# Formation and Decomposition of Zinc Cellulose Xanthate in Acid Media

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## Synopsis

Complex formation between zinc ($5 \times 10^{-2}$–$5 \times 10^{-4}M$) and cellulose xanthate and its effect upon the rate of dexanthation by $0.25M$ sulfuric acid were studied. The determinations were based on spectrophotometric measurements on dilute solutions of cellulose xanthate with $\gamma$-numbers from 140 to 30. The results showed that the tendency of the xanthate groups to enter into complexes with zinc increased as the $\gamma$-number decreased. The stabilization toward decomposition by acid produced by complex formation was also found to vary with the $\gamma$-number and was much smaller at low than at high $\gamma$-numbers. These findings indicate that cellulose xanthate, because of local differences in the steric arrangement of potential ligand groups along the molecule, can form a whole set of zinc complexes, differing in thermodynamic stability and reactivity toward acid.

## INTRODUCTION

The fact that zinc sulfate has a profound effect upon the fiber formation process during viscose spinning has been known since the introduction by Napper[1] in 1911 of Müller-type spinning baths containing zinc. The mechanisms by which zinc sulfate exerts its action are, however, still incompletely understood. This is due in part to the fact that zinc has an effect upon most of the concomitant physical and chemical processes that occur during viscose spinning, so that the effect of zinc becomes strongly dependent upon the spinning conditions. It is, however, also due to lack of basic knowledge about the equilibrium between zinc and cellulose xanthate and the kinetics of the acid decomposition of zinc cellulose xanthate.

Most previous studies concerned with the role of zinc in viscose spinning have been carried out by measurements on spinning filaments of various diameters.[2-9] As the overall spinning process is composed of interrelated physical and chemical processes, experiments of this type are not suited for the elucidation of an individual chemical step. The kinetics of the decomposition of zinc cellulose xanthate has been studied by Chikowski[10] using model filaments obtained by coagulation of viscose in saturated sodium sulfate and by Gröbe, Jost, and Klare[11] using model filaments as well as slurries of zinc cellulose xanthate. By spectrophotometric measurements on thin films, Phifer[12] demonstrated the presence of a complex between cellulose xanthate and zinc and followed the acid decomposition of

zinc cellulose xanthate. Even with this film technique, it is likely that the rate of the overall process is partly determined by the rate of diffusional processes.

In a previous paper, some results from a study of complex formation between zinc and cellulose xanthate using spectrophotometric measurements on dilute xanthate solutions were reported.[13] It was found that cellulose xanthate showed a strong tendency to enter into complexes with zinc. The results also indicated zinc to have an even greater stabilizing effect on the acid decomposition than that expected from the extent of complex formation. This previous study was rather preliminary, however, and the results did not permit a full discussion of the complex formation or the kinetics of the decomposition in the presence of zinc. In order to elucidate these questions further, the study was extended in the present work to cover a wide range of concentrations of zinc and xanthate samples with a wide range of γ-numbers (100 DS).

## EXPERIMENTAL

### Cellulose Xanthate

Cellulose xanthate with a high degree of substitution was prepared according to Geiger and Weiss.[14] The freshly prepared viscose was divided into samples, each of which provided sufficient viscose (5 to 10 g) for one experiment. The samples were stored in small plastic cups at −30°C. From the frozen samples, dilute solutions of cellulose xanthate, free from interfering viscose by-products, were prepared as previously described.[15] The γ-number of this viscose was 138. As determined according to Dolby, Dunbrant, and Samuelson,[16] 50% of the xanthate groups were primary. The γ-number of each cellulose xanthate sample was determined spectrophotometrically.[17]

Solutions of cellulose xanthate of lower γ-number were obtained from the highly substituted viscose by ripening or by partial decomposition by acid. Ripening was carried out at a cellulose concentration (0.06%) low enough to prevent rexanthation.[16,18] Immediately before use, the ripened solutions were purified by allowing them to pass through a column containing a strongly basic anion exchange resin in hydroxide form (Dowex 2-X 8, OH⁻).

Partial decomposition by acid was carried out by making a purified solution containing highly substituted cellulose xanthate 2.0$M$ with respect to hydrochloric acid. After a predetermined length of time, a solution of sodium hydroxide, sufficient to make the solution slightly alkaline, was suddenly added. The clear solution was diluted with water and used in the experiments without further treatment.

### Spectrophotometric Measurements

In zinc-containing acid media, the xanthate groups are present as three different species: undissociated free xanthic acid groups (HX), dissociated

xanthate groups (X), and complexed xanthate groups (ZnX). The relative amounts of these species were determined spectrophotometrically, using a Beckman DB-G spectrophotometer provided with a lin/log recorder (Beckman Model 105) and a stopped-flow apparatus, similar to that previously described.[19] The latter contained two motor-driven syringes by means of which a dilute solution of cellulose xanthate and an acid solution were simultaneously fed to a small mixing chamber connected to a flow cell (Hellma 176-QS). The capacity of the cell was 0.5 ml, which corresponded to a calculated mean residence time in the cell of 0.28 sec. The recorder traces obtained showed the absorbance of the reaction mixture under steady-state conditions in the flow cell, as well as the decrease in the absorbance during the decomposition (after the flow was stopped). The absorbance values were corrected for turbidity as previously described.[15] All measurements were carried out at 25°C.

The molar absorptivity of the complexed xanthate groups was determined using the extrapolation method previously described.[19] Since the absorption bands of dissociated and complexed xanthate groups almost coincide, these measurements had to be carried out in the presence of acid.[13]

It should be possible to determine the relative amounts of the three xanthate species (HX, X, and ZnX) from absorbance measurements at three wavelengths if the appropriate molar absorptivities were known. The molar absorptivities, however, are known to be slightly different for different samples of cellulose xanthate.[15,20] Because of this, and of the fact that the absorption bands of two of the species (X and ZnX) overlap, such a straightforward determination would be likely to give seriously erroneous results. In this work, therefore, the extent of complex formation was calculated from the spectral shift produced by substituting zinc for magnesium, under the assumption that the degree of dissociation, $[X]/([HX] + [X])$, was independent of the presence of complexed xanthate groups and that magnesium sulfate exerted only a normal salt effect.[10,13] All measruements were carried out in the presence of acid, that is, under conditions such that complex formation was accompanied by a large spectral shift.[13] The calculations were carried out by solving eq. (1), (2), and (3) for two sets of absorbance data, one obtained by measurement on zinc-free and the other on zinc-containing xanthate solutions of equal acidity, ionic strength, and $\gamma$-number:

$$A(276) = (1200\alpha_1 + 9600\alpha_2 + 2590\alpha_3)\, b[X]_T \tag{1}$$

$$A(303) = (15900\alpha_1 + 1200\alpha_2 + 11700\alpha_3)\, b[X]_T \tag{2}$$

$$1 = \alpha_1 + \alpha_2 + \alpha_3 \tag{3}$$

Where $A(\lambda)$ refers to the absorbance of the solution at the wavelength given within parenthesis; $\alpha_1$, $\alpha_2$, and $\alpha_3$ are the fractions of dissociated (X), free acidic (HX), and complexed (ZnX) xanthate groups, respectively; $b$ is the optical path length of the cell; and $[X]_T$ is the total concentration of xanthate groups. The coefficients are molar absorptivities for the dif-

ferent xanthate species as determined previously or in the present work.[15] From measurements in zinc-free media ($\alpha_3 = 0$), the degree of dissociation, $\alpha_1/(\alpha_1 + \alpha_2)$, was first calculated. This value was then used to calculate $\alpha_1$, $\alpha_2$, $\alpha_3$, and $[X]_T$ from absorbance data obtained by measurements in the presence of zinc. The numerical calculations were carried out on a UNI-VAC 1108 digital computer.

## RESULTS AND DISCUSSION

### The Molar Absorptivity of Complexed Xanthate Groups

Results from the determination of the molar absorptivity of xanthate groups complexed with zinc are shown in Figure 1. The underlying experiments were carried out in the presence of $5 \times 10^{-3}M$ sulfuric acid, using a sample of $\gamma$-number 51 obtained by ripening of the highly substituted cellulose xanthate. Except at the highest concentration of zinc ($1M$), the solutions contained zinc and magnesium sulfate in a total concentration of $0.5M$. From the ordinate intercepts, the molar absorptivities were calculated, assuming the molar absorptivity of the dissociated xanthate group
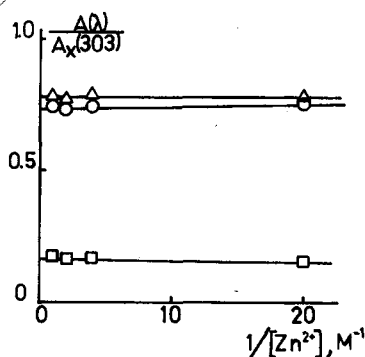


Fig. 1. The absorbance $A(\lambda)$ of weakly xanthate solutions containing zinc sulfate at (O) 303, (△) 298, and (□) 276 nm in relation to the absorbance at 303 nm of the corresponding alkaline xanthate solutions, $A_x(303)$.

(X) at 303 nm to be 15900 cm l./mole.[17] The values at 276 and 303 nm were introduced in eqs. (1) and (2). The molar absorptivity at the absorption maximum of the complexed groups (298 nm) was calculated to be 12300 cm l./mole. This and the other values are slightly lower than those obtained by Phifer[12] using a quite different method. Similar measurements carried out on other xanthate samples and at a higher concentration of sulfuric acid ($0.02M$), however, gave results in good agreement with those reproduced in Figure 1.

### Complex Formation with Cellulose Xanthate of Various $\gamma$-numbers

Complex formation with zinc was studied using cellulose xanthate samples of various $\gamma$-numbers. Most of the experiments were carried out using
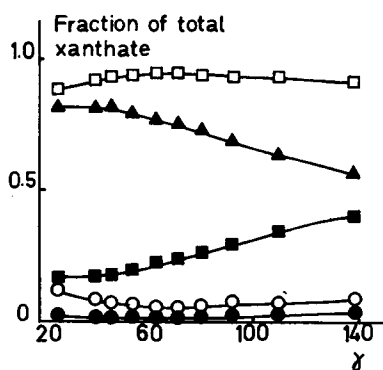
Fig. 2. Relative amounts of the different xanthate species (X, (O) (●); HX, (□) (■); ZnX, (▲)) in solutions of cellulose xanthates of various $\gamma$-numbers, containing $0.25M$ sulfuric acid and $0.05M$ magnesium sulfate (open symbols) or $0.05M$ zinc sulfate (filled symbols).

xanthate solutions containing $0.25M$ sulfuric acid and zinc and magnesium sulfate in a total concentration of $0.05M$. These conditions are similar to those used in some recent viscose spinning processes.[21]

As previously shown, addition of even a small amount of zinc sulfate to an acid solution of cellulose xanthate produced a large displacement of the absorption spectrum of the solution. This could be explained by complex formation between zinc ions and xanthate groups.[13] In the present work, this effect of adding zinc was found to be quite different with xanthate samples of varying $\gamma$-numbers. This can be illustrated by the following example. By exchange of $0.05M$ magnesium sulfate for $0.05M$ zinc sulfate, the absorbance ratio $A(303)/A(276)$ changed from 0.27 to 1.40 for a xanthate with $\gamma$-number 138, whereas the corresponding change was from 0.27 to 2.65 for a xanthate with $\gamma$-number 40. The ability of the xanthate groups to complex with zinc thus seems to increase with a decrease in the $\gamma$-number.

Figure 2 gives the relative amounts of the different xanthate species as determined in the presence and absence of zinc for a series of xanthate samples of various $\gamma$-numbers, obtained by ripening of a highly substituted xanthate. It is evident that the fraction of complexed xanthate groups, when compared at equal conditions, increased considerably as the $\gamma$-number decreased. Figure 2 also shows that at the concentration of acid used, the fraction of dissociated xanthate groups was low. The error eventually introduced in the calculations by assuming the degree of dissociation to be independent of the presence of complexed xanthate groups should accordingly be negligible.

As seen from Figure 3, the fraction of complexed xanthate groups was found to vary with the $\gamma$-number in the same manner at widely different concentrations of zinc and, hence, at different extents of complexation. The effect was thus not peculiar to a certain system and must consequently

TABLE I
Distribution of Xanthate Groups Between Primary ($\gamma_6$) and Secondary ($\gamma_{2,3}$)
Hydroxyl Groups During Ripening of a Highly Substituted Viscose at a
Cellulose Concentration of 0.06%

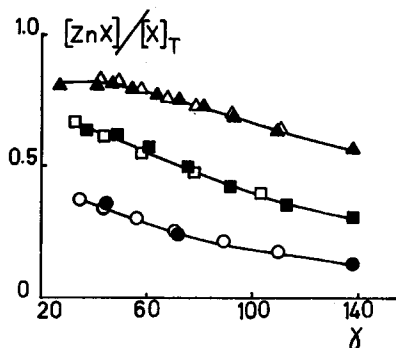| $\gamma_{tot}$ | 138 | 110 | 92 | 81 | 72 | 64 | 55 |
|---|---|---|---|---|---|---|---|
| $\gamma_6$ | 82 | 80 | 76 | 72 | 69 | 64 | 55 |
| $\gamma_{2,3}$ | 56 | 30 | 16 | 9 | 3 | 0 | 0 |



Fig. 3. Fraction of complexed xanthate groups at different concentrations of zinc in the presence of 0.25$M$ sulfuric acid as determined on ripened samples (filled symbols) or during decomposition by acid (open symbols): (O) (●) 5 × 10$^{-4}M$ ZnSO$_4$; (□) (■) 5 × 10$^{-3}M$ ZnSO$_4$; (△) (▲) 5 × 10$^{-2}M$ ZnSO$_4$.

be ascribed to a change in the inherent properties of the cellulose xanthate. Besides results from experiments with ripened cellulose xanthate, Figure 3 includes results from measurements carried out during decomposition by acid in the presence of zinc. From the results given, it is evident that the tendency of the xanthate groups to enter into complexes with zinc varied with the $\gamma$-number in the same manner irrespective of whether the $\gamma$-number was decreased by ripening or by decomposition by acid.

Under the ripening conditions used, the secondary xanthate groups were split off at a much higher rate than the primary xanthate groups.[18] This can be seen from the results given in Table I. Similar differences in the reactivity between different types of xanthate groups toward decomposition by acid do not seem to exist.[15] From this, and a comparison between the results given in Figure 3 and Table I, it is obvious that the observed effect cannot be ascribed to a difference in the complex formation ability of primary and secondary xanthate groups. It must be suggested, therefore, that it was the decrease in the density of xanthate groups along the macromolecular backbone per se, which was responsible for the observed increase in the fraction of complexed xanthate groups. Such a variation can be explained if it is assumed that a large set of complexes can be formed between a zinc ion and a xanthate group, and that these complexes may differ in stability because of differences in the steric arrangement of neighboring, potential ligand groups such as hydroxyl or xanthate groups. According

TABLE II

Fraction of Complexed Xanthate Groups in Samples of Cellulose Xanthate Obtained by
Partial Dexanthation by Ripening or by Decomposition with $2M$ HCl[a]

| | $[ZnX]/[X]_T$ | | | |
| | Ripened | | Decomposed by acid | |
| $\gamma$ | a | b | a | b |
|---|---|---|---|---|
| 138 | 0.56 | 0.30 | | |
| 72 | 0.75 | 0.52 | 0.70 | 0.46 |
| 30 | 0.81 | 0.65 | 0.77 | 0.55 |

[a] As determined in the presence of $0.25M$ sulfuric acid and (a) $0.05M$ ZnSO$_4$ or (b) $0.005M$ ZnSO$_4$.

to this explanation, the results suggest that the most stable complexes would be those in which the zinc ions can coordinate both a xanthate group and one or more hydroxyl groups.

According to results previously reported, ripening and partial decomposition by acid produce cellulose xanthates with their xanthate groups differently distributed along the molecules.[20]   In view of the explanation suggested, ripening and decomposition by acid would be expected to give xanthates with different complex formation properties. . As seen from Figure 3, however, significant differences of this type did not appear under the experimental conditions used.   Results from other experiments, in which the partial decomposition by acid was carried out at much higher acidity ($2M$ HCl), showed that the different distribution of the substituents along the molecules in ripened samples and in samples decomposed by acid had consequences for the complex formation ability of the xanthate groups. This can be seen from the results presented in Table II.   As will be evident from the discussion in the next section, the samples compared in Table II showed quite different decomposition behavior in the presence of zinc. The results obtained thus lend some support to the explanation offered. In this case, with the samples decomposed by acid, the measurements were carried out on solutions containing some chloride ions, and the activity of zinc, therefore, would be slightly lower than in the experiments with the ripened samples.   According to available stability constants[22] and the observed dependence of the fraction of complexed groups on the concentration of zinc, the effect of complex formation between zinc and chloride should be too small to obviate the significance of the observed effect.

## Kinetics

Figure 4 shows the effect of increasing amounts of zinc upon the rate of decomposition in solutions containing $0.25M$ sulfuric acid.   The fraction of complexed xanthate groups, as well as the retarding effect of zinc observed in the experiment at $0.005M$ zinc sulfate, are in excellent agreement with previous results from experiments with a freshly prepared viscose of about the same $\gamma$-number (see Table II, ref. 13).
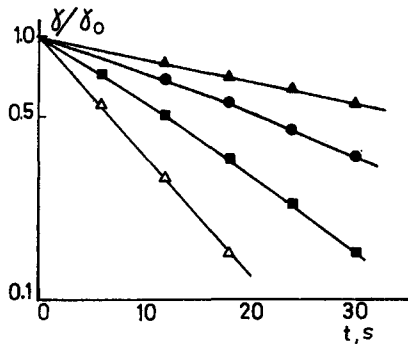
Fig. 4. Decomposition of a sample of ripened cellulose xanthate ($\gamma_0 = 72$) in $0.25M$ sulfuric acid free from zinc ($\triangle$) or containing $5 \times 10^{-4}M$ ($\blacksquare$), $5 \times 10^{-3}M$ ($\bullet$), or $5 \times 10^{-2}M$ ($\blacktriangle$) $ZnSO_4$.
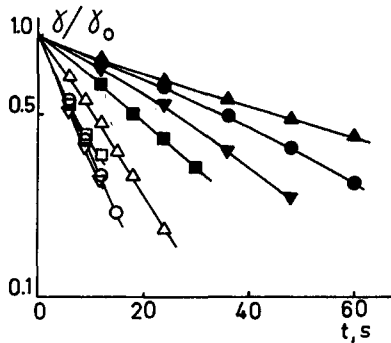


Fig. 5. Decomposition of freshly prepared ($\gamma_0 = 138$) and ripened samples of cellulose xanthate in $0.25M$ sulfuric acid free from (open symbols) or containing $0.05M$ zinc sulfate (filled symbols): ($\triangle$) ($\blacktriangle$) $\gamma_0 = 138$; ($\bigcirc$) ($\bullet$) $\gamma_0 = 72$; ($\triangledown$) ($\blacktriangledown$) $\gamma_0 = 47$; ($\square$) ($\blacksquare$) $\gamma_0 = 27$.

In the presence of zinc, the course of the decomposition differed from that of a first-order reaction. This can be seen from the increase in slope (negative) with time of reaction shown by the pertinent curves in Figure 4. Similar results were described in a previous paper, in which it was suggested that the deviation from a first-order reaction was due to a decrease in the fraction of complexed groups, as the local concentration of xanthate groups decreased during the decomposition.[13] As seen in Figure 3, however, the fraction of complexed xanthate groups increased rather than decreased during the decomposition. The explanation previously offered, therefore, cannot be correct.

In order to further elucidate the influence of zinc upon the decomposition kinetics, the retarding effect of certain amounts of zinc was studied in experiments with samples of varying $\gamma$-number. Examples of results from this type of experiment are shown in Figure 5. Although the rate of decomposition in the absence of zinc was different with the different samples, an examination of the results will clearly show that zinc exerted a more
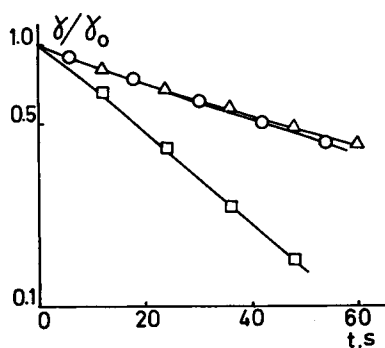
Fig. 6. Decomposition of cellulose xanthates in $0.25M$ sulfuric acid containing $0.05M$ zinc sulfate: ($\triangle$) freshly prepared xanthate, $\gamma_0 = 138$; (O) freshly prepared xanthate, partially decomposed by acid, $\gamma_0 = 30$; ($\square$) freshly prepared xanthate, partially decomposed by ripening, $\gamma_0 = 27$.

pronounced retarding effect with samples of high $\gamma$-number, i.e., with samples having a lower content of complexed xanthate groups. Evidently, the tendency of the xanthate groups to enter into complexes with zinc and the stability of the complexes formed toward decomposition by acid varied in opposite directions with a variation in the $\gamma$-number.

Except at the highest $\gamma$-number, the samples used in the experiments to which Figure 5 refers contained almost exclusively primary xanthate groups. The variation of the stability of the complexed xanthate groups with the decrease in the $\gamma$-number during ripening can thus not be ascribed to the concomitant increase in the relative amount of primary xanthate groups (cf. Table I).

Results suggesting that the distribution of the substituents along the macromolecular backbone is an important factor in determining the extent of stabilization produced by complexation with zinc are shown in Figure 6. These results show that in the presence of zinc, a sample with a $\gamma$-number of about 30 decomposed at a much lower rate if it was prepared from a highly substituted xanthate by partial decomposition by acid than if prepared by ripening. Evidently, in the complexed form, randomly distributed xanthate groups, such as those obtained by ripening of a highly substituted xanthate at low cellulose concentration, have a higher reactivity than nonrandomly distributed xanthate groups such as those obtained by acid decomposition.[20]

As ripening of a technical viscose results in both a decrease in the $\gamma$-number and a redistribution of the xanthate groups along the molecules, zinc would be expected to exert a stronger inhibitory effect during spinning of a freshly prepared viscose than of a ripened viscose. Previous results from spinning experiments in the presence and absence of a small amount of zinc are in agreement with this expectation.[13]

It is noteworthy that the large difference in reactivity shown by the two samples with $\gamma$-numbers of about 30 (Fig. 6) was not accompanied by a cor-
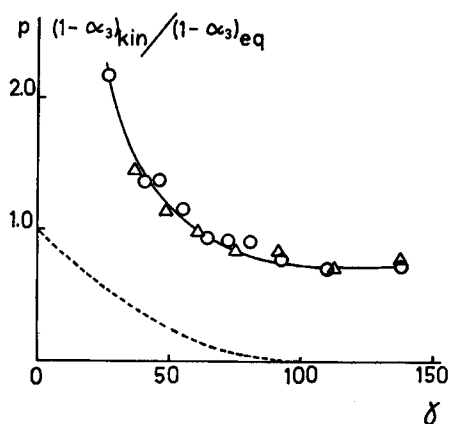
Fig. 7. Values of $(1 - \alpha_3)_{kin}/(1 - \alpha_3)_{eq}$ for cellulose xanthates of various $\gamma$-numbers in solutions containing 0.25 $M$ sulfuric acid and 0.05 $M$ zinc sulfate (O) or 0.005$M$ zinc sulfate ($\triangle$), and the fraction of substituted glucose residues, p(- - -), which have an un-substituted neighbor.

responding difference in the extent of complexation. As shown in Table II, at the beginning of the reaction period, the ripened sample had 81% of its xanthate groups present as complexed groups, which can be compared with 77% for the other sample and 56% for the original, highly substituted xanthate. Obviously, the influence of zinc upon the kinetics of the dexanthation process is fairly complicated and is determined by factors other than those determining the extent of complexation.

It seems to have been common practice to assume that the rate of dexanthation decreases in proportion to the extent of complex formation.[7,13,23] The present results indicate this approach to be unreliable. It may be convenient, however, to discuss the inhibitory effect of zinc in terms of a kinetically apparent extent of complex formation. If, for this purpose, it is assumed that the complexed xanthate groups are stable toward decomposition by acid, the ratio between the rate of decomposition in the presence of zinc to that in the absence of zinc should give the fraction of xanthate groups not engaged in complex formation with zinc. It should thus be possible to write

$$[(d\gamma/dt)_{Zn}/(d\gamma/dt)_{Mg}]_{\gamma} = (1 - \alpha_3)_{kin} \qquad (4)$$

where the subscript $\gamma$ indicates that the reaction rates are measured at equal $\gamma$-numbers.

Values calculated according to eq. (4), using initial rates of reaction determined in experiments with ripened samples, are compared in Figure 7 with corresponding values designated $(1 - \alpha_3)_{eq}$, calculated from the spectra of the reaction mixtures according to eqs. (1)–(3). Results from measurements at two different concentrations of zinc, $5 \times 10^{-2}$ and $5 \times 10^{-3}M$, have been included in the diagram. The results obtained at a still

lower concentration of zinc ($5 \times 10^{-4}M$), where the stabilization was comparatively low, showed the same general appearance, though with more scatter.

It is evident from Figure 7 that the ratio $(1 - \alpha_3)_{kin}/(1 - \alpha_3)_{eq}$ deviates from unity, which implies that a determination of the fraction of complexed xanthate groups from a comparison of reaction rates would give erroneous results in most instances. At low $\gamma$-numbers, even a fairly high extent of complex formation could be completely overlooked, whereas at high $\gamma$-numbers the kinetic approach would result in an overestimate of the fraction of complexed groups. The present results might thus offer an explanation for some of the contradictory conclusions arrived at in previous investigations on the role of zinc in viscose spinning.

The observation that $(1 - \alpha_3)_{kin}/(1 - \alpha_3)_{eq}$ was considerably larger than unity at low $\gamma$-numbers would mean that zinc could be expected to influence the fine structure of viscose rayon filaments spun in the presence of zinc, even in those cases in which a retardation in the rate of dexanthation could not be observed. An obvious mechanism by which this influence can be exerted is by way of complex formation with xanthate groups on different molecules.[24-26]

At high $\gamma$-numbers, the ratio $(1 - \alpha_3)_{kin}/(1 - \alpha_3)_{eq}$ was found to be smaller than unity (Fig. 7). This would mean that the complexed groups were completely stable and, furthermore, exerted a stabilizing influence upon neighboring uncomplexed xanthate groups. This conclusion is in agreement with results from preliminary measurements reported in a previous paper.[13] It also offers a partial explanation for the observation that zinc exerted a stabilizing effect during spinning which, according to the kinetic approach and the observed contents of zinc in the spinning filaments, corresponding to an apparent coordination of more than four xanthate groups per zinc ion.[13]

As discussed in connection with Figure 6, the variation of $(1 - \alpha_3)_{kin}/(1 - \alpha_3)_{eq}$ with the $\gamma$-number must be connected in some way or the other with the distribution of the substituent along the molecules. In Figure 7, a curve has been included which gives the fraction $p$ of randomly distributed primary xanthate groups positioned at anhydroglucose units having at least one unsubstituted neighboring anhydroglucose unit. At $\gamma$-numbers below about 70, this curve would apply fairly well to the ripened samples used in the actual experiments. As can be seen, this curve and the curve representing $(1 - \alpha_3)_{kin}/(1 - \alpha_3)_{eq}$ have similar shapes, indicating that the presence of neighboring unsubstituted anhydroglucose units increases the reactivity of the complexed groups, while, at the same time, it increases the tendency of the xanthate groups to enter into complexes with zinc (cf. Fig. 3).

It seems to be more plausible to assume that hydroxyl groups on neighboring anhydroglucose units have a destabilizing effect upon the complexed xanthate groups than to assume a pronounced stabilizing effect of complexed groups on neighboring xanthate groups. However, the results

do not permit an elucidation of the mechanism by which neighboring unsubstituted anhydroglucose units exert their action.

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