Acid Decomposition of Highly Substituted Cellulose Xanthate

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Synopsis

The acid decomposition of cellulose xanthate was studied spectrophotometrically with a stopped-flow technique. The reactivity of the xanthate groups was found to decrease with an increase in the viscose γ number. This was explained by the occurrence of stabilizing interactions exerted between closely spaced xanthate groups. With uniformly substituted xanthates this effect began to be noticeable at γ numbers above 50. At higher γ numbers partial decomposition by acid resulted in an uneven distribution of xanthate groups along the chain molecules. Another feature of cellulose xanthate is that the degree of dissociation at constant acid concentration decreases with an increase in the γ number. This can be ascribed to variations in the dielectric constant inside the macromolecules.

INTRODUCTION

As was recently reported, a stopped-flow technique in combination with a spectrophotometric determination of xanthate can be used to study the rapid decomposition by acid of low molecular weight xanthates as well as of cellulose xanthate. This technique also made possible a determination of the dissociation equilibrium of the xanthic acids.[1,2]

With cellulose xanthate the decomposition and the dissociation behavior were much more complicated than with simple low molecular weight xanthates. This can largely be explained by the fact that cellulose xanthate is a polyelectrolyte and that the change in the composition of the macromolecules resulting from acidification and decomposition affected the properties of the medium surrounding the fixed xanthate groups. The decomposition behavior, however, could not be fully accounted for with samples of a high degree of substitution, indicating that other effects were also involved.[3]

Earlier studies were mainly confined to cellulose xanthate with γ numbers below 70 (the γ number is defined as 100 D.S.). In the present work xanthates with γ numbers up to and slightly higher than 150 have been included, and the results will be used to elucidate further the decomposition kinetics and the acid strength of cellulose xanthic acid.

EXPERIMENTAL

The kinetics of the decomposition were studied spectrophotometrically by using the stopped-flow technique referred to above. The decomposition

was followed by absorbance measurements at two wavelengths, carried out during successive, repetitive runs. The wavelengths used corresponded to the absorption maxima of undissociated (276 nm) and dissociated (303 nm) xanthate groups. From the recorded absorbance values determined at these wavelengths the total concentration of xanthate and the degree of dissociation of the xanthic acid during the reaction period were calculated. The molar absorptivity of the xanthic acid group in cellulose xanthate of γ number 150 was determined as 10,700 at 276 nm and as 1900 at 303 nm. These values were used for calculations in experiments with xanthate samples of initial γ number above 100. With other samples calculations were carried out by using the molar absorptivities previously tabulated. Those values which referred to the unripened viscose were used with samples of initial γ number between 100 and 60, and those which referred to the ripened viscose were used with samples of lower initial γ number.[2]

In some of the experiments the absorbance measurements were carried out on slightly turbid solutions. In such runs a correction was applied for the influence of scattering. The evaluation of this correction and also detailed descriptions of the apparatus and experimental techniques used have been published previously.[2]

In all experiments acid was present in a large excess over the xanthate, so that the hydrogen ion concentration was unaffected by the decomposition and was constant over the reaction period.

Cellulose Xanthate

The highly substituted cellulose xanthate used in most of the runs was prepared according to Geiger and Weiss.[4] Alkali cellulose was xanthated for 3 hr at 20–25°C with 500% CS_2 (calculated on cellulose). The xanthate was dissolved in 10% sodium hydroxide at 20°C for 1 hr, and the solution was kept at 2°C for 12 hr. The solution was then mixed (1:1) with 30% aqueous sodium hydroxide and emulsion-xanthated with 200% CS_2 for 12 hr at 20°C. The batch was divided into samples and stored at $-65°C$ to avoid dexanthation.[2,5]

The viscose obtained by this procedure contained considerable amounts of viscose byproducts and some unreacting carbon disulfide. In order to obtain pure solutions of cellulose xanthate, the viscose was diluted with water and filtered through a paper filter. This freed the solution from droplets of carbon disulfide. Viscose byproducts and dissolved carbon disulfide were then removed by passing the filtered solution through an ice-cooled column containing an anion exchange resin (Dowex 2-X8, OH⁻, 30–50 mesh). Ice-cooled deionized distilled water was used in all dilution steps.

THEORETICAL CONSIDERATIONS

According to Katchalsky et al., the electrostatic potential of a stretched polyion in a solution of given ionic strength is directly proportional to the

number of charged groups per unit length of the macromolecule.[6] If this applies to cellulose xanthic acid, the dissociation equilibrium should be represented by the following expression:[3]

$$pk_a = pH + \log (1 - \alpha)/\alpha = pK_0 + \lambda\alpha\gamma \qquad (1)$$

where k_a is the formal dissociation constant, K_0 an intrinsic dissociation constant characteristic of the ionizable group, and α the degree of dissociation. The factor λ is a proportionality constant, which relates the variation in pk_a caused by electrostatic interactions to the variation in the number of ionized xanthate groups per 100 anhydroglucose units, $\alpha\gamma$.

Decomposition of xanthates by acid most probably involves a bimolecular reaction between xanthate anions and hydrogen ions.[7,8] On the assumption that the significant hydrogen ion concentration is that prevailing in the region close to the xanthate groups and that all of the substituents in cellulose xanthate have the same reactivity, the following rate expression can be derived:[3]

$$d \log \gamma/dt = -0.4343kK_0 (1 - \alpha) \qquad (2)$$

where k is the second-order reaction-rate constant.

Equation (2) does not rely on any assumptions concerning the relation between the charge density and the polyion potential.   Electrostatic interactions are, instead, implicitly accounted for by using the xanthic acid group as an acid–base indicator in determining the local hydrogen ion concentration.

As shown in a previous paper, the value of pK_0 defined according to eq. (1) increased with an increase in the number density of undissociated xanthic acid groups along the macromolecular backbone, $(1 - \alpha)\gamma$.[3] This effect, referred to as the acidic group effect, was ascribed to a decrease in the effective dielectric constant with an increase in the local concentration of undissociated, rather nonpolar, acid groups, i.e., to a medium effect within the macromolecules.

A variation in the effective dielectric constant should also affect the second-order rate constant.   Since the decomposition and dissociation reactions both involve dissociated xanthate groups and hydrogen ions, it is reasonable to assume that a variation in the effective dielectric constant would affect both these reactions to the same extent.   This means that the product kK_0, which can be regarded as the first-order rate constant for the decomposition of the uncharged acid, can be assumed to be virtually independent of medium effects.   Previous results strongly support the validity of this assumption.   Thus, in several experiments with cellulose xanthate, in which K_0 varied considerably during the decomposition, the product kK_0 was found to be almost constant.[3] Similarly, with pentyl xanthate a change in the reaction medium causing large variations in the dissociation constant produced only small changes in kK_0.[9] Furthermore, in studying the decomposition of ethyl and n-propyl xanthates by acetic acid in aqueous dioxane King and his co-workers found that the second-order rate constant,

multiplied by relevant values for the acidity constant of acetic acid, was remarkably constant over a wide range of dioxane concentrations.[10,11] These results point out that the value of the product kK_0 calculated according to eq. (2) can be used as a measure of the reactivity of the xanthate groups in cellulose xanthate.

RESULTS AND DISCUSSION

Decomposition

In Figure 1 the curves denoted A and C represent the decomposition of cellulose xanthate from two unripened viscoses of different degrees of xanthation. At the acid concentration used the degree of dissociation was low during the decompositions and varied within the same range with both samples. The large difference in the specific rate of reaction $(d\gamma/\gamma dt)$ evident from Figure 1 corresponded to a large difference in the value of the product kK_0 [eq. (2)].

The xanthate samples A and C differed widely in the degree of substitution but contained almost equal relative amounts of primary and secondary xanthate groups. The difference in reactivity can therefore only be explained by the fact that the number of substituents and their locations along the macromolecules were different in the two samples. An influence of these factors upon the reactivity must be explained by the action of some kind of short-range intramolecular interactions between neighboring xanthate groups or between xanthate groups and hydroxyl groups.

At low γ numbers the xanthate groups in cellulose xanthate possess a reactivity quite similar to that of ethyl xanthate.[2] Hence, the comparatively high reactivity of sample C (Fig. 1) cannot be explained by a destabilization of the xanthate groups caused by interactions with hydroxyl groups. This statement does not exclude the possibility of interactions between hydroxyl groups and dissociated xanthate groups as proposed by Cichowski.[12] Within the acidity range studied in the present work, how-
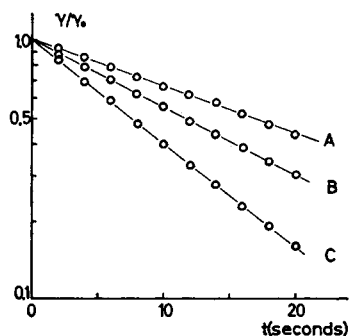

Fig. 1. Decomposition of cellulose xanthate from different viscoses in $0.5M$ HCl containing $0.5M$ NaCl at 25°C: (A) fresh viscose, $\gamma_0 = 155$; (B) viscose A partially decomposed by reaction in $0.1M$ HCl, $\gamma_0 = 82$; (C) fresh viscose, $\gamma_0 = 73$.

ever, this type of interaction is completely negliglible and need not be considered. It is very probable, therefore, that the interactions occurred between neighboring xanthate groups and that these resulted in a stabilization toward decomposition by acid. Since in alkaline media no influence of the degree of substitution upon the dexanthation kinetics has been observed,[13] it is likely that these interactions occur only in the presence of undissociated xanthic acid groups.

The presence of a stabilizing influence between neighboring substituents offered a simple explanation of the results given in Figure 1. Sample A contained very nearly two primary and one secondary xanthate group per two anhydroglucose units. All of the substituents in this sample were thus closely spaced and certainly much more so than in sample C. Accordingly, the low rate of dexanthation observed with sample A should be caused by a high frequency of close-neighbor interactions. These would prevent a random splitting off of the xanthate groups and promote the maintenance of a high proportion of short close-neighbor spacings. Thus, even after partial decomposition sample A would contain closely spaced xanthate groups, and this would explain the fact that the specific rate of dexanthation was constant despite the fact that the average γ number decreased to less than 50% of its initial value.

The extent to which the stabilization effect was maintained during decomposition by acid depends upon the electrolyte composition of the reaction mixture. This can be seen by comparing the specific rates of reaction of samples A and B in Figure 1. The xanthate sample denoted by B was obtained from sample A by partial decomposition in $0.1M$ hydrochloric acid. This fractional decomposition step was carried out in batch and was interrupted by neutralization. The neutral solution was then used in experiments with the stopped-flow technique, yielding the results reproduced in the diagram. As can be seen, in $0.5M$ hydrochloric acid sample B decomposed at a higher specific rate than the original sample A. Evidently, the stabilizing effect was decreased during decomposition in the weaker acid medium. This indicates that the originally very short close-neighbor distances in sample A were retained more effectively during decomposition at the higher acid concentration. The reaction mixtures compared differed both in acidity and total electrolyte concentration. Probably both factors contributed to the observed difference in the magnitude of the stabilizing effect: the acidity by changing the degree of dissociation, and the electrolyte concentration by virtue of a salting-out effect.

The effect upon the decomposition caused by varying the distance between the neighboring xanthate groups was studied in a series of experiments with xanthate samples having the substituents randomly spaced along the chain molecules. Xanthates ranging in γ number from about 150 to 50 were obtained by aging at room temperature (20–23°C) a stock solution prepared from purified, highly substituted viscose and air-free, deionized, distilled water. Aliquots of this stock solution were taken at certain times during the aging period, and the acid decomposition of the xanthate

was studied. The xanthate samples used in the individual experiments thus originated from the same stock solution and differed only in the extent of dexanthation that occurred during aging.

As shown in a previous investigation, primary and secondary xanthate groups split off at equal rates during decomposition by acid.[2] In the
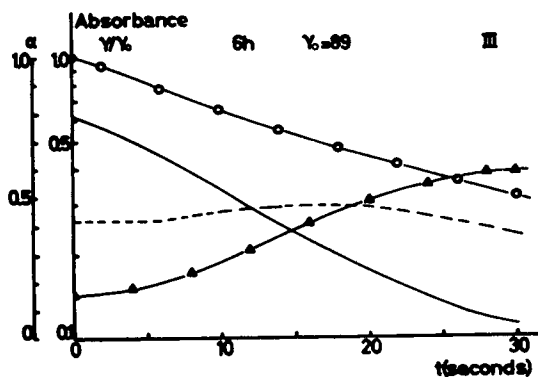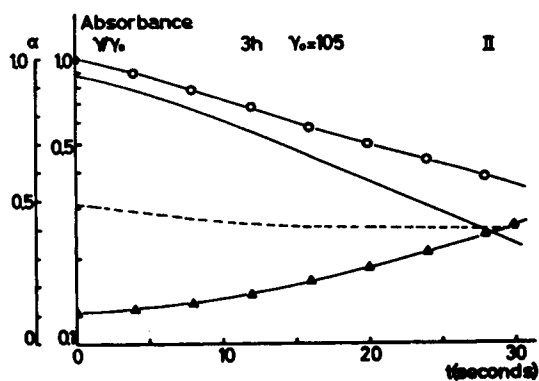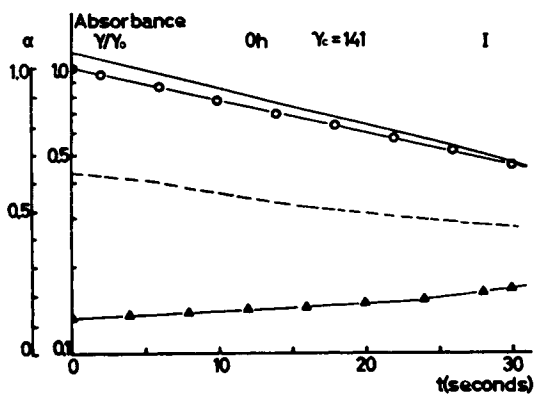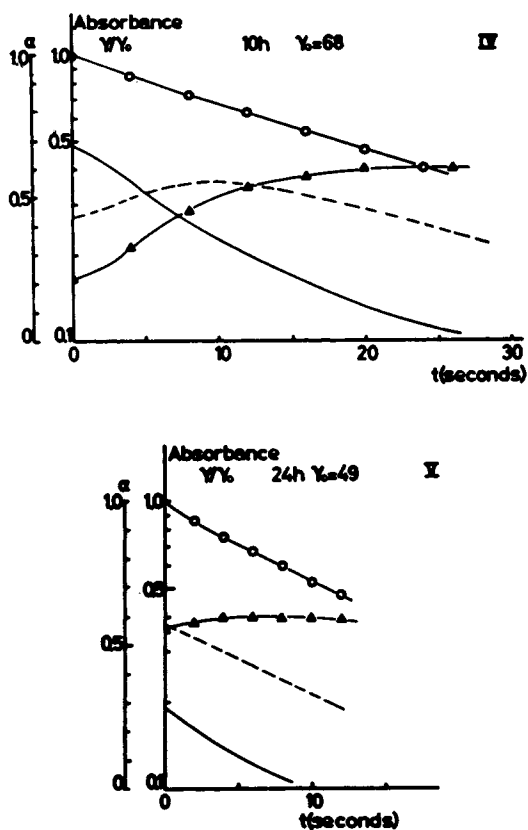
Fig. 2. Decomposition of unaged (I) and aged (II–V) cellulose xanthate from a highly substituted viscose in 0.05M HCl containing 0.05M NaCl (——) absorbance at 276 nm (reproduced recorder trace); (- - -) absorbance at 303 nm (reproduced recorder trace); (O) γ/γ_0; (△) α. Aging times and γ numbers given in the diagrams.

subsequent discussion, therefore, it is sufficient to consider the aging as a process by which the number of substituents along the chain molecules was lowered. According to Andersson and Samuelson, dexanthation in alkaline media is determined by the same kinetics, irrespective of the degree of substitution.[13] It can be concluded, therefore, that aging resulted in a random elimination of substituents from different locations along the macromolecules. In the original, highly substituted xanthate almost all of the anhydroglucose units (more than 90%) were substituted in the 6 position. This xanthate, and also all aged samples, can consequently be considered uniformly substituted along the macromolecules.

The results from the decomposition experiments are given in Figure 2. In the following discussion the xanthate samples used in the different runs will be identified by the Roman numerals given in the diagrams. It is evident from the reproduced recorder traces that dexanthation both by
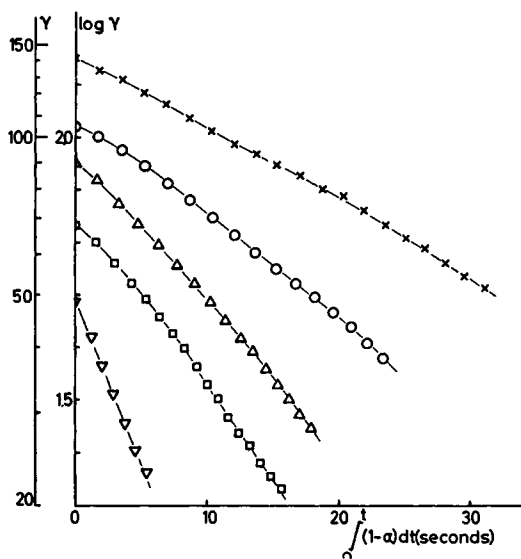
Fig. 3. Decomposition of unaged and aged cellulose xanthate (same experiments as in Fig. 2). Sample number: ($\times$) I; (O) II; ($\triangle$) III; ($\square$) IV; (∇) V.

aging and by acid decomposition strongly affected the behavior of the xanthate.

An analysis of the decomposition of the original (I) and aged (II–V) xanthate samples according to the kinetic model [eq. (2)] is given in Figure 3. If the kinetic model were obeyed, the decompositions in this type of diagram would be represented by straight lines with a common slope equal to $-0.4343kK_0$. This was obviously not the case. Except for sample V the decomposition curves were nonlinear. The curvature observed corresponded to an increase in kK_0 during the decomposition. This behavior is in agreement with previous results obtained with fresh viscoses having γ numbers in the range of about 60–70.[3]

Dexanthation by aging also resulted in an increase in slope, i.e. in the value of the product kK_0. As can be seen by comparing the slopes of the decomposition curves at equal γ numbers, this increase was considerably larger than that which occurred during decomposition by acid. These results show that partial dexanthation by acid and by aging yielded products with different reactivities. In view of the fact that in acid media different types of xanthate groups decompose at equal rates, only a difference in the localization of the substituents along the macromolecules could affect the kinetics of the acid decomposition. Since the original and aged samples were uniformly substituted along the macromolecules, it must be concluded that at least with samples I–IV the xanthate groups were split off in a nonrandom fashion during decomposition by acid. It is evident that this could occur only by stabilizing close-neighbor interactions. The same conclusion can be arrived at, without claiming equal reactivities of

primary and secondary xanthate groups, merely by confining the discussion to samples III–V, in which between 94–100% of the substituents were primary xanthate groups.

The results obtained with samples III and IV show that primary xanthate groups attached to adjacent anhydroglucose units are sufficient y closely spaced for close-neighbor interactions to occur. In an earlier investigation differences in reactivity were observed between cellulose xanthate from unripened and ripened viscoses with γ numbers of about 70 and 50, respectively.[3] In view of the present results these differences can be ascribed to the increase of the spacings between neighboring xanthate groups during ripening. With the ripened viscoses used in the earlier experiments no increase in the reactivity was observed during decomposition by acid. This and the linear decomposition curve observed with sample V (Fig. 3) strongly indicate that intramolecular interactions exert no stabilizing influence upon the decomposition of uniformly substituted xanthates of γ numbers below 50.

In several recent spinning processes the viscose is spun without ripening and at rather high γ numbers. The results point out that in these processes the stabilizing effect plays an important role in determining the rate at which cellulose is regenerated. In conventional viscose rayon processes, however, in which ripened viscoses of γ number below 50 are spun, a similar influence would not be operative.

The question of the nature of the close-neighbor interactions remains. In a previous paper it was shown that the decomposition of pentamethylene dixanthate in solutions of constant acidity was considerably retarded when its concentration was increased above a certain limit. This was ascribed to association of xanthic acid molecules. Under experimental conditions such that the solutions turned turbid the low reactivity was ascribed to an enrichment of xanthate molecules in agglomerates inaccessible to hydrogen ions.[9] A similar mechanism does not appear likely in the case of cellulose xanthate, in which the xanthate groups are fixed. In this case it may, instead, be assumed that neighboring xanthate groups become associated owing to the formation of intramolecular hydrogen bonds. As can be demonstrated with molecular models, this suggestion is consistent with steric requirements and the observation that primary xanthate groups attached to adjacent anhydroglucose units can exert a stabilizing influence upon one another. Granted the reaction mechanism proposed by Foss[14] and by Lewis,[15] which involves an attack by a proton on the oxygen atom of the ionized xanthate group, association of a charged (X^-) and an uncharged (HX) xanthate group, forming a type of structure ($-X-H\cdots X-)^-$, should stabilize the dissociated xanthate group and result in a decreased reactivity.

No experimental evidence of the formation of hydrogen bonds between xanthic acid molecules in water seems to have been reported. The presence of such bonds is not improbable, however, since in several other compounds the presence of both strong and weak $S-H\cdots S$ hydrogen

bonds has been established.[16]   It may be mentioned that dithioacetic acid
has been shown to be strongly associated in the liquid state.[17]   It may also
be mentioned that dimerization of bisulfite ions, in part caused by an S—H
···S hydrogen bond, even in relatively dilute aqueous solutions has been
suggested.[18]

In a cellulose xanthate molecule the local xanthate concentration can
reach rather high values.   If the molecule is assumed to occupy a cylinder
about 15 Å in diamter, the local xanthate concentration in a sample of γ
number 70 can be estimated as $1.25M$, which is about 60 times that of a
saturated aqueous solution of ethyl xanthic acid.   Although this simple
comparison between the local concentration of xanthate groups and the
solubility of a low molecular weight xanthic acid can be debated, it suggests
that there is, very likely, an intramolecular association between xanthate
groups in cellulose xanthate.

Dissociation Equilibrium

The plots in Figure 2 of the degree of dissociation showed that the disso-
ciation equilibrium of cellulose xanthic acid was displaced during decompo-
sition by acid (at constant acidity).   As can be seen by comparing the
diagrams, large changes in the acid properties of the xanthate were also
produced by aging.

In Figure 4 values for the formal acidity constant (pk_a), calculated from
the results given in Figure 2, have been plotted against the number density
of undissociated xanthic acid groups along the chain molecules.   It can be
calculated from Figure 2 that the charge density of the xanthate molecules
(proportional to $\alpha\gamma$) varied to a very limited extent during the decomposi-
tions and was of the same magnitude in all runs.   The overall variation in
$\alpha\gamma$ was from 12.3 to 26.6 which, according to previous estimates of the value
of the term $\lambda\alpha\gamma$ of eq. (1), would correspond to variations in pk_a of a magni-
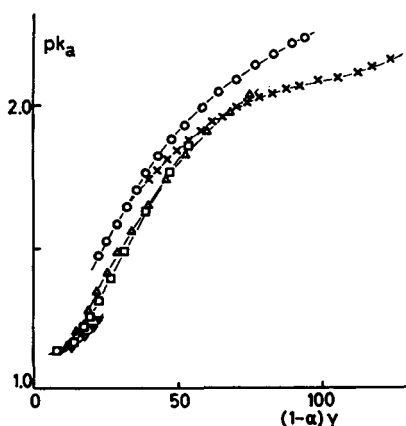

Fig. 4. Variation of pk_a with $(1 - \alpha)\gamma$ during acid decomposition of unaged and aged
cellulose xanthate (same experiments as in Fig. 2). Sample number: ($\times$) I; ($\bigcirc$) II;
($\triangle$) III; ($\square$) IV; (∇) V.

tude comparable to the experimental error.[3]   The contribution fron electrostatic effects to the variation in pk_a can accordingly be neglected, and the observed variations in pk_a can be ascribed to an influence of the acidic group effect, referred to in the theoretical section.   The dependence of pk_a on $(1 - \alpha)\gamma$ compares well with previous results obtained with xanthate samples of other origin (cf. Fig. 6, Törnell[3]).   This and the observation that the variation in pk_a was similar with all of the samples lent further support to the significance of this effect.

In Table I the pk_a values determined for the aged samples (II–V of Fig. 4) were compared at equal γ numbers with pk_a values determined after partial decomposition of sample I by acid.   This comparison showed that, except at the lowest γ number, the influence of the acidic group effect was practically independent of existing differences between the distribution of substituents along the molecules.   This suggested that the acidic group effect was caused by interactions of a long-range type, as compared with the stabilizing close-neighbor interactions discussed above.   In view of this the difference between the pk_a values determined at the lowest γ number must be ascribed to rather large differences in the local degree of substitution, which is in agreement with the results from the decomposition experiments.

As mentioned in the theoretical section, the acidic group effect can be ascribed to variations in the local dielectric constant inside the macromolecules.   Some observations of the light scattering of dilute solutions of cellulose xanthate lend support to this explanation.   In one experiment 100 ml of a purified solution of a highly substituted xanthate containing 0.06% cellulose was rapidly poured into 100 ml of a well-stirred $0.25M$ hydrochloric acid.   This resulted immediately in turbidity.   The turbid solution showed the typical bluish appearance characteristic of colloidal solutions containing scattering particles with diameters smaller than or comparable to the wavelength of natural light.   About 30 sec after acidification 30 ml of $1M$ sodium hydroxide were added.   The turbidity disappeared instantaneously, and the solution again became clear.

At the acid concentration prevailing in the turbid solution the main part of the xanthate groups was present in the undissociated free acid form.

TABLE I

Formal Dissociation Constant of Cellulose Xanthic Acid Obtained by Aging and Decomposition by Acid from a Highly Substituted Viscose of γ Number 141[a]

	pk_a	
γ number	Aging	Decompn. by acid
105	2.24	2.07
89	2.04	2.01
68	1.86	1.88
49	1.24	1.70

• Same experiments as in Figure 2.

Evidently, transformation of dissociated xanthate groups into uncharged xanthic acid groups brought about a change in the scattering properties of the xanthate molecules. According to the theory of light scattering, this can be explained by a change in the dielectric constant of the scattering particles.[19]

No similar effect was observed on acidification of a solution of CMC. These results show that the xanthic acid group is much less polar and, hence, less hydrated than the carboxylic acid group. The nonpolar character of the xanthic acid group, reflected also in the low solubility of low molecular weight xanthic acids in water, might be an important factor in determining the polymer–polymer interactions involved in viscose spinning. This would be true at least in the undoped spinning of highly substituted viscoses, in which the filaments become completely acidified before any considerable decomposition of the xanthate has occurred.[20] Under these conditions the fiber formation, besides the mechanical properties and swelling of the xanthic acid gel, would be determined to a large extent by the number and properties of the xanthic acid groups attached to the macromolecules. The nonpolar character of the xanthic acid groups explains, for example, why during spinning in a weak sulfuric acid bath filaments are formed more easily from highly substituted viscoses than from viscoses of a lower degree of substitution.[20]

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