

## Use of Thin Films in Ultraviolet Studies of Cellulose Xanthate\*

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### Synopsis

A procedure for the study of the chemistry of viscose based on ultraviolet measurements of a film of cellulose xanthate has been developed. To illustrate the range of usefulness of the technique, spectra of various compounds formed with cellulose xanthate, including metal salts, organic derivatives, and an acid form, the influence of solvation on several cellulose xanthate compounds, and formation and decomposition curve of cellulose xanthate derivatives are presented. Possible applications of the technique include a study of the acid decomposition of cellulose xanthate, the influence of additives, new derivatives, and the xanthation mechanism. It is also probable that the method can be used in the study of other systems where fast reaction mechanisms are involved and suitable absorption characteristics are present.

### INTRODUCTION

Although the spinning of viscose (a sodium hydroxide solution of sodium cellulose xanthate) into rayon and cellophane is well founded scientifically as far as the qualitative aspects are concerned, there has been little quantitative work done on the chemical reactions taking place in the spinning process. Cellulose xanthate does not readily lend itself to study because of the speed of its reactions, difficulties encountered as a result of production of complex insoluble mixtures when almost any reaction occurs, and complications from diffusion processes. Previous studies have as a result been concentrated on model compounds and, to a limited degree, on very dilute solutions of cellulose xanthate.

The value of model compound studies to an understanding of the cellulose xanthate system can only be verified by direct studies of cellulose xanthate and viscose. Past studies have indicated that such factors as degree of substitution, degree of polymerization, cellulose xanthate concentration, etc., have an effect on the nature of reactions of cellulose xanthate.<sup>1,2</sup>

Dilute cellulose xanthate studies are limited by detection methods to those which do not produce an appreciable amount of insoluble material, a situation which does not exist very often, and to those which proceed at a relatively slow rate.

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Sodium cellulose xanthate has an absorption maximum in the ultraviolet spectral region of  $303\text{ m}\mu$  with an extinction coefficient of 15,900.<sup>3</sup> The extremely high extinction coefficient permits spectral measurements to be made on very dilute solutions or a very short light path. The latter was accomplished by casting a thin film of a cellulose xanthate solution on a quartz optical flat. The thickness of the film can be calculated assuming the Beer-Lambert law is valid and that the concentration of the xanthate solution is known. On most conventional recording spectrophotometers the maximum measurable absorbance is in the order of 2.0, which corresponds to a film thickness in the order of  $1\text{--}2\ \mu$  for a normally substituted spinning age viscose. This report is a description of the development of this technique into a practical method for studying the chemistry of viscose.

## EXPERIMENTAL

### Initial Experiments

In the experiments run while exploring the possibilities of adapting the idea to practice, spinning bath (aqueous  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ ) was placed in both cells of the standard cell holder of a Beckman DK spectrophotometer. A thin film of normal viscose was spread on a small rectangular piece of an optical flat which was slid down the front face of the quartz cell in the sample light path.

These initial experiments revealed several facts.

(1) The film was so thin that diffusion of the gases produced in the reaction was sufficiently rapid to eliminate clouding of the film. Thus no background was obtained from this source. It was necessary to cover a larger area of the plate than just that portion in the light path since bath would diffuse slowly between the plate and the film, producing clouding.

(2) Ion exchanging of the viscose<sup>3</sup> to remove the interference due to by-product sulfur compounds was generally desirable.

(3) The absorbance disappeared very rapidly at first (faster than the response time of the instrument) and then more slowly, taking several minutes at room temperature to disappear completely.

(4) When the bath also contained zinc sulfate, the initial rapid drop in absorbance was less than that obtained in zinc-free baths, and a longer time elapsed before the absorbance totally disappeared.

### Development of the Method

Due to the time involved in performing the operation of sliding the plate in and replacing the cover of the instrument, and the difficulty of ascertaining the initial absorbance of the film, a modification of the equipment was necessary. A small hole was drilled in the top of the sample compartment suitable for the introduction of a hypodermic syringe needle. It was lined up in such a way that the needle would extend to the bottom of the sample cell in a corner outside of the normal light path. Arrange-

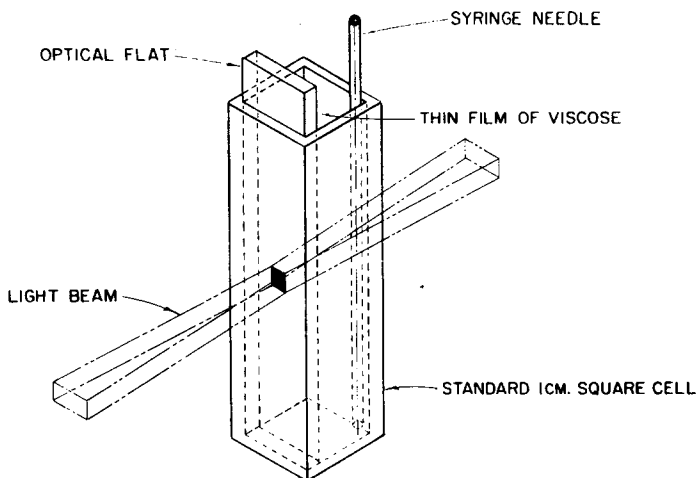


Fig. 1. Schematic drawing of the cell and optical flat arrangement.

ments were also made for maintaining a constant temperature. Figure 1 shows a schematic drawing of the spectrophotometer cell and optical flat.

In practice, a thin film of ion exchanged viscose was cast on an optical flat and slid down the front face of a cell. After making suitable corrections for the baseline, the absorbance could be determined at  $303\text{ m}\mu$ . When the solution to be reacted with the xanthate is injected in the cell, no change in the absorbance occurs until the solution rising in the cell crosses the light path. With practice, an injection can be made without excessive turbulence at a rate which crosses an approximately 1 mm. light path height in the order of 0.02 sec. The meniscus will have the effect of producing a very high absorbance but, since it is in the light path for only a very short time interval, the recorder will show only a slight response to this.

After the injection of the reacting solution, two possibilities exist: either the absorbance at one wavelength can be followed or repetitive scans of the spectrum can be run. If a rapid change is occurring in the spectrum, such as decomposition, the spectra tend to be skewed toward the direction of the scan. If the maximum of the spectrum is to be determined, this must be corrected for.

### Casting of the Film

Optical flats, 1 mm. thick, cut so that they will just slide into a conventional 1 cm. quartz absorption cell, have been found to be very satisfactory for introducing the viscose sample. A drop of viscose is placed on the plate and spread with a glass stirring rod. With practice, an operator can cast a film of a desired thickness. To prevent diffusion between the plate and viscose film, the film should extend to the edges of the plate and above the final liquid level. Care must be used to avoid an excess on the upper end of the plate since this will result in flow downward and a chang-

ing in the absorbance of that portion in the light path. Efforts to design an automatic film caster have thus far been unsuccessful.

### Reaction Techniques

The study of the reaction of cellulose xanthate with various reactants can be carried on in several different ways.

(1) Aqueous or nonaqueous solutions of possible reacting materials are placed in both reference and sample cells with an optical flat with the xanthate film in the sample cell and a blank optical flat in the reference. This is applicable where the solvent and reactant do not have high ultraviolet absorption.

(2) Where high ultraviolet absorption is a problem, the reaction can be performed externally on the film and excess reactant removed by washing before placing the sample in the cell. From a practical standpoint, this technique can be used only to prove the existence of a derivative and has little value for mechanism studies.

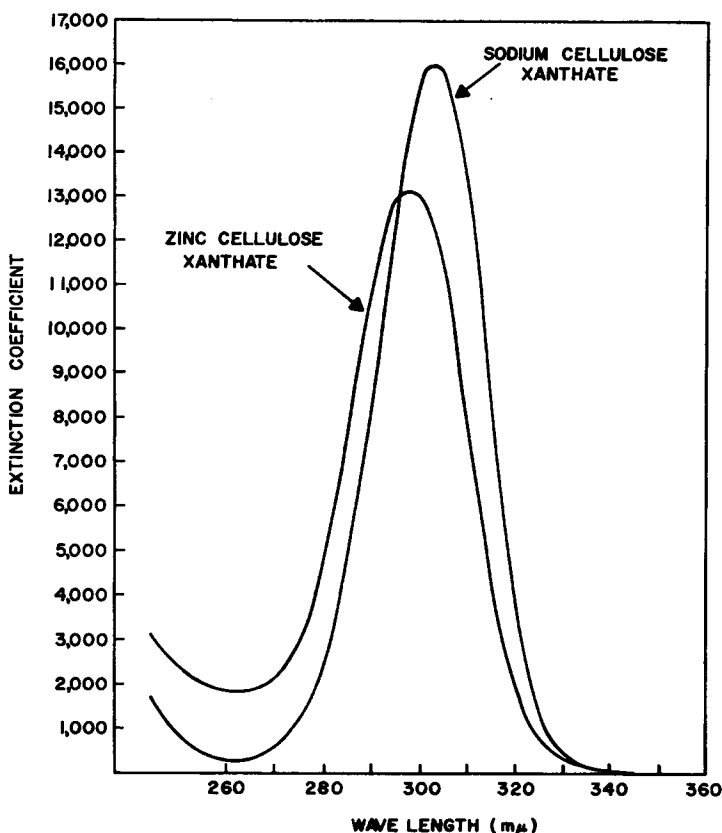


Fig. 2. Ultraviolet spectra of sodium and zinc cellulose xanthate. The absorption maxima are at 303 and 298 mμ, respectively.

(3) In the gas-phase reaction, the film is exposed to the vapor of a possible reacting material either in the absorption cell or externally.

### Diffusion Characteristics

Diffusion apparently occurs at a rate very much greater than can be observed when the film technique is used. This is based on the following observations.

(1) A calculation of the total molecular thickness indicates that a film  $2.0 \mu$  thick is in the order of 200 cellulose molecular thicknesses.

(2) When the xanthate ion is converted into another species with a spectrum different from that of the xanthate ion by an ionic reaction which is obviously fast, such as reaction with acid, the loss of absorbance at  $303 \text{ m}\mu$  and the increase of absorbance at the different wavelength is equal to the response time of the recorder. Experiments with a very fast recorder have indicated that the time required for diffusion and reaction is less than the time for the solution to cross the light path.

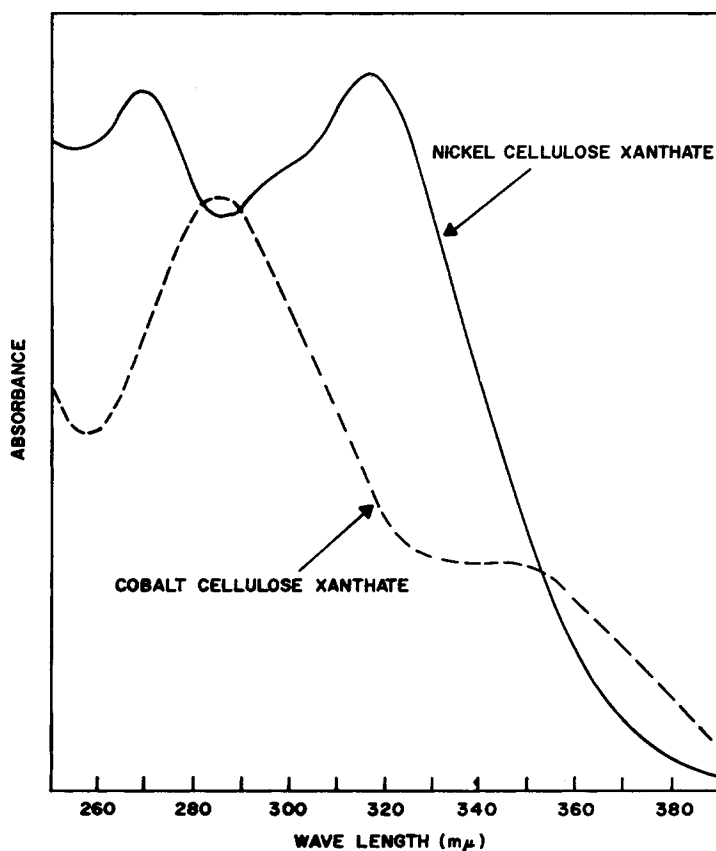


Fig. 3. Ultraviolet spectra of nickel and cobalt cellulose xanthate.

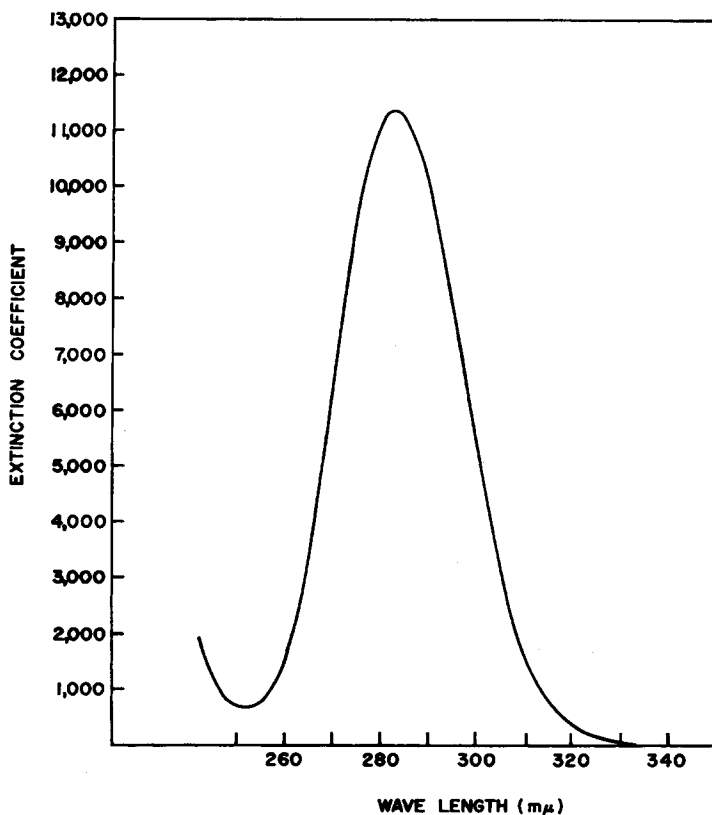


Fig. 4. Ultraviolet spectrum of *S*-methyl cellulose xanthate. The absorption maximum is at 280 mμ.

(3) If diffusion were slow, results would be expected to vary with film thickness. No demonstrable difference has ever been observed as a result of using films whose absorption at 303 mμ is varied from 0.2 to 2.0.

Heat production due to reaction was of some concern due to the fact that certain of the studies involved neutralization of approximately 8% sodium hydroxide in the viscose film with acid. To prove that it was so rapidly dissipated that it did not interfere in kinetics studies, results were compared between acid treatment of a normal viscose film and one which had been previously washed with 25% sodium sulfate to remove the alkali. No difference was observed between the two systems.

For purposes of making calculations, it is recognized that the film may change in thickness from shrinkage (or swelling) but, because of adherence to the rigid quartz plate, it is assumed that no change occurs in lateral directions. Any change of absorbance, therefore, is attributable to reactions of absorbing chromophores in the light path. The concentration of the reacting solution is taken to be the same in the film volume as it is in the remainder of the cell. Any consumption of the reacting solution is

assumed to be immediately replenished from the major bulk of the solution through rapid diffusion. No change in the concentration of the reacting solution is apparent, since so little xanthate is present compared to the amount of reactants. This set of conditions implies that pseudo first-order kinetics would be observed, and, therefore, changes in film thickness during the course of the reaction would not affect the kinetic analysis.

## APPLICATIONS OF THE TECHNIQUE

### Xanthate Spectra and Extinction Coefficients

It is known<sup>4</sup> that when derivatives of model compound xanthates are formed shifts in the ultraviolet absorption spectra take place. The film technique allows similar observations on polymeric or insoluble xanthates. If the xanthate ion can be converted into a new species with no decomposition, no change in the total number of absorbing species occurs but only a change in the absorbing characteristics. Thus, the extinction coefficient

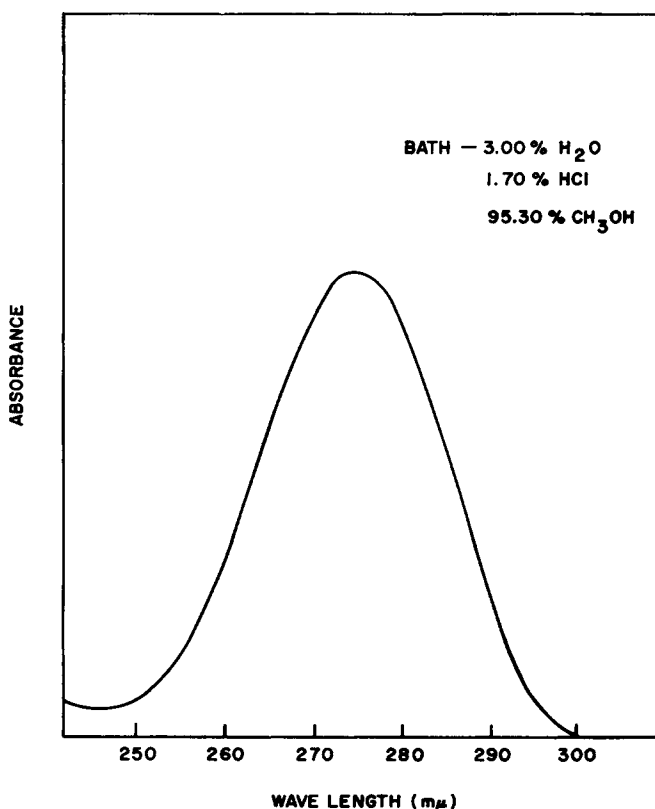


Fig. 5. Ultraviolet spectrum of cellulose xanthic acid prepared from exposing a sodium cellulose xanthate film to a solution containing 1.70% HCl, 3.00% H<sub>2</sub>O, and 95.30% methanol. The maximum is at 273.9 mμ.

can be calculated by comparing the ratios of the new absorbance to the original absorbance of the sample.

Figure 2 contains the spectrum of sodium cellulose xanthate from viscose after ion exchange to remove the by-product sulfur compounds and the spectrum of zinc cellulose xanthate prepared by treating this film with 10% zinc sulfate. There is no evidence of decomposition during the course of this reaction since the original amount of xanthate ion absorbance is obtained again if the film is treated with 1.0 *N*NaOH solution. The shift to

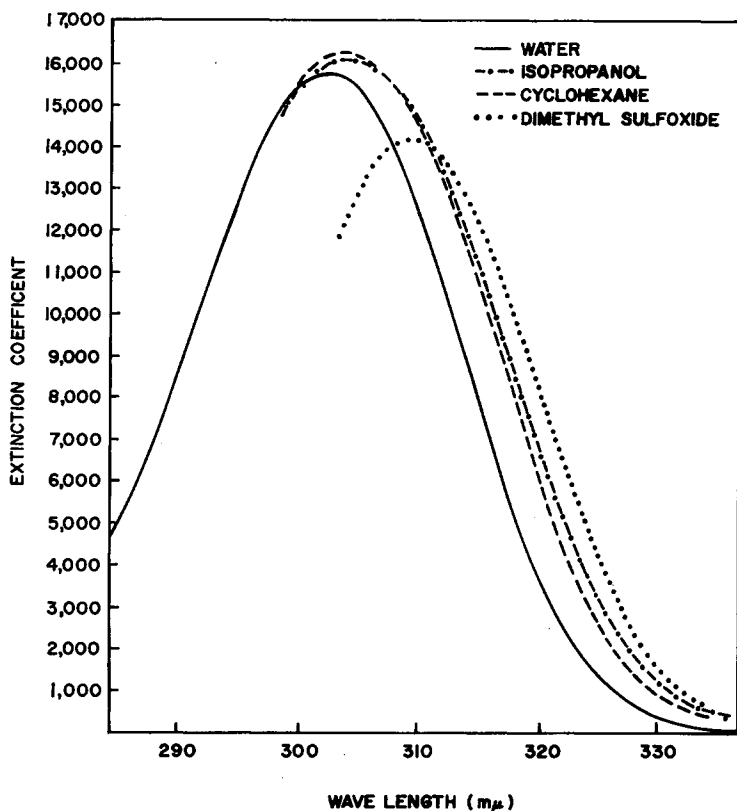


Fig. 6. Influence of water, isopropanol, cyclohexane, and dimethyl sulfoxide on the ultraviolet absorption of sodium cellulose xanthate.

a lower wavelength maximum and lower extinction coefficient is apparently due to the formation of a weak bond between the xanthate and zinc ion.

It has been presumed that cobalt and nickel ions form compounds similar to the zinc compound, but ample evidence to prove that the character of the compounds is different is given in Figure 3.

Figure 4 is the spectrum of the methyl derivative of cellulose xanthate. This spectrum is virtually identical with that of other similar derivatives, such as *S*-methyl ethyl xanthate, etc.<sup>4</sup>



The aqueous cellulose xanthic acid has an absorption maximum at 273  $m\mu$  as shown in Figure 5 and compares with the spectrum of ethyl xanthic acid.<sup>4</sup>

### Solvation Effect

A relatively little known effect which can easily be studied by the film technique is the influence of solvation on the position of the absorption maximum of an insoluble system. Figure 6 gives the spectrum of sodium cellulose xanthate in contact with water, isopropyl alcohol, cyclohexane, and dimethylsulfoxide. The shift of the spectrum in the alcohol or cyclohexane would appear to indicate that the xanthate ion is normally associated with water in aqueous solution. The drastic shift in dimethyl sulfoxide implies that a totally different type of solvation occurs in this system.

The effect of water and cyclohexane on zinc cellulose xanthate is shown in Figure 7. The very slight shift toward longer wavelengths when water is present would indicate only slight solvation of the xanthate group in aqueous zinc cellulose xanthate. This compound may be regarded as only slightly ionized and what solvation occurs is associated with the ionized portion.

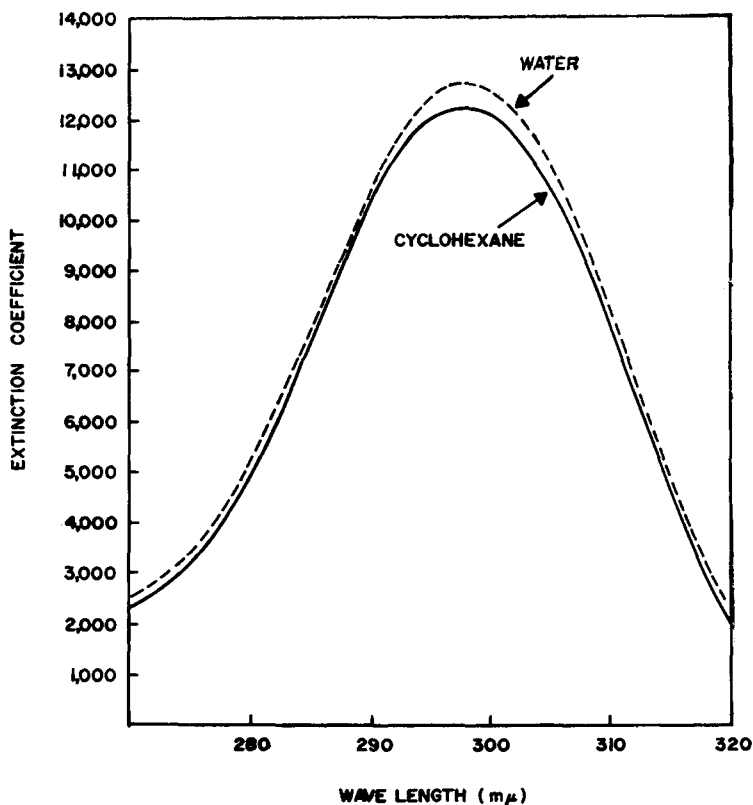


Fig. 7. Influence of cyclohexane on the ultraviolet absorption of zinc cellulose xanthate.

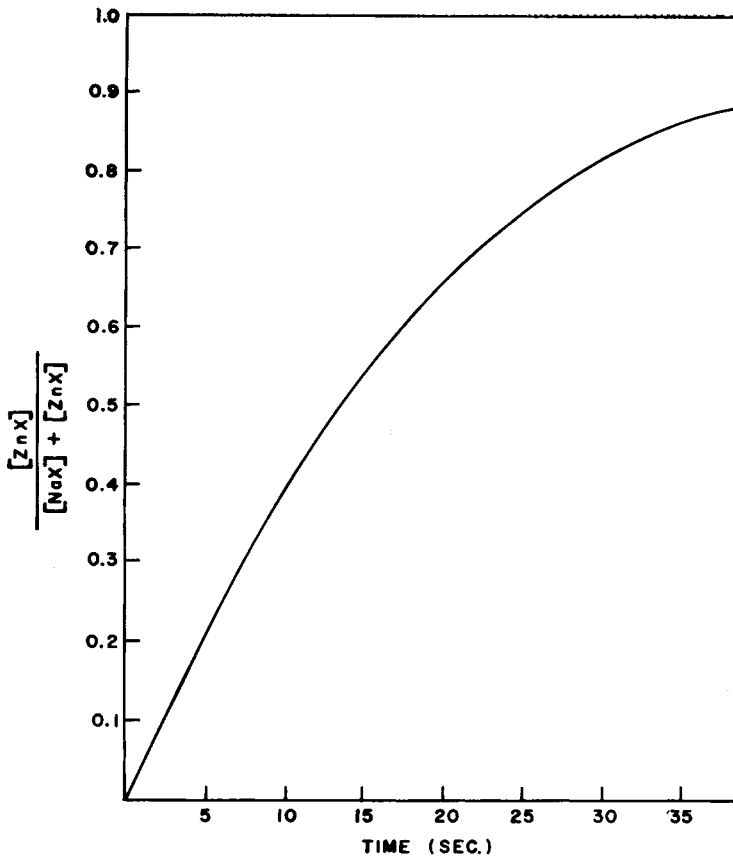
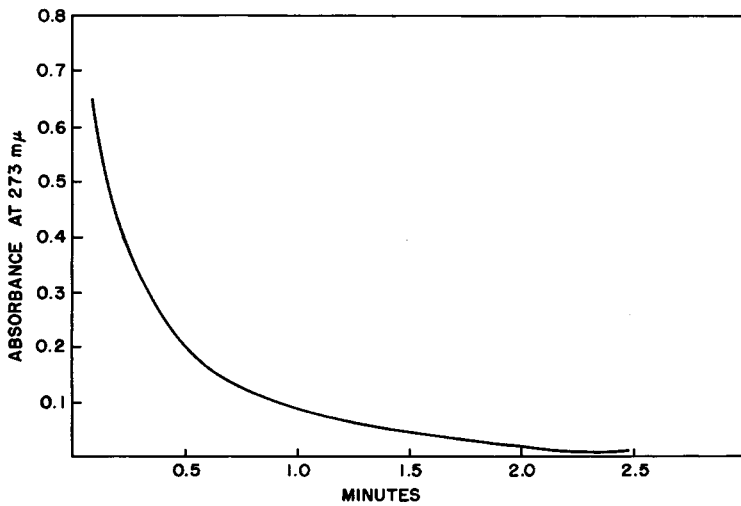


Fig. 8. Formation of zinc cellulose xanthate at 23°C.

Fig. 9. Decomposition of cellulose xanthic acid in 0.394N H<sub>2</sub>SO<sub>4</sub> at 10°C.

### Formation Rates

In all the cases where the xanthate ion and a derivative prepared from the xanthate ion have maxima at different wavelengths, it is evident that simultaneous equations can be set up and solved for the concentration of the xanthate ion and derivative.

If the rate of formation proceeds at a level which the recording instrument can follow, it is thus possible to calculate the rate of formation of the derivative. An illustration of this is given in Figure 8, which shows the formation of zinc cellulose xanthate. A film of ion-exchanged viscose was prepared and the spectrophotometer was adjusted to scan the 303–298  $m\mu$  region repeatedly. The film was then treated with 10% zinc sulfate solution and the effect on the absorption at the two wavelengths recorded. This technique is similar to one employed by Klein<sup>4</sup> to study the acid decomposition of ethyl xanthate.

### Decomposition Rates

Perhaps one of the most useful applications of the ultraviolet film technique is the study of the acid decomposition of the xanthate. Figure 9 is the decomposition curve obtained when sodium cellulose xanthate is treated with dilute sulfuric acid. Figure 10 is the acid decomposition curve of zinc cellulose xanthate.

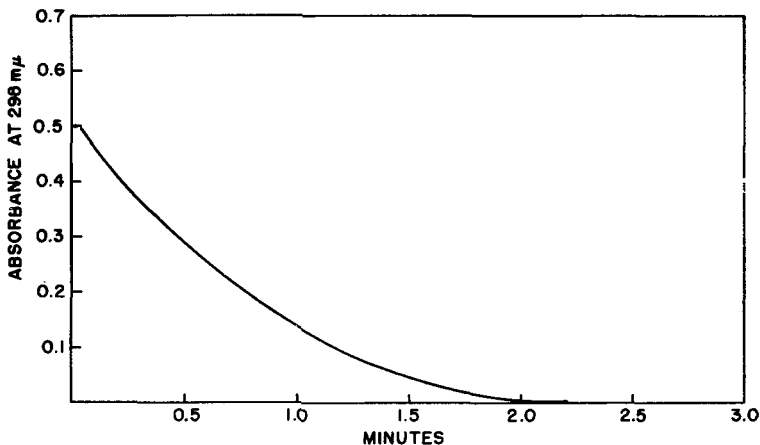


Fig. 10. Decomposition of zinc cellulose xanthate in 0.394*N*  $H_2SO_4$  at 10°C.

Another application for the technique is in the direct study of the thermal decomposition of viscose. This is illustrated in Figure 11. The wavelength of 295  $m\mu$  was chosen since the trithiocarbonate ion, which is a decomposition product of thermal aging, has negligible absorbance at this point.<sup>3</sup>

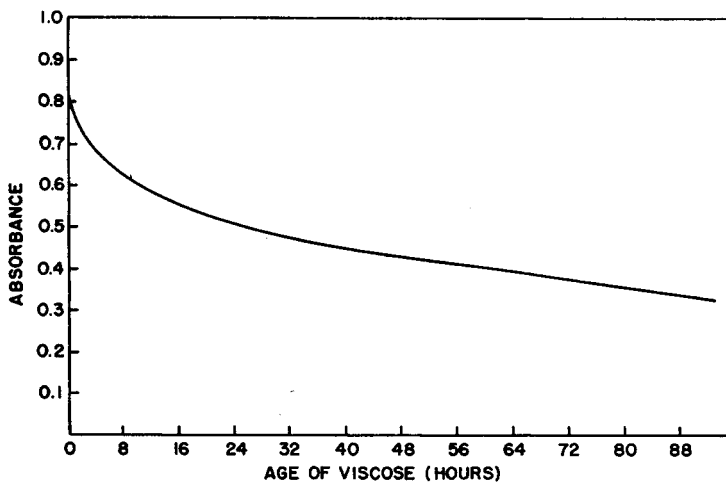


Fig. 11. Thermal decomposition of sodium cellulose xanthate in 6.6% NaOH at 19°C.

### LIMITATION OF THE PROCEDURE

The ultraviolet film technique may usually be satisfactorily applied only if the absorbing species is insoluble or almost insoluble in the reacting system. In special cases, where the absorbing species does not rapidly diffuse into the reacting media, certain studies can be made; for example, the conversion of cellulose xanthic acid back to sodium cellulose xanthate with a sodium hydroxide solution.

If gaseous products are produced or, perhaps, diffusion is a potential problem, the technique is limited to those species with an extinction coefficient of greater than about 1000 as less than this would require a much thicker film.

When working with viscose, by-product sulfur compounds on occasion can cause difficulties due to creation of unusual background absorption. Ion exchanging of the viscose is the simplest way to eliminate this trouble if only the reaction of the xanthate is to be studied.

The use of certain types of surfactants in the pulp from which the viscose is prepared can lead also to some background problems.

Finally, with certain types of systems, problems are encountered with reproducibility. These are usually traceable to the fact that the reactions involved are extremely complex and variables are not closely enough controlled.

### References

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### Résumé

On a développé un procédé pour étudier la chimie de la viscosité basée sur des mesures dans l'ultraviolet d'un film de xanthate de cellulose. Pour illustrer le domaine d'emploi de cette technique, on présente des spectres de composés différents formés avec la xanthate de cellulose, y compris les sels métalliques, des dérivés organiques et une forme acide, ainsi que l'influence de la solvation sur plusieurs composés de xanthate de cellulose et les courbes de formation et de décomposition de dérivés du xanthate de cellulose. Des applications possibles de cette technique supposent une étude de la décomposition acide du xanthate de cellulose, l'influence des additifs, des nouveaux dérivés et des mécanismes de xanthation. Il est aussi probable que la méthode peut être utilisée dans l'étude d'autres systèmes où existent des mécanismes de réactions rapides et où il existe des caractéristiques d'absorption convenables.

### Zusammenfassung

Ein Verfahren zur Untersuchung der Chemie der Viskose durch Ultraviolettmessungen eines Cellulosexanthatfilmes wurde entwickelt. Zur Illustration des Anwendungsbereiches dieser Methode werden Spektren mit Cellulosexanthat gebildeter Verbindungen, nämlich Metallsalze, organische Derivate sowie einer sauren Form angegeben, ebenso der Solvatationseinfluss auf verschiedene Cellulosexanthatverbindungen und die Bildungs- und Abbaukurven der Cellulosexanthatderivate. Unter die möglichen Anwendungen dieser Methode fällt auch eine Untersuchung der sauren Zersetzung von Cellulosexanthat, der Einfluss von Additiven, neue Derivate und der Xanthatierungsmechanismus. Es ist ausserdem wahrscheinlich, dass diese Methode zur Untersuchung anderer Systeme mit schnellen Reaktionsmechanismen und geeigneten Absorptionscharakteristika verwendet werden kann.

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