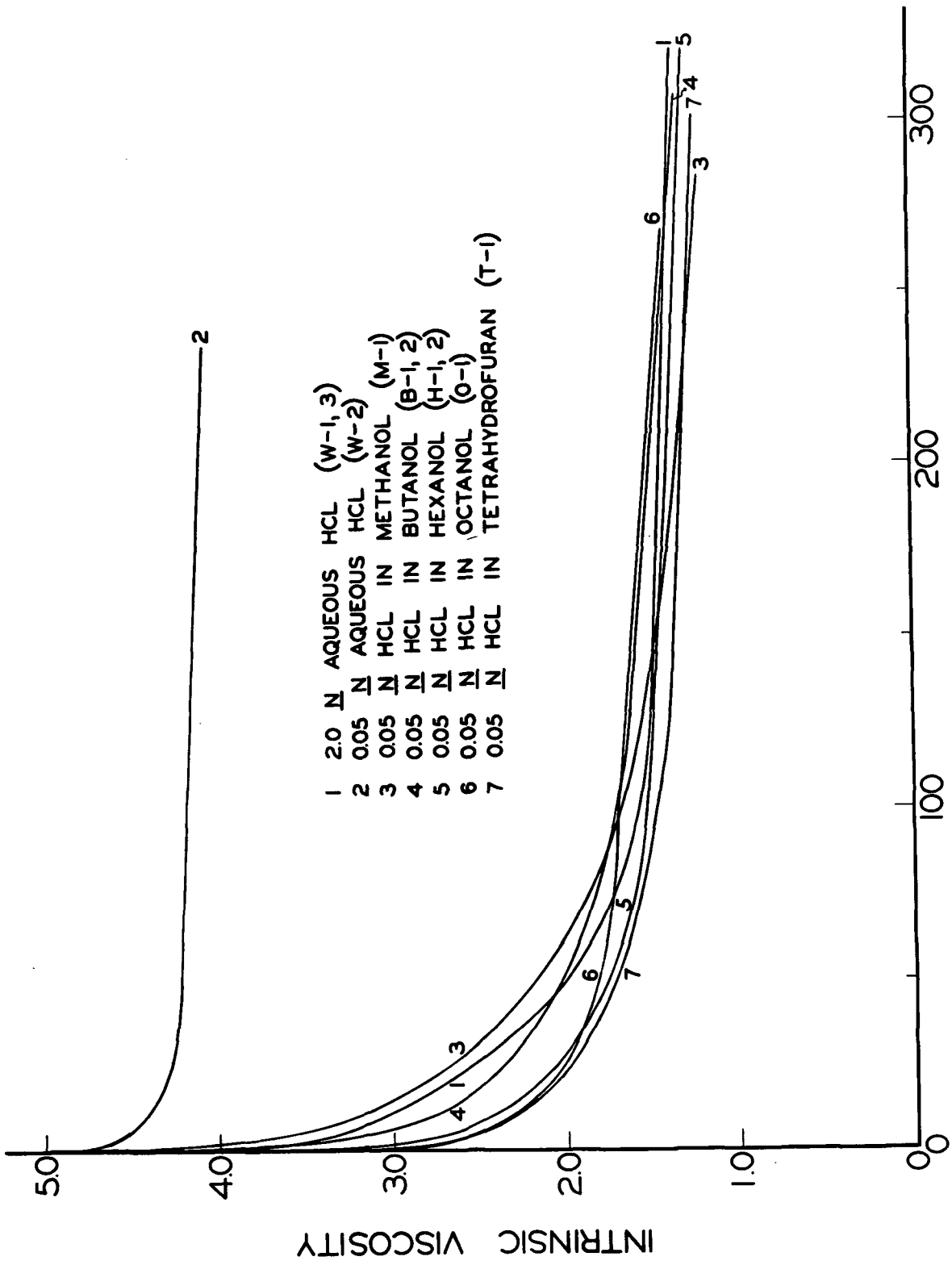


Figure 16

Intrinsic Viscosity Versus Time of Treatment at 30°C.

(Individual Curves With Experimental Points Are Given in Figures 24 Through 30.)

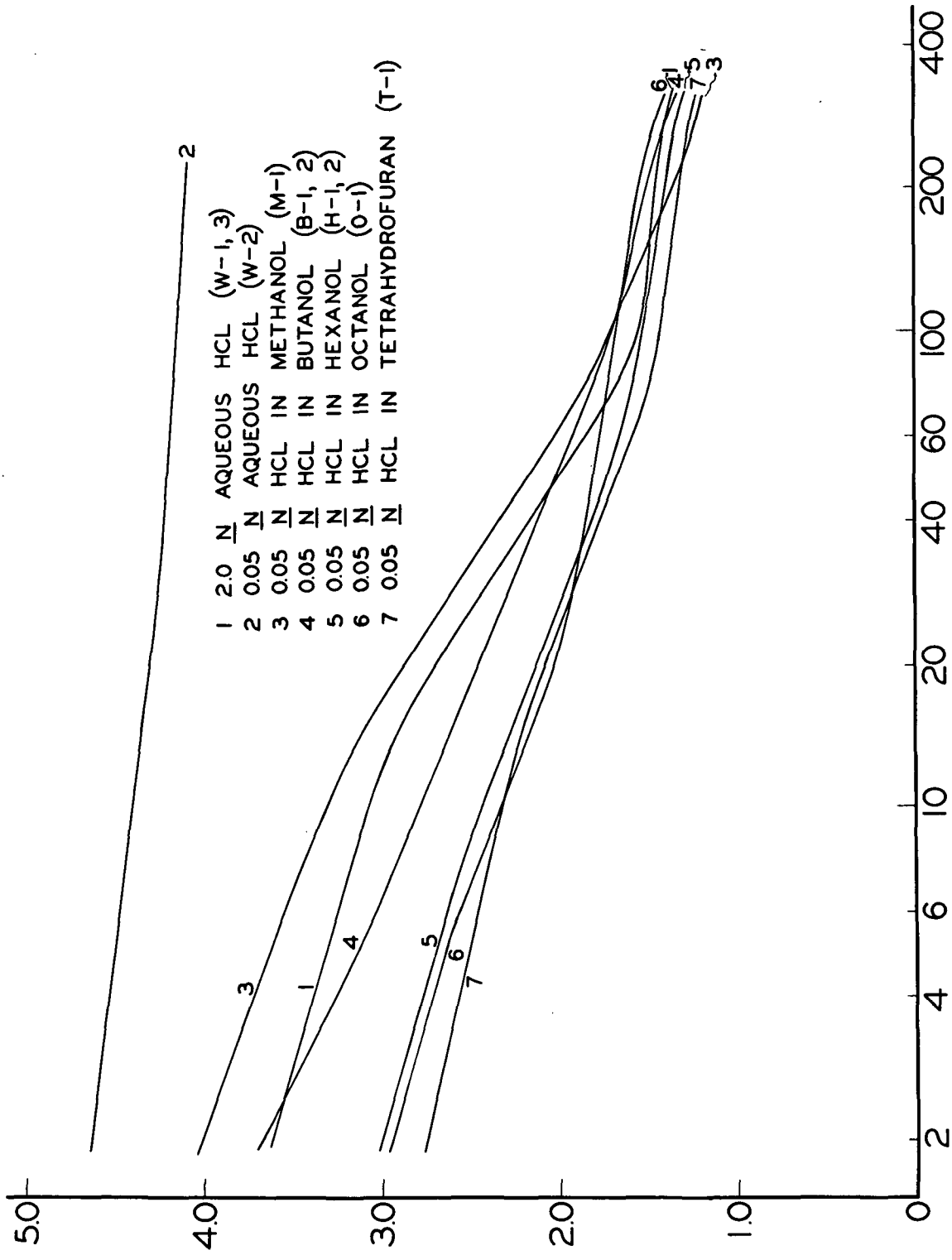


Figure 17

Intrinsic Viscosity Versus Time of Treatment at 30°C.

(Individual Curves with Experimental Points Are Given in Figures 24 Through 30.)

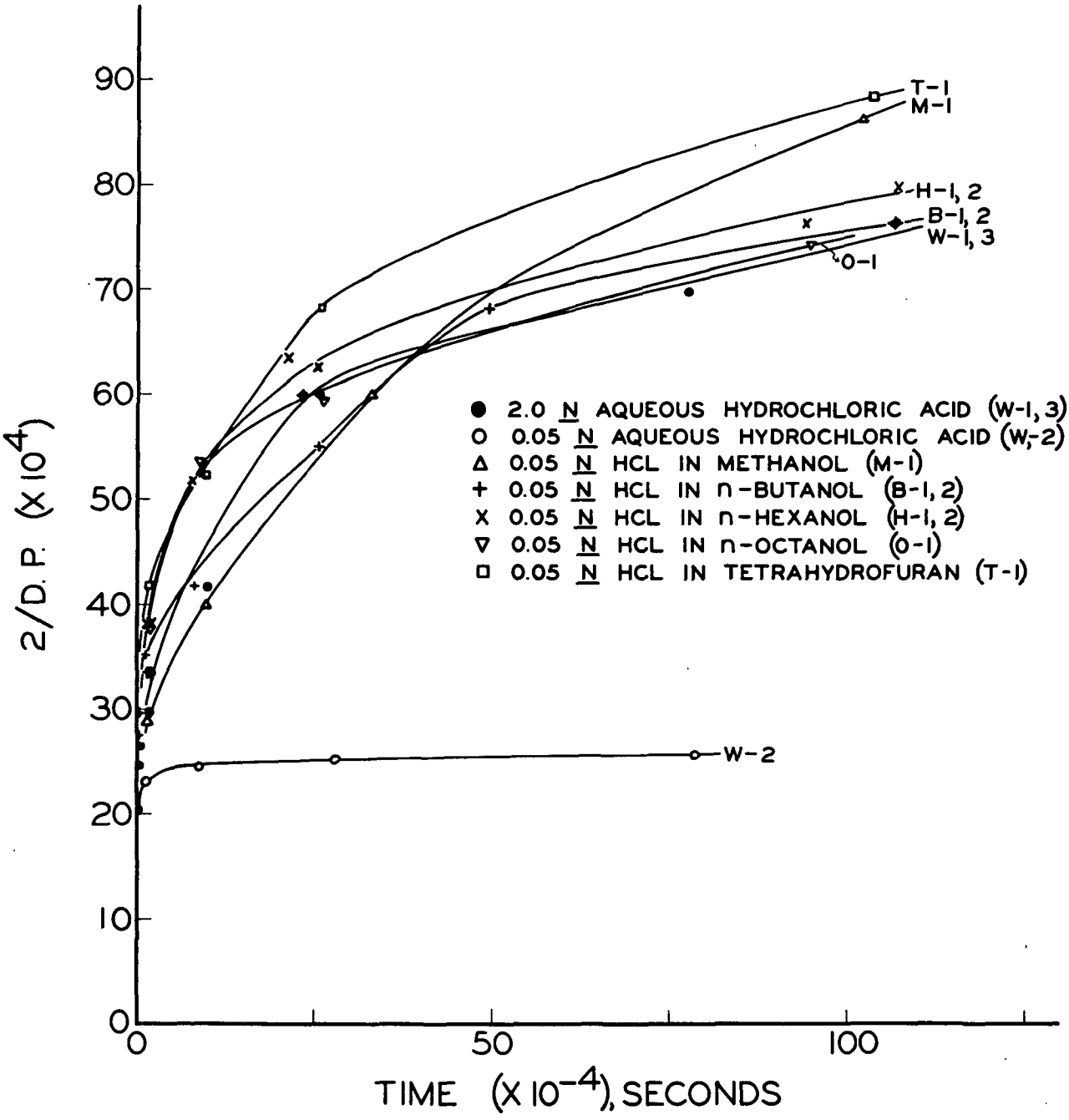


Figure 18

2/D.P. Versus Time of Treatment at 30°C.

TABLE XXV

REACTION CONSTANTS FOR DEGRADATION STUDIES

Liquid	Acidity, N	k,* sec.$^{-1}$x10^{8}
Water	2.0	1.63
Water	0.05	0.28
Methanol	0.05	3.60
n-Butanol	0.05	1.33
n-Hexanol	0.05	1.70
n-Octanol	0.05	2.30
Tetrahydrofuran	0.05	2.23

*Measured over the interval t 60x10^{4} to t 90x10^{4} seconds.

Copper Number

Table XXIV gives the copper numbers found for each sample. Figure 19 shows the variation of the copper number of the degraded linters with the time of treatment. Figure 20 shows the variation of copper number with $1/[\eta]$.

Aldehyde Number

Table XXIV gives the aldehyde numbers found. Figures 21 and 22 show the variation of aldehyde number with time and $1/[\eta]$, respectively.

Carboxyl Content

The carboxyl content, determined using silver O-nitrophenolate, is given for three samples in Table XXVI. The samples tested were the original linters, linters degraded 262 hours in acidified hexanol, and linters degraded 288 hours in acidified tetrahydrofuran.

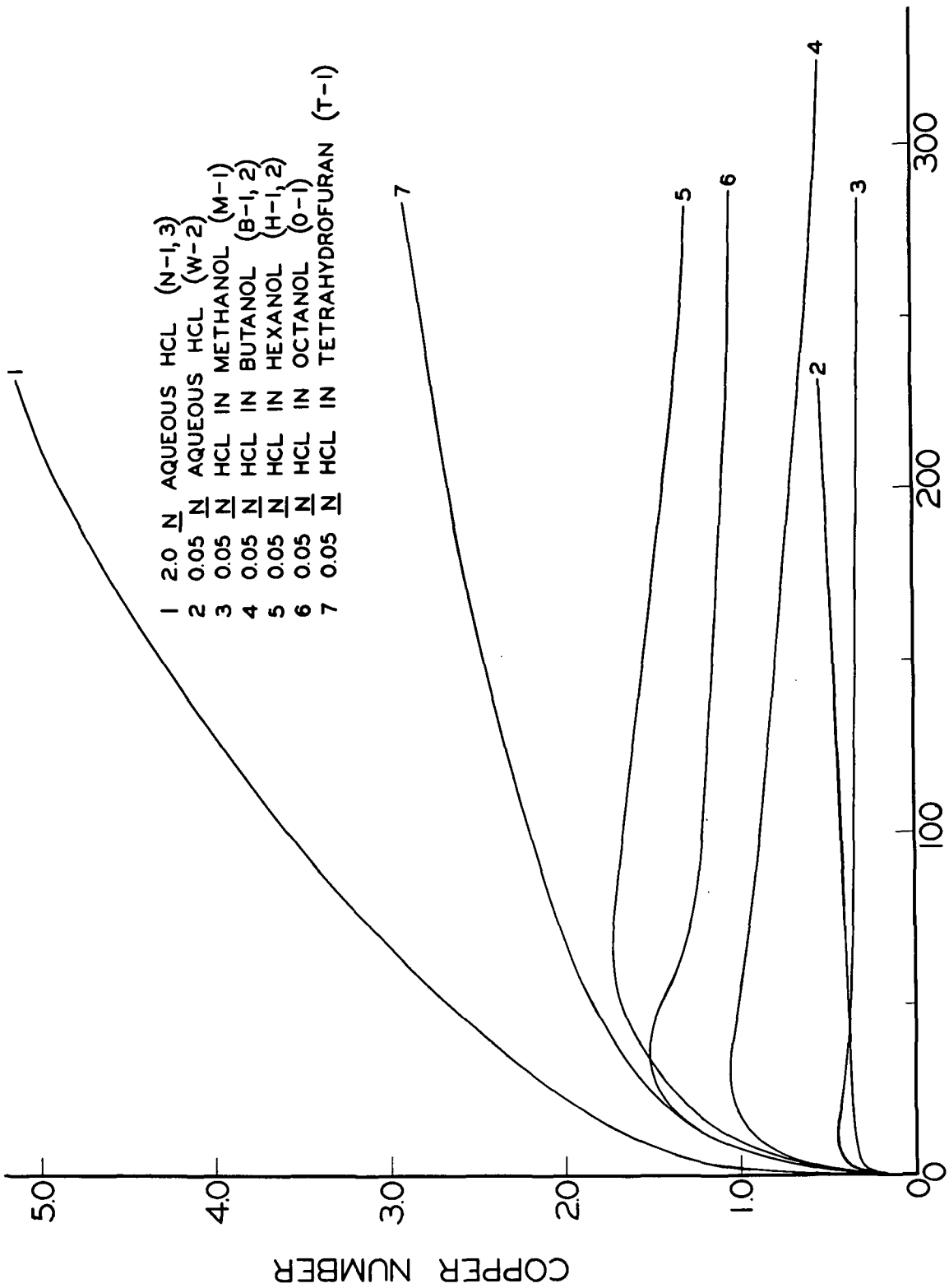


Figure 19

Copper Number Versus Time of Treatment at 30°C.

(Individual Curves With Experimental Points Are Given in Figures 24 Through 30.)

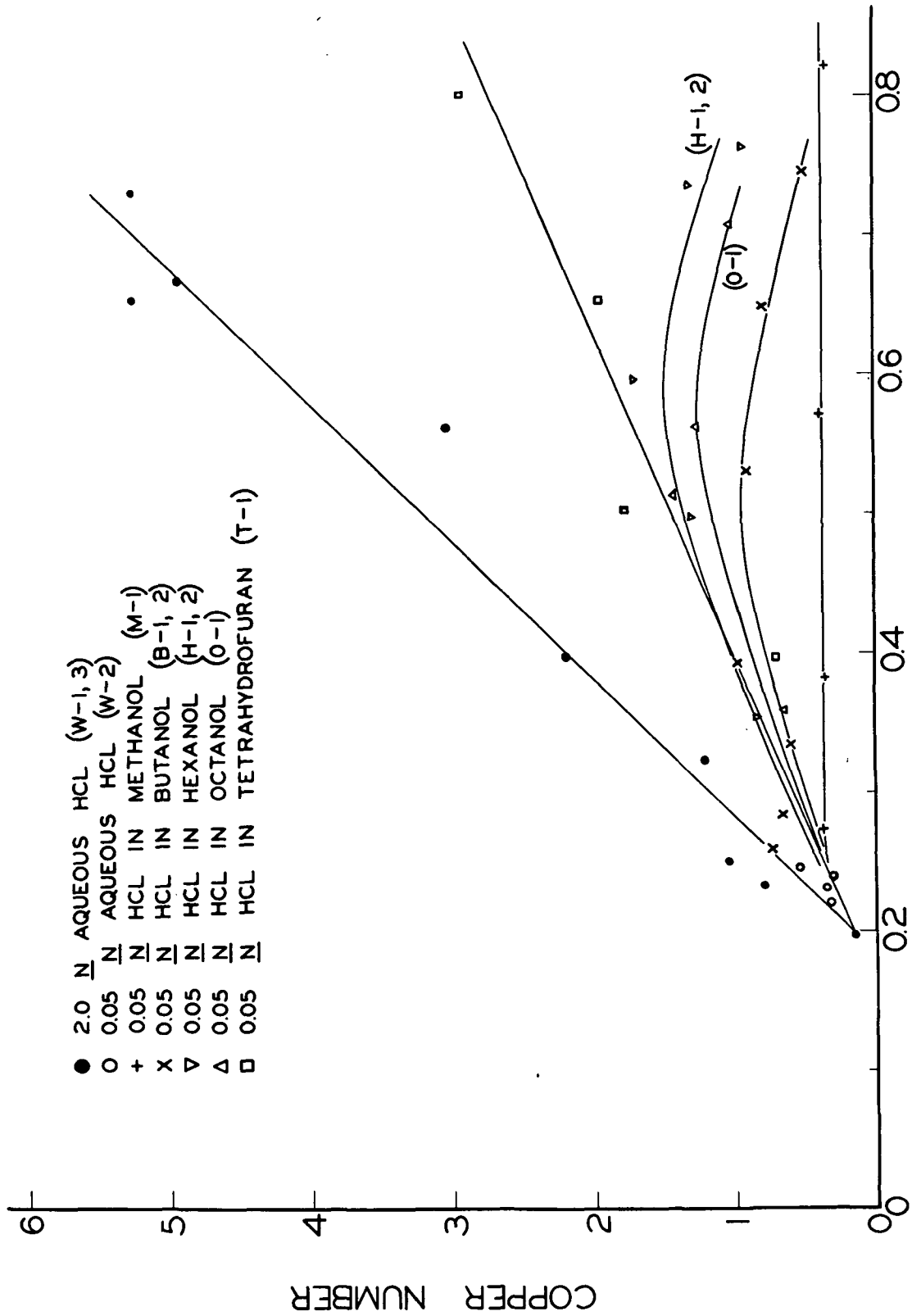


Figure 20

Copper Number Versus Reciprocal Intrinsic Viscosity

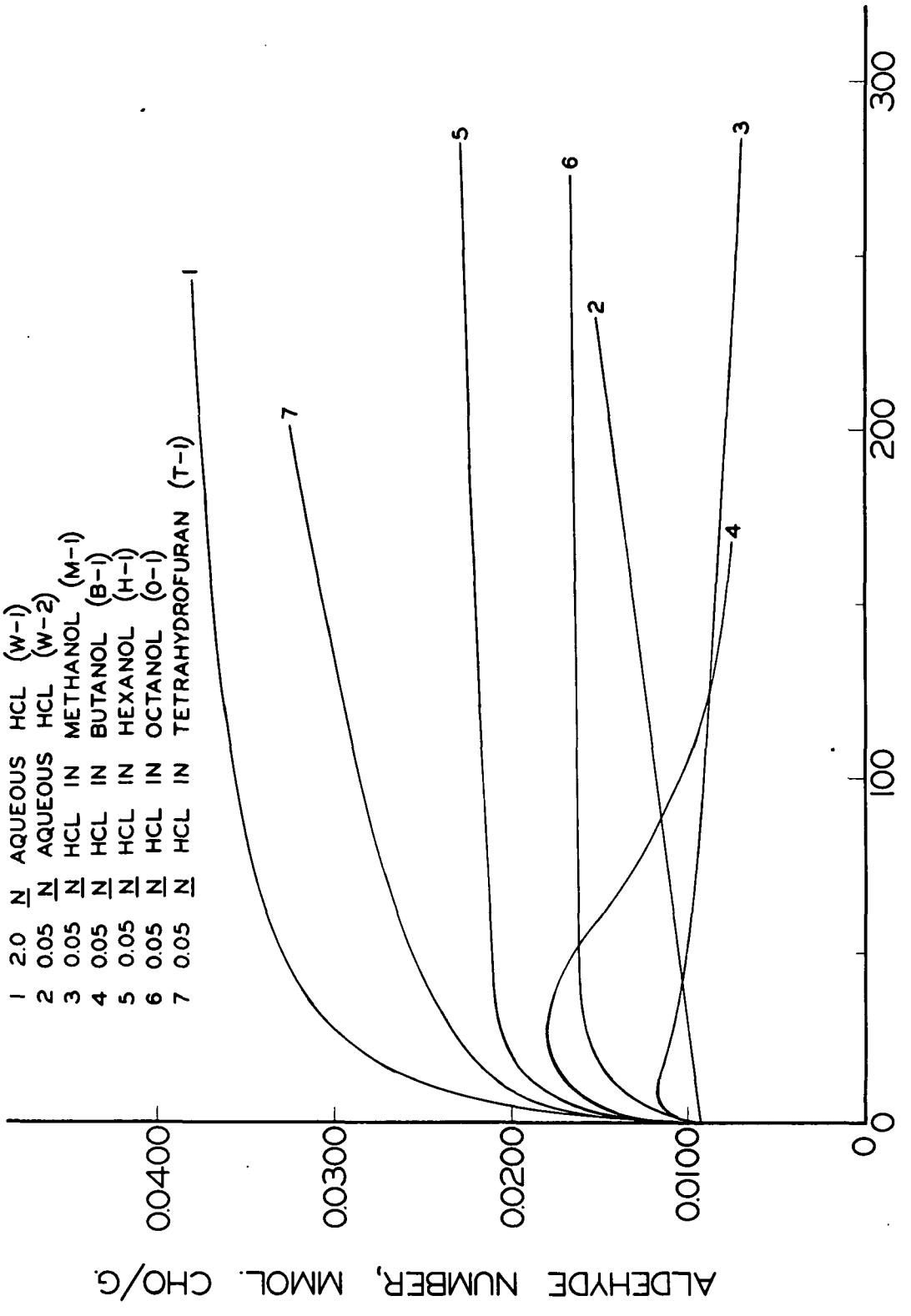


Figure 21

Aldehyde Number Versus Time of Treatment at 30°C.

(Individual Curves With Experimental Points Are Given in Figures 24 Through 30.)

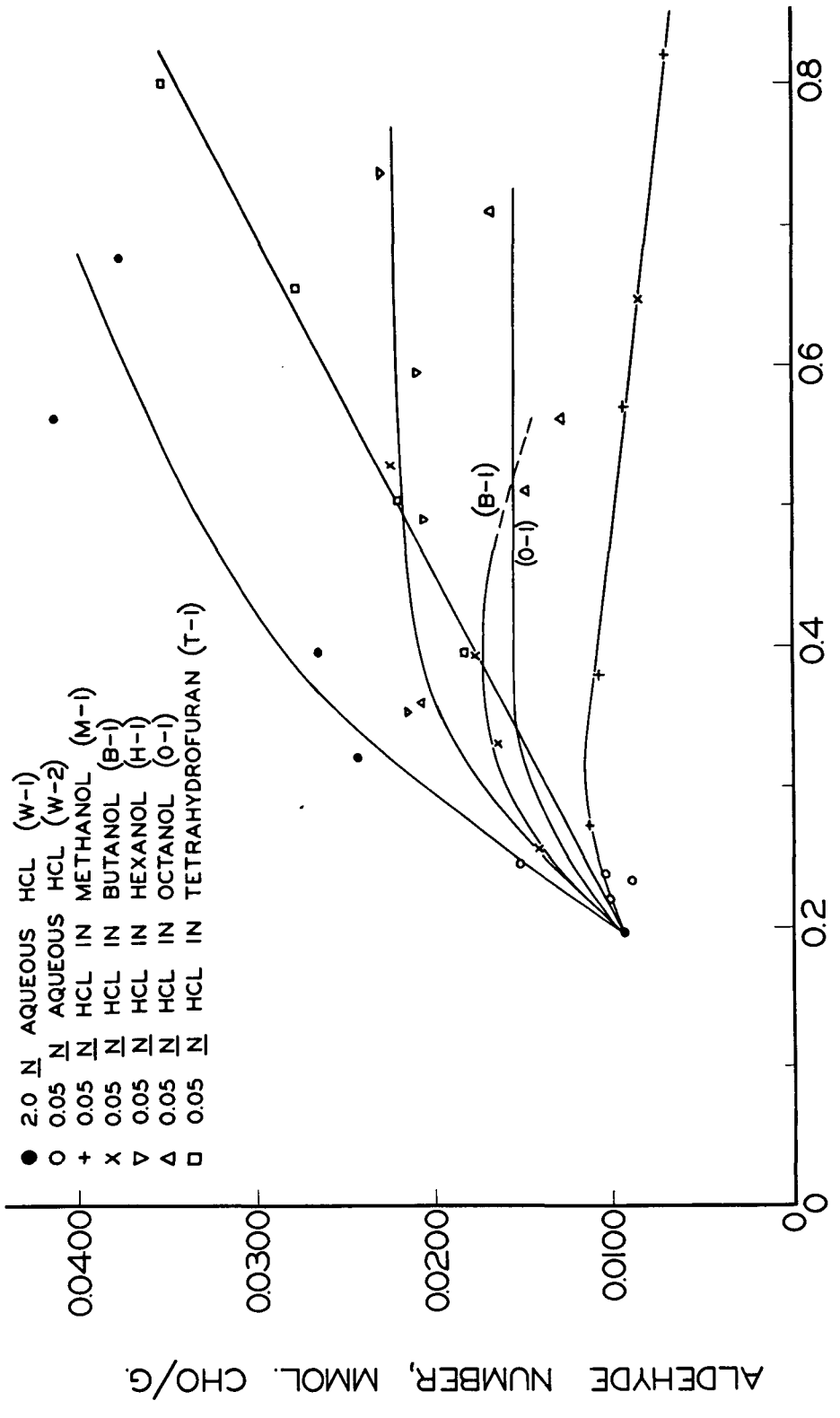


Figure 22

Aldehyde Number Versus Reciprocal Intrinsic Viscosity

TABLE XXVI

CARBOXYL CONTENTS

Sample	Carboxyl Content, mmol.CHO/g.	Difference in CHO Content Between Linters and Degraded Sample, mmol.CHO/g.
Linters	0.006	---
Linters degraded 262 hr. in hexanol + 0.05 N HCl	0.002	-0.004
Linters degraded 288 hr. in tetrahydrofuran + 0.05 N HCl	0.014	+0.008

The decrease in carboxyl content of the linters degraded in acidified hexanol may have been caused by esterification. The increase in the carboxyl content of the linters degraded in acidified tetrahydrofuran may have been caused by oxidation of aldehydric groups. Two observations support this view. Table XVIII indicated that oxidizing compounds were formed in acidified tetrahydrofuran. In Figure 22, at a reciprocal intrinsic viscosity of 0.8 (corresponding to 288 hours degradation), the aldehyde number of linters degraded in acidified tetrahydrofuran is 0.035 mmol. CHO per g. An extrapolation of the curve for hydrolysis in 2.0 N hydrochloric acid indicates that the aldehyde number at 288 hours should be 0.045 mmol. CHO per g. The difference of 0.010 mmol. CHO per g. compares favorably with the difference in carboxyl content between the original linters and the linters degraded in acidified tetrahydrofuran.

YIELD OF DEGRADED LINTERS

A summary of the recovery of insoluble and soluble cellulose is given in Table XXVII. Insoluble cellulose includes all solid samples recovered

TABLE XXVII

RECOVERY OF SOLUBLE AND INSOLUBLE CELLULOSE

Series	Study	Weight of Linters Recovered, g.	Soluble Cellulose[a] Recovered, g.	Total Weight, g.	Initial Weight of Linters, g.	Recovery, %
I	W-1	17.49	0.015	17.50	17.69	99.0
I	B-1	31.39	0.042	31.43	32.55	96.6
II	W-2	15.60	0.006	15.61	15.55	100.3
II	M-1	15.03	0.014	15.04	14.94	100.7
II	H-1	23.76	0.064	23.82	24.32	98.1
II	O-1	22.27	0.073	22.35	22.61	98.8
II	T-1	15.93	0.262	16.20	16.15	100.4
III	W-3	15.00	0.024	15.03	13.63[b]	110.0
III	B-2	13.31	0.041	13.35	12.23[b]	109.1
III	H-2	15.98	0.074	16.05	14.90[b]	107.7
IV	W-4	5.83	0.004	5.83	5.81	100.4
IV	M-2	6.94	0.009	6.95	6.93	100.5
IV	B-3	5.37	0.019	5.38	5.32	101.2

[a] Measured by hydrolyzing the filtrates, determining the apparent concentration of glucose by the reducing power of the hydrolyzate, and converting the value to an equivalent concentration of cellulose.

[b] Initial weights are in doubt and are believed low.

plus any known losses in filtration. The term "soluble cellulose," refers to solubles in the filtrates expressed as an equivalent concentration of cellulose. The calculation was made by determining the reducing power of the solutions after hydrolysis, expressing the value as an equivalent concentration of glucose, and converting the glucose concentration to an equivalent concentration of cellulose, (see section on Hydrolysis of Model Compounds, p. 69 ff.). The total weight of soluble cellulose was found by multiplying the volumes of liquors found by the concentration of soluble cellulose in each liquor.

In some of the liquors, solubles were measured by evaporation of the liquors to constant weight at 80°C. under vacuum. The methanol-water extraction liquors contained sodium salts from the neutralization step, necessitating a correction in the solids found. The data with comparative values of soluble cellulose are given in Table XXVIII. Except for some scattered samples, the values found by evaporation were much higher. The summative data given in Table XXVII indicate that the losses measured by hydrolysis gave values which are of the right order of magnitude.

Loss-time curves were calculated for Series I, II, and III from: (a) The initial weight of linters added and the samples recovered. (b) The volume of all liquid added or removed. (c) The volume of all methanol-water extractions. (d) The concentration of soluble cellulose in all liquid samples. Figure 23 shows the percentage loss as a function of the time of treatment. Reproducibility between duplicate curves was poor but the losses found represent only very small

TABLE XXVIII

DETERMINATION OF SOLUBLES IN LIQUORS

Comparison of Values Found by Hydrolysis and by Evaporation

Samples	Solids by Evaporation,[a] mg./ml.	Solubles by Hydrolysis,[b] mg./ml.	Ratio Net Solids/Solubles by Hydrolysis
W-1-Ff[c]	0.048	0.019	2.53
W-3-Af	0.116	0.041	2.83
W-3-Cf	0.152	0.037	4.11
W-3-Df	0.170	0.039	4.36
W-4-Af	0.086	0.030	2.87
M-1-Df	0.076	0.025	3.04
M-1-Dm[d]	0.020	0.011	1.82
M-2-Af	0.026	0.027	0.96
M-2-Am	0.111	0.017	6.53
B-1-Ff	0.102	0.021	4.86
B-1-Fm	0.123	0.029	4.24
B-2-Df	0.116	0.030	3.87
B-3-Af	0.020	0.030	0.67
B-3-Am	0.141	0.068	2.07
H-1-Df	0.306	0.037	8.27
H-1-Am	0.112	0.001	10.2
H-1-Bm	0.140	0.010	14.0
H-1-Cm	0.183	0.028	6.53
H-1-Dm	0.446	0.113	3.95
H-2-Df	0.908	0.034	26.7
O-1-Bf	1.161	0.016	72.6
O-1-Cm	0.237	0.057	4.16
O-1-Dm	0.541	0.153	3.53
T-1-Df	0.284	0.732	0.39
T-1-Dm	0.354	0.164	2.16

[a] Determined by drying to constant weight at 80°C. under vacuum and correcting for any sodium salts present.

[b] Samples hydrolyzed for six hours in 1.0 N HCl and the reducing power determined by Somogyi's method.

[c] Filtrates are designated by adding a lower-case f to the code number for the corresponding fiber sample.

[d] Methanol-water extraction liquors are designated by adding a lower-case m to the code number of the corresponding fiber sample.

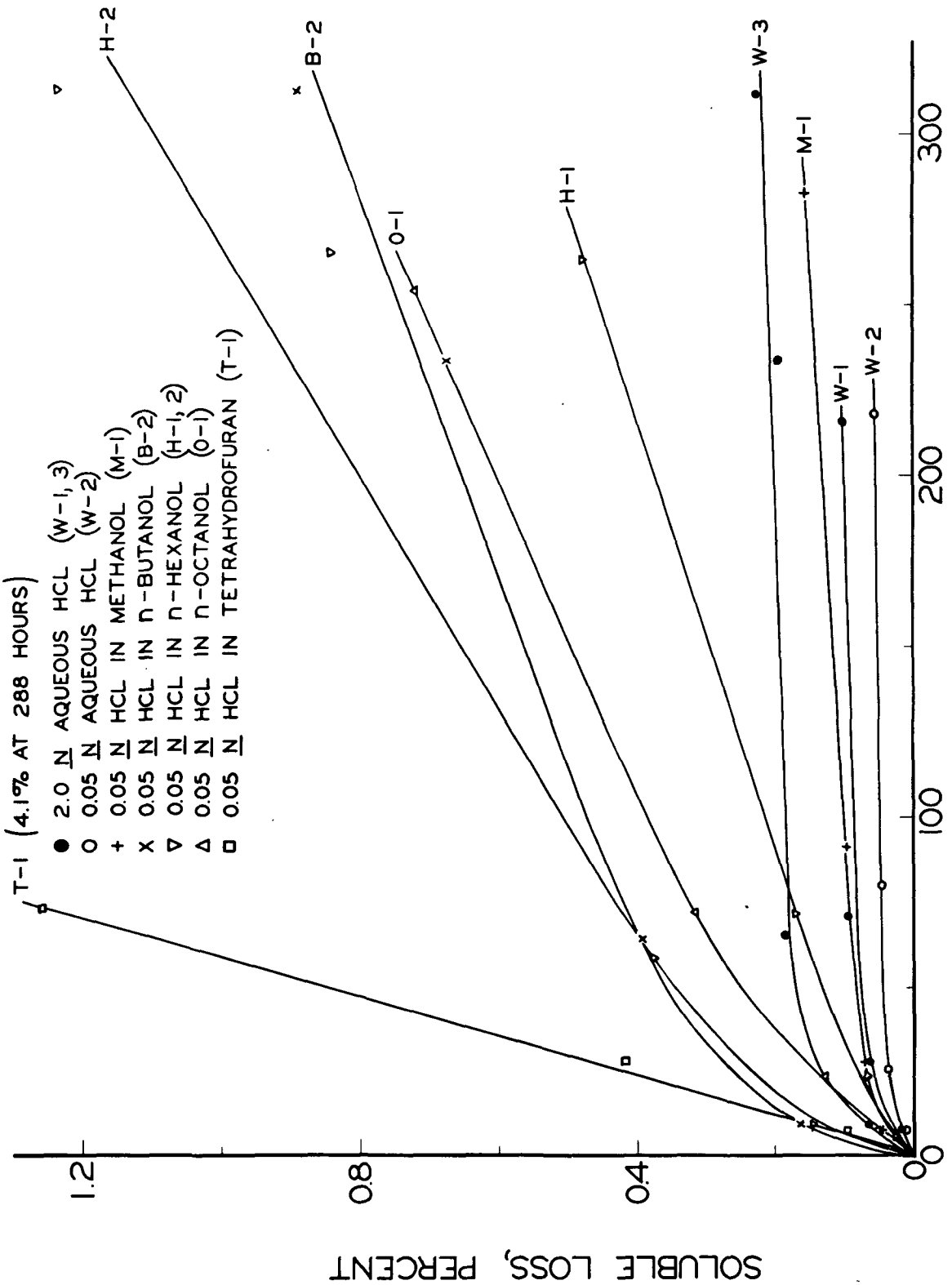


Figure 23

Soluble Losses Versus Time of Treatment at 30°C.

quantities. It may be that experiments in which the losses were greater would show better agreement.

The data for soluble cellulose from Study B-1 were very scattered and duplicate determinations differed by several hundred per cent. It is believed that the scatter was caused by the very small liquor samples (20 to 40 ml.) taken in this experiment as later experiments in which the volumes of liquor taken were about 100 ml. showed good agreement. The curve for Study B-1 was not included in Figure 23 for this reason.

LIMIT HYDROLYSIS

Cotton linters and three degraded linter samples were subjected to a "limit" hydrolysis using the method (2.5 N boiling hydrochloric acid for 15 minutes) suggested by Battista (44) and the results are given in Table XXIX. The intrinsic viscosities of the four samples before hydrolysis varied from 5.08 to 1.41. After hydrolysis, the intrinsic viscosities of all the samples were essentially equal. Battista stated that a mild hydrolysis would lead to recrystallization and that a mildly prehydrolyzed sample would be more resistant to further, drastic hydrolysis than the original sample. On the basis of these data, recrystallization did not occur during the experiments.

CHANGES IN THE LIQUID PHASE

Acidity

Observations of the variations of acidity during degradation were divided into two parts: the sorption of acid which occurred

TABLE XXIX

LIMIT HYDROLYSIS OF LINTER SAMPLES

2.5 N HCl, 100°C., 15 minutes

Sample	Sample Yield,[a] %	Limit Hydrolysis Yield, %	Over-all Yield, %	Intrinsic Viscosity Before Limit Hydrolysis	Intrinsic Viscosity After Limit Hydrolysis
Linters	100.0	94.8	94.8	5.08	1.02
W-1-F[b]	99.9	94.5	94.4	1.50	1.00
W-2-D[c]	99.95	92.4	92.4	4.09	1.02
O-1-D[d]	99.3	93.0	92.3	1.41	0.96

[a] Determined from Figure 23.
[b] Degraded 216 hours in 2.0 N hydrochloric acid.
[c] Degraded 218 hours in 0.05 N hydrochloric acid.
[d] Degraded 263 hours in octanol containing 0.05 N hydrogen chloride.

on mixing acidified liquids and linters, and the changes in acidity during the remainder of an experiment. Mixing changes were measured by determining the acidity of the liquids just before adding them to the cellulose and by determining the acidity of the liquid phase within one-half hour of mixing. The data are given in Table XXX. The initial acidity of the liquid has been corrected for the dilution by unacidified liquid present on the cellulose. Acidities of the liquid phase were determined during some of the studies and are listed in Table XXXI. The decrease in acidity with time is comparable to similar decreases observed in studying the reaction between alcohols and hydrogen chloride in the absence of cellulose and there is no reason to believe that the presence of cellulose has changed the reactions.

Water Content

An attempt was made to measure the changes in water content of the liquid phase on mixing linters and acidified liquid and the data obtained are given in Table XXXII.

SUMMARY OF DEGRADATION STUDIES

Viscosity of the Degraded Linters

Degradation of cotton linters occurred in all the acidified liquids used. The rate of degradation in acidified, nonaqueous liquids was much greater than the rate of degradation in aqueous acid of the same acid concentration. The rate of degradation in

TABLE XXX

ACID SORPTION BY CELLULOSE FROM ACIDIFIED LIQUIDS

Liquids Were Acidified With Hydrogen Chloride

Liquid	Total Volume of Liquid,[a] cc.	Initial Acidity,[b] N	Acidity After Mixing, N	Weight of Cellulose, g.	Acid Sorbed by Cellulose, meq./g.
Water	916	1.920	1.902	17.69	0.933
Water	892	0.0498	0.0489	15.55	0.052
Water	834	1.994	1.984	13.63	0.611
Water	153	1.961	1.990	5.81	0.746
Methanol	887	0.0504	0.0498	14.94	0.036
Methanol	307	0.0490	0.0483	6.93	0.031
n-Butanol	840	0.0454	0.0443	32.55	0.028
n-Butanol	857	0.0442	0.0432	12.33	0.066
n-Butanol	301	0.0502	0.0490	5.32	0.068
n-Hexanol	913	0.0473	0.0437	24.32	0.135
n-Hexanol	862	0.0551	0.0529	14.90	0.128
n-Octanol	909	0.0467	0.0438	22.61	0.117
Tetrahydrofuran	899	0.0477	0.0408	16.15	0.384

[a] Includes unacidified liquid wetting the cellulose.
[b] Acidity has been corrected for dilution caused by unacidified liquid added with the cellulose.

TABLE XXXI

VARIATIONS IN ACIDITY DURING DEGRADATIONS

Temperature, 30°C.

Study	Time, hr.	Acidity, N
0.05 N HCl in methanol (Study M-1)	0.5	0.0498
	66	0.0479
	160	0.0463
0.05 N HCl in n-butanol (Study B-1)	0.5	0.0432
	307	0.0421
0.05 N HCl in n-hexanol (Study H-1)	0.5	0.0529
	287	0.0511

TABLE XXXII

CHANGES IN THE WATER CONTENT OF THE LIQUID PHASE ON MIXING CELLULOSE AND ACIDIFIED LIQUIDS

Study	Water Brought in With Liquid, mg.	Water Brought in With Cellulose, mg.	Total, mg.	Water Found in Liquid Phase After Mixing, mg.	Difference, mg.
0.05 N HCl in methanol	1070	450	1520	1220	-300
0.05 N HCl in hexanol	1150	100	1250	1440	+190
0.05 N HCl in octanol	350	70	420	640	+220
0.05 N HCl in tetrahydrofuran	130	300	430	420	- 10

2.0 N hydrochloric acid was about as rapid as the rate of degradation by 0.05 N hydrogen chloride in methanol. A rough estimate of the initial rates of degradation in liquids acidified with 0.05 N hydrogen chloride was made by comparing the viscosity changes during the first ten hours of reaction. The values are given in Table XXXIII. The changes, beginning with the smallest, ranked: water, methanol, butanol, hexanol, octanol, and tetrahydrofuran. Within the limits of experimental error, there was no difference in the leveling-off viscosity found for 2.0 N hydrolysis and any of the nonaqueous liquids used (see Figure 16). The value, about 1.25, is somewhat higher than the limit viscosity of 1.00 found using Battista's method (see Table XXX).

Copper and Aldehyde Numbers of the Degraded Linters

The general character of the copper and aldehyde numbers is sufficiently similar so that discussion of the results can be made together. The results found for hydrolysis are normal and show only differences caused by the different acidities used. The values found for degradation in tetrahydrofuran (Study T-1) are similar to those found for hydrolysis except for somewhat lower values at corresponding degrees of degradation. In all degradations carried out in alcoholic media, there was an initial increase in copper number of the residues during the first 24 hours. After this time the reducing power of the residue either decreased or leveled off and tended to approach a

TABLE XXXIII

SUMMARY

Liquid	Ten Hour Viscosity Change From Figure 16	Acid Sorbed by Cellulose, From Table XXX, meq./g.	Soluble Losses at 288 hr., From Figure 23, %	Reaction Constants at $t=75 \times 10^4$ sec., From Table XXV, $sec.^{-1}(\times 10^8)$
Water	0.67	0.052	0.05	0.28
Methanol	1.79	0.035	0.13	3.60
n-Butanol	2.28	0.054	0.75	1.33
n-Hexanol	2.63	0.132	0.79	1.70
n-Octanol	2.75	0.117	0.80	2.30
Tetrahydrofuran	2.76	0.384	4.10	2.23

steady value after extended degradation. The steady values found from Figure 19, at 300 hours for the four alcohols were: methanol, 0.3; butanol, 0.5; hexanol, 1.2; and octanol, 1.1. The comparative value found by extrapolation for 2.0 N hydrolysis was 5.7.

Soluble Losses

The soluble losses were under 1.2% for all of the studies except degradation in tetrahydrofuran. The comparative values at 288 hours are given in Table XXXIII. At constant acidities, degradations in nonaqueous media showed higher losses than did degradations made in aqueous acid. The losses for degradation in methanol were lower than the losses for degradations made in other alcohols. Losses in acidified tetrahydrofuran were much higher.

Changes in the Liquid Phase During Degradation

Mixing cellulose and acidified liquids produced a decrease in the amount of acid titratable in the liquid phase. A comparison of all degradations using 0.05 N hydrogen chloride is repeated in Table XXXIII. Water, methanol, and butanol produced the smallest sorption while the sorption in hexanol and octanol was over twice as high. The amount of acid sorbed from tetrahydrofuran was much higher than from any other liquid acidified with 0.05 N hydrogen chloride.

DISCUSSION

Alcoholysis has been stated by Reeves and co-workers (22, 25) to be an unique reaction in which the cellulose molecule is split by acid-catalyzed alcohol with the formation of a nonreducing alkyl glycoside. The work of Assaf, Haas, and Purves (8) indicated that cellulose was almost inaccessible to alcohols larger than butanol. If the mechanism suggested by Reeves occurred in degrading cellulose with acidified alcohols, then differences in the reaction with homologous alcohols should be noted as the molecular weight of the alcohols increased. An increase in the molecular weight of the alcohol should lead to a decrease in the amount of cellulose solubilized because a smaller portion of the cellulose would be attacked. The viscosity of the residue should be higher because more of the long chains originally present in the cellulose would not be accessible to the larger alcohols.

Cotton linters were degraded in this study with four acidified alcohols: methanol, n-butanol, n-hexanol, and n-octanol. The same leveling-off viscosity was found for all four alcohols. The amount of cellulose solubilized during the degradations was smallest for degradations made in methanol and larger for the other alcohols. Under the mechanism of alcoholysis suggested by Reeves and co-workers, the copper numbers of the residues should decrease slightly during the degradation. This behavior was not observed.

The data which have been presented in this work do not fit the mechanism of alcoholysis in three points. There was no difference in the leveling-off viscosity when different alcohols were used. There was no decrease in the amount of cellulose solubilized as the molecular weight of the alcohol used increased. Finally, changes in the copper numbers of the residues did not indicate that non-reducing groups were formed in one reaction. It does not seem possible, therefore, that alcoholysis occurs in the system studied here.

A new explanation can be suggested. The system in question must of necessity contain traces of water. In such a system, the 1-4 links are split by acid-catalyzed hydrolysis. The reducing groups formed by the hydrolysis then react with the acidified alcohol to form nonreducing groups, probably glycosides. In addition, in such a two-phase system containing acid, the concentration of acid at the cellulose-liquid interface is increased by a sorption of acid by the cellulose. The amount of sorption is dependent on the nature of the liquid phase.

This proposed mechanism agrees with the results of this work in the following points. The same leveling-off viscosity would be reached in every alcohol because the cellulose was actually degraded by hydrolysis. The amounts of cellulose solubilized during the degradations would not decrease as the molecular weight of the alcohols increased but would depend on other factors which will be discussed later. Finally, the formation of nonreducing groups

involves two simultaneous reactions. The increase in the copper number followed by a decrease or leveling off is also typical of two simultaneous reactions. Further, the very slight increase observed when methanol was used indicates that in this case the second reaction was faster then when other alcohols were used. This behavior also agrees with the slightly greater reactivity of methanol compared to the higher alcohols.

The hypothesis developed can be extended to cover the degradation of cellulose by acidified tetrahydrofuran. In this case, the degradation of cellulose proceeded by hydrolysis but the reducing groups formed were not converted to nonreducing groups in a second reaction. The slight difference between the reducing power of hydrolyzed linters and linters degraded in tetrahydrofuran at similar degrees of degradation was probably caused by a secondary oxidation of some of the aldehyde groups.

Support for the hypothesis that increased rates of degradation in nonaqueous media are caused by a preferential sorption of acid by the cellulose is of a general nature. In this work the degradation medium was a two-phase system consisting of cellulose plus sorbed water and acid as the solid phase and the nonaqueous liquid containing water and acid as the liquid phase. In this system there will be a partition between the cellulose and the liquid for the available acid. Cellulose, with three hydroxyl groups on each glucose unit, will be favored in this partition as the polarity of

the liquid decreases. The concentration of acid at the interface of the two-phase system will thus depend on the polarity of the liquid. As the acidity increases at the interface, the rate of degradation should increase. The increase would be noted by a more rapid decrease in the viscosity of the residue and in greater soluble losses.

In Table XXXIII the liquids studied are listed in order of decreasing polarity. The viscosity changes agreed in every case with the hypothesis, increasing as the polarity of the liquid decreased. The determination of soluble losses was not as accurate as that of viscosity change. However, losses were least for 0.05 N hydrolysis, somewhat higher for acidified methanol, higher for the other three alcohols, and very high for acidified tetrahydrofuran. The values for the sorption of acid by cellulose from the various liquids agreed only partially with the hypothesis. The values measured were very small, however, and the technique used had not been developed to measure such small changes. Cellulose in water, methanol, and butanol showed much smaller sorption values than did cellulose in the other alcohols. Again, the value for sorption from tetrahydrofuran was much higher. The reaction constants show the same trend with the marked exception of the value for degradation in acidified methanol. Methanol has been found in the past to show properties out of line with the other members of the series. These results cannot be said to give definite proof of the hypothesis that increased rates of degradation in nonaqueous media are caused by increased sorption of acid from the liquid. It is believed, however, that there is fair evidence of such a phenomenon.

Alcoholysis of cellulose might still occur if a truly anhydrous system could be maintained throughout the degradation. Such a system seems very difficult, if not impossible, to achieve.

The data do indicate some dependence of the reducing power of the degraded linters on the accessibility of the residues to alcohols of different molecular weights. The heterogeneous hydrolysis of cellulose is considered to yield crystalline cellulose in which further reaction is limited to the surfaces of the crystallites. The interior of the crystallites is not considered to be accessible to any molecule. The reducing power of the degraded linters must therefore represent reducing groups at the surface of the crystallites. If the "surface" is without depth, then the same percentages of reducing groups should be covered by octanol as are covered by methanol. The relative values of the copper numbers at 300 hours degradation were given on p. 98 and from them the percentages of reducing groups covered by the several alcohols were calculated to be: methanol, 95%; butanol, 91%; hexanol, 79%; and octanol, 81%. Figure 19 indicates that the curves of copper number versus time had very nearly leveled-off so that the differences should primarily represent differences in the accessibility of the reducing groups to the alcohols. The results suggest that the "surfaces" of the degraded linter crystallites are disordered enough to exhibit different accessibilities to molecules of different size.

SUMMARY AND CONCLUSIONS

1. Techniques were developed for the preparation of alcohols and cellulose samples containing minimum quantities of water. It was not possible to prepare anhydrous materials, nor was it possible to maintain water contents below 0.2% in alcohols acidified with hydrogen chloride.

2. The alcoholysis of cellulose was studied by degrading cotton linters at 30°C. with methanol, n-butanol, n-hexanol, and n-octanol, using 0.05 N hydrogen chloride as the catalyst. Comparative degradation studies were made using 0.05 and 2.0 N aqueous hydrochloric acid and tetrahydrofuran acidified with 0.05 N hydrogen chloride.

3. It was found that degradations in acidified organic liquids produced the same leveling-off viscosities although the change in viscosity during the first ten hours was greater as the molecular weight of the alcohol used increased. The soluble losses found in the studies were less than one per cent for 200 hours except in the study using tetrahydrofuran. The soluble losses were greater for those studies made in organic liquids. The reducing values of the residues of linters degraded in alcohols showed and increase during the early stages of degradation, then leveled off or decreased. This behavior was in direct contrast to that for hydrolysis in which the reducing value of the residue increased steadily. The reducing value of the highly degraded residues from the studies made in alcohols were related to the alcohol used. The smaller alcohols gave residues with lower reducing values.

4. It is believed that alcoholysis as a distinct reaction did not exist under the conditions used in this study. There was no evidence that the accessibility of the cellulose to alcoholysis was a function of the molecular weight of the alcohol. Further, the initial increases in reducing power of the residues argues against such a mechanism.

5. It is suggested that degradations of cellulose in acidified alcoholic media are actually initiated by traces of water present in the system and that nonreducing cellulose is formed by condensation of the alcohol with the reducing groups formed on hydrolysis of the 1-4 links.

6. It is suggested that the accelerated rates of degradation found in organic liquids are caused by a sorption of acid from the non-aqueous phase by the cellulose so that the effective acidity at the cellulose-liquid interface is much higher than that measured in the liquid phase.

7. Comparison of the reducing values of the leveling-off residues from the studies using alcohols indicates that a portion of the highly degraded residue is accessible only to the smaller alcohols.

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APPENDIX

REMOVAL OF WATER FROM COTTON LINTERS

A sample of linters was placed in the solvent removal apparatus and dehydrated with two successive methanol soaks. The water and methanol content of the dehydrated linters were measured directly and also calculated from the volumes and water contents of the filtrates. The water-methanol ratios were measured or calculated for each step. The following tabulation summarizes the experiment.

Initial condition of linters:

Solids at 80°C. under vacuum	48.0%
Dry weight of linters	18.84 g.
Weight of water in the linters	20.41 g.

First Soak:
100 ml. of methanol containing 0.60 mg. H_2O/ml.

First Filtrate:
61 ml. of wet methanol containing 260 mg. H_2O/ml.

Second Soak:
150 ml. of methanol containing 0.60 mg. H_2O/ml.

Second Filtrate:
153 ml. of wet methanol containing 30.3 mg. H_2O/ml.

Conditions of dehydrated linters:

Solids at 80°C. under vacuum	32.4%
Water content by Karl Fisher reagent	0.8%
Methanol content by fuchsin test	68.8%
	102.0%

Water balance:

Initial:	
From Linters	20.41 g.
First Soaking:	
Methanol	0.06 g.
Total	20.47 g.

Water balance (Continued)

First filtration:	
Filtrate	15.88 g.
Remaining on linters	4.59 g.
Second soaking:	
Methanol	0.09 g.
Total	4.68 g.
Second filtration:	
Filtrate	4.63 g.
Remaining on linters	0.05 g.

Methanol balance:

Initial:	
From linters	0.0 g.
First soaking:	
Methanol	79.15 g.
Total	79.15 g.
First Filtration:	
Filtrate	37.68 g.
Remaining on linters	41.47 g.
Second soaking:	
Methanol	118.80 g.
Total	160.27 g.
Second Filtration:	
Filtrate	119.63 g.
Remaining on linters	40.64 g.

The composition of the linters as determined from the above calculations was: solids, 31.6%; water, 0.1%; and methanol, 68.3%. The agreement with the experimentally determined values is well within experimental error. The water-methanol ratios calculated from the above tabulation were: first filtrate, 260 mg. per ml.; remainder on linters after first soak, 90.1 mg. per ml.; second filtrate, 30.3 mg. per ml.; and remainder on linters after second soak, 1.2 mg. per ml. A portion of the differences are probably caused by cumulative errors in the calculations.

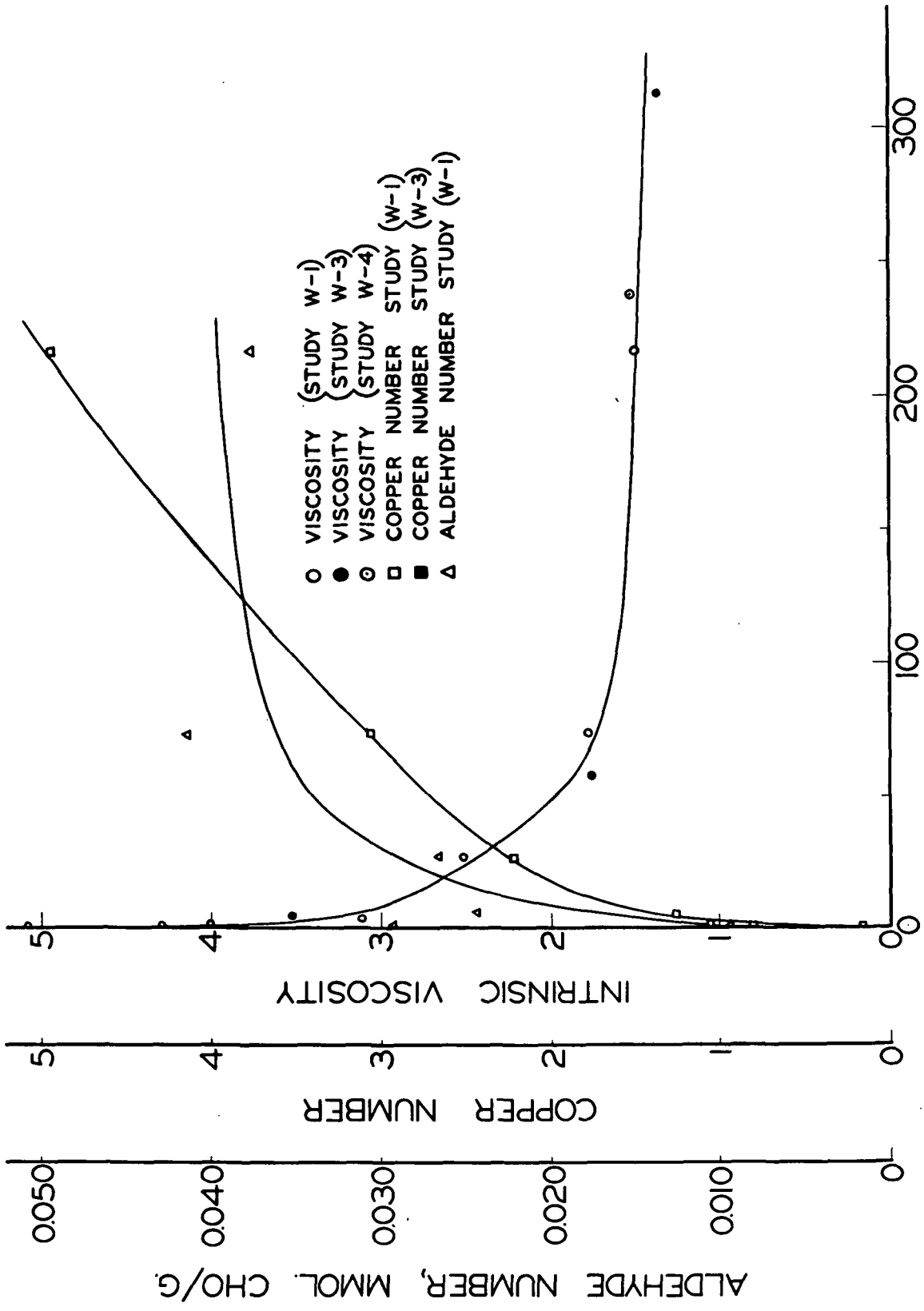

Figure 24

Hydrolysis of Cotton Linters, Properties of Residues, 2.0 N Aqueous HCl at 30°C. (Studies W-1,3,and 4)

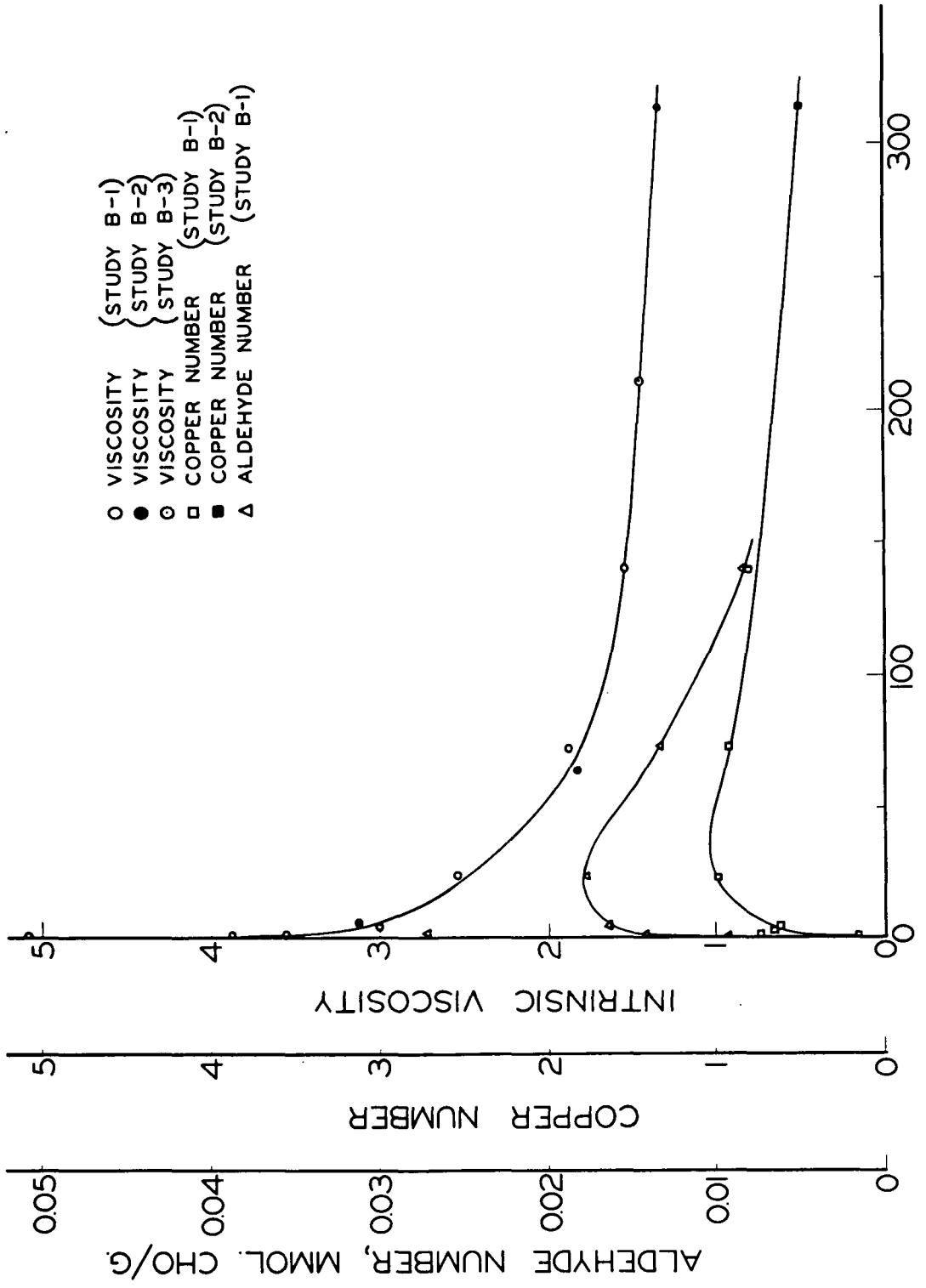

Figure 25

Degradation of Cotton Linters, Properties of Residues, 0.05 N HCl in n-Butanol at 30°C. (Studies B-1,2,and 3)

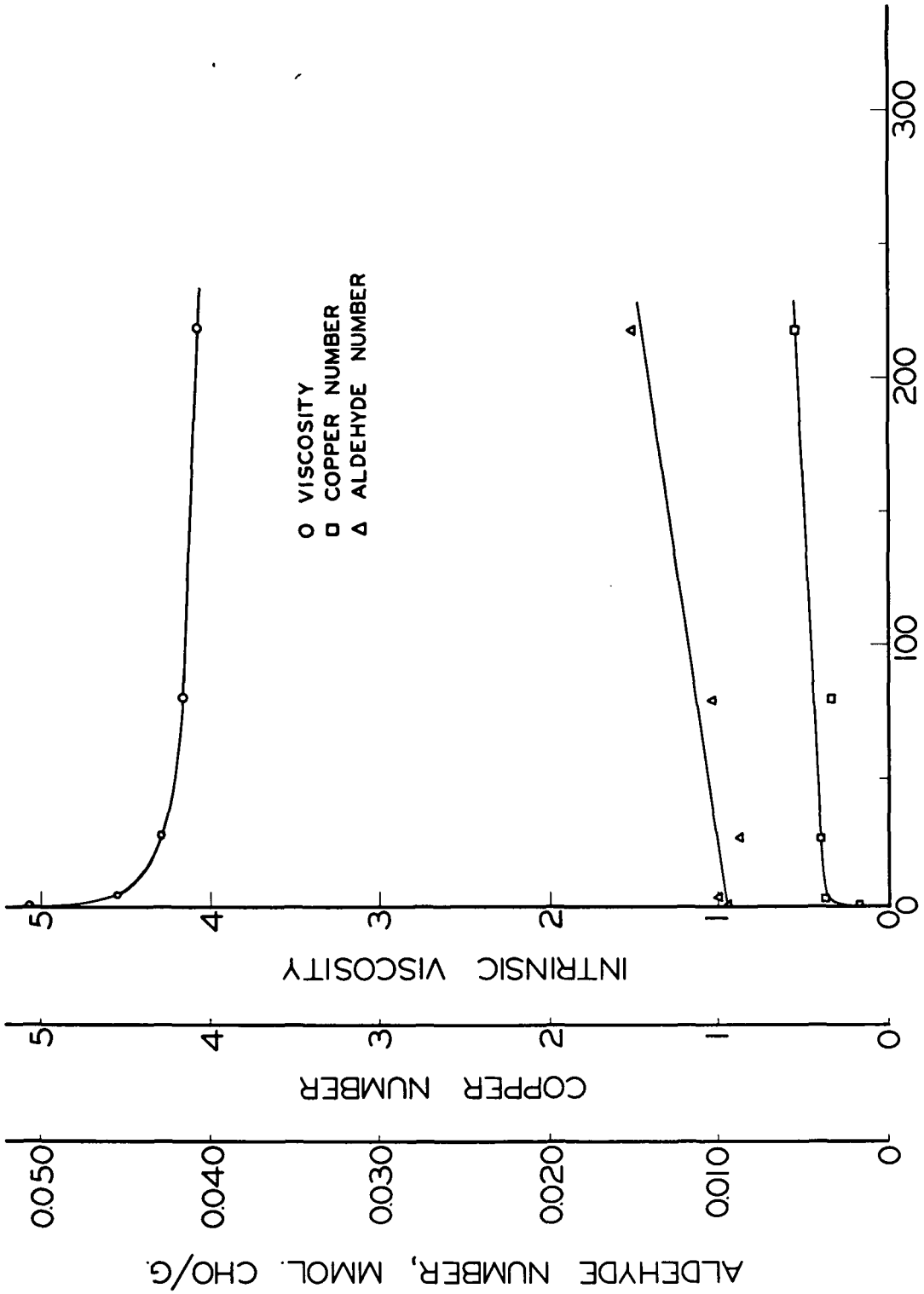

Figure 26

Hydrolysis of Cotton Linters, Properties of Residues, 0.05 N Aqueous HCl at 30°C. (Study W-2)

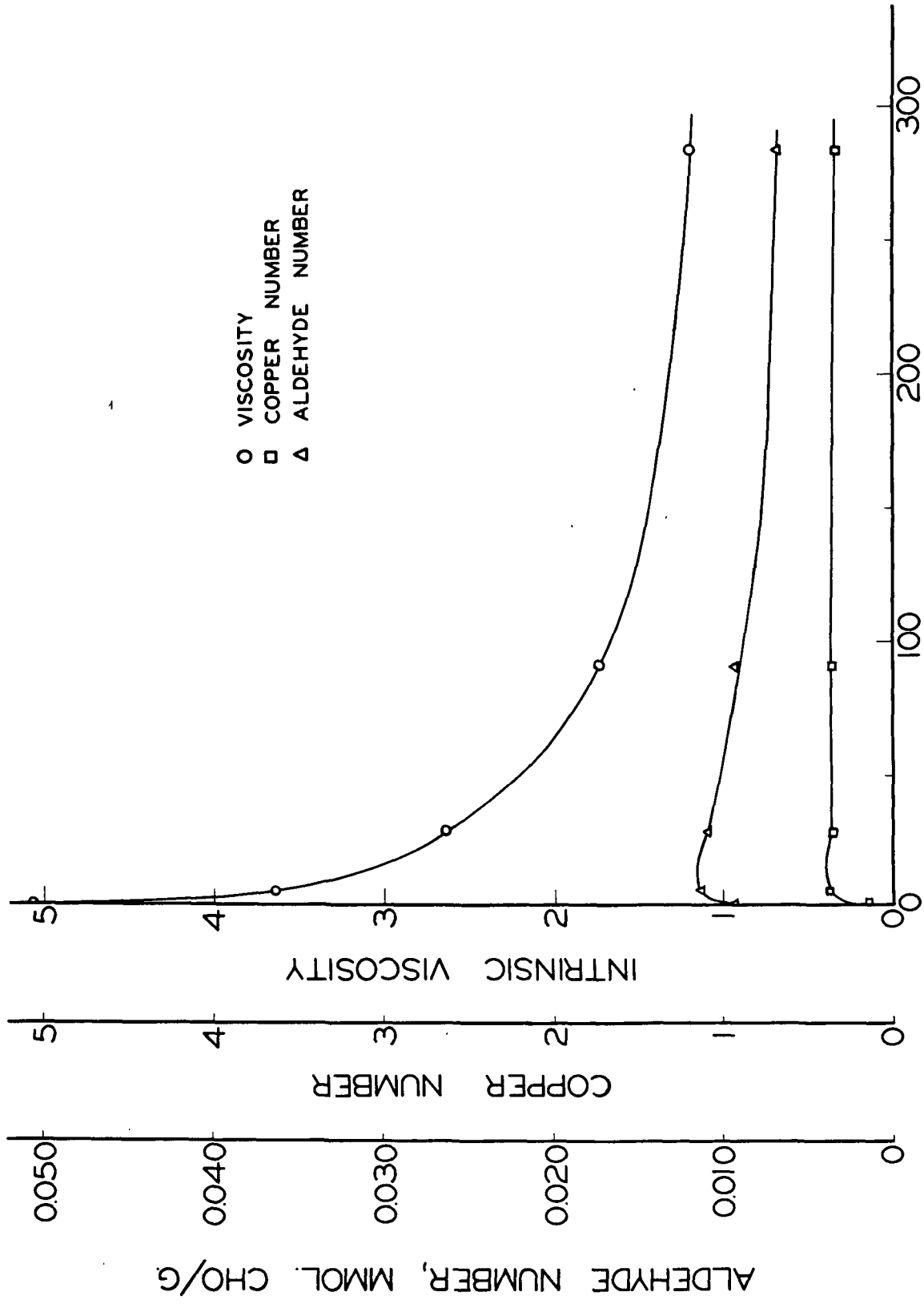

Figure 27

Degradation of Cotton Linters, Properties of Residues, 0.05 N HCl in Methanol at 30°C. (Study M-1)

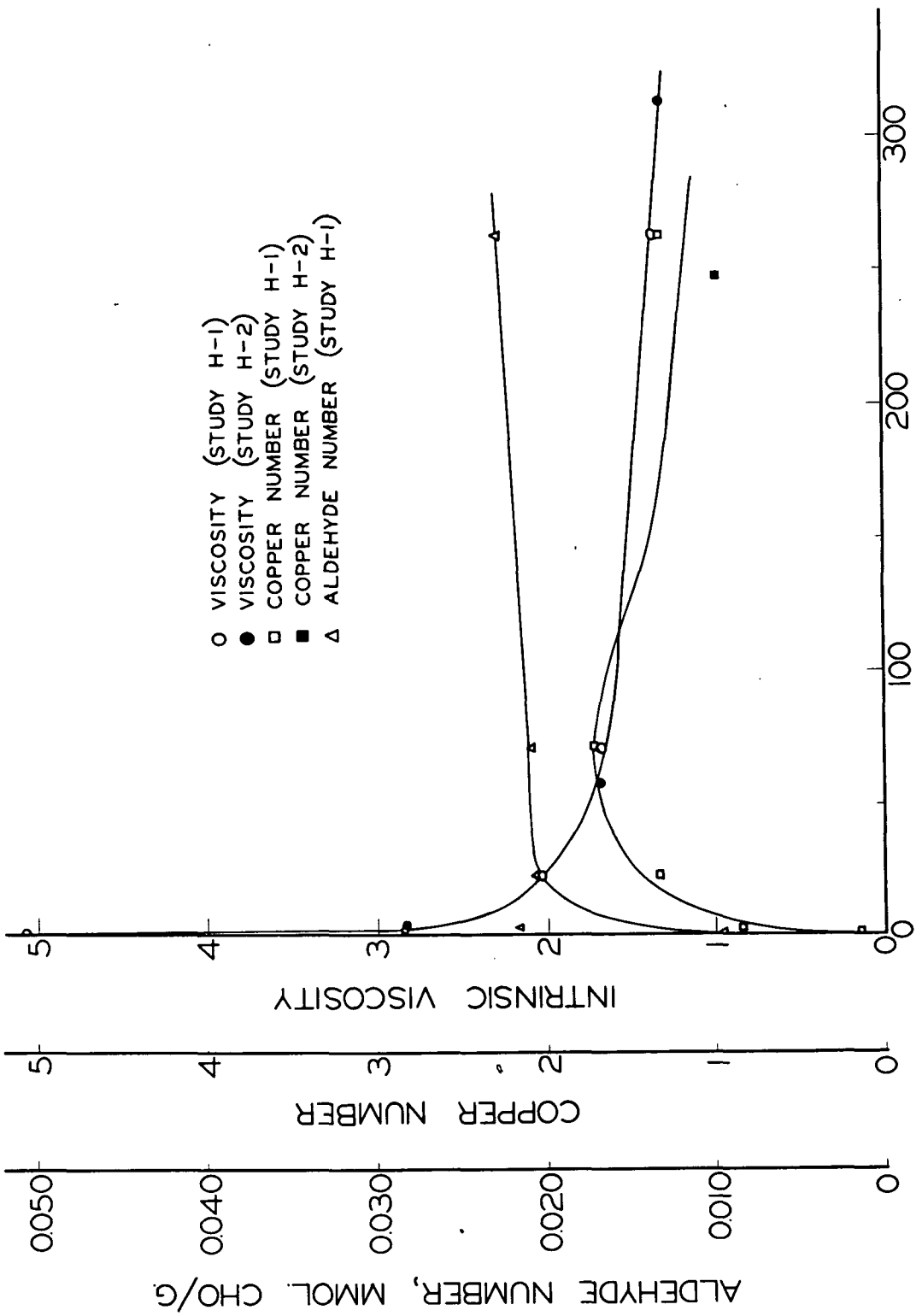

Figure 28

Degradation of Cotton Linters, Properties of Residues, 0.05 N HCl in n-Hexanol at 30°C. (Studies H-1, and 2)

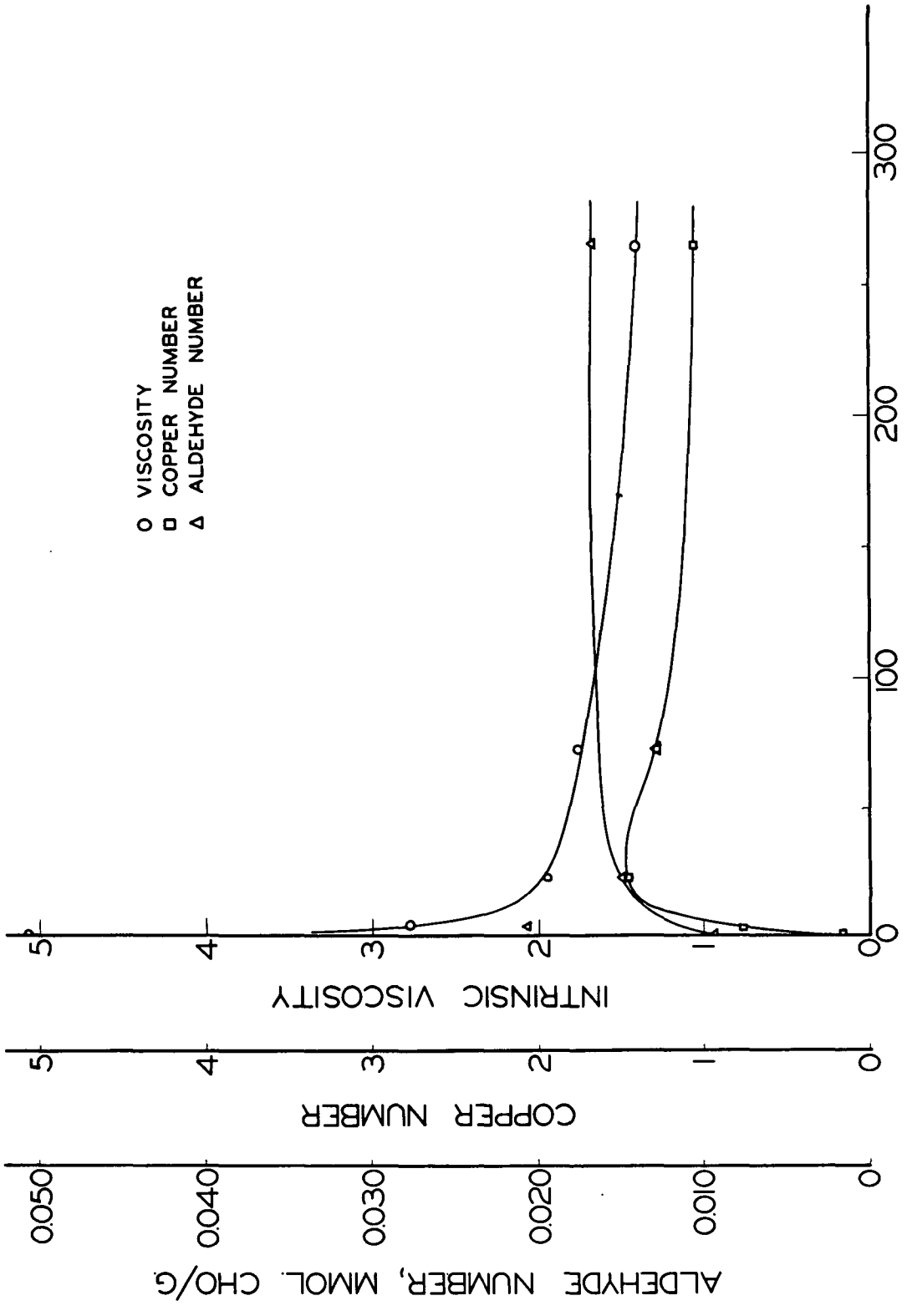

Figure 29

Degradation of Cotton Linters, Properties of Residues, 0.05 N HCl in n-Octanol at 30°C. (Study 0-1)

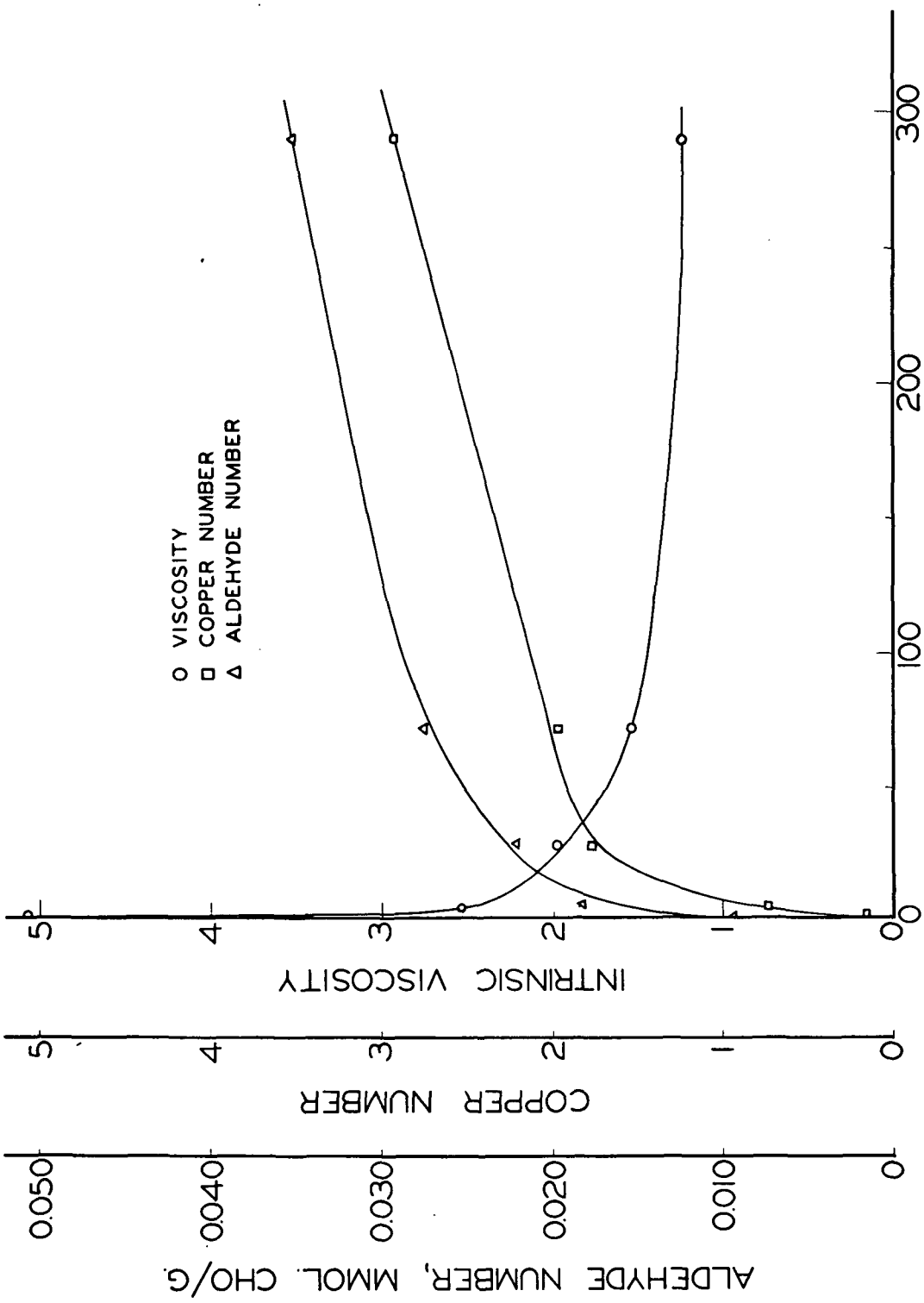

Figure 30

Degradation of Cotton Linters, Properties of Residues, 0.05 N HCl in Tetrahydrofuran at 30°C. (Study T-1)