

Factors Affecting the Solution Properties of Cellulose Acetate

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Synopsis

Absorbance measurements on concentrated solutions of cellulose 2¹/₂-acetates in acetone show that the apparent absorbance is almost entirely due to turbidity. The size of the scattering particles is comparable with the wavelength of light. Sedimentable fractions are responsible for the anomalous viscosity of concentrated solutions of cellulose acetates as well as for their turbidity. These sedimentable fractions are enriched in xylan and mannan acetate. Solubility differences found for sediments rich in either xylan or mannan acetate, and extraction experiments with polar and nonpolar solvents revealed that more polar impurities, such as xylan acetates, are responsible for turbidity, while less polar impurities, such as mannan acetates, are responsible for false viscosity. A hypothesis based on solvent interaction and polymer incompatibility has been advanced to coordinate these and earlier findings.

I. INTRODUCTION

It is a well known fact of industrial importance that solutions of cellulose acetates exhibit differences in appearance and rheological behavior depending upon the origin and the purity of the cellulose from which they are made. The extraordinary increase in viscosity with increasing concentration exhibited by solutions of cellulose acetates made from impure celluloses is frequently referred to^{1,2} as "false viscosity." It has been shown that this false viscosity may be caused by the presence of carboxyl groups and polyvalent metal ions,^{3,4} by polydispersity,⁵ the distribution of substituents, and by mannan.^{1,6} The cause of turbidity and color, however, does not appear to be so well defined, nor is the influence of xylan acetates on the solution properties of cellulose acetate well known.

The object of this work was to investigate the turbidity of cellulose acetate solutions and to attempt to ascertain its cause. Special attention has been given to the influence of xylan acetates. It was hoped that a study of the solution properties of various cellulose acetates would lead to a hypothesis for turbidity and anomalous viscosity which would be compatible with all the isolated pieces of information found by earlier workers.

II. EXPERIMENTAL METHODS

The cellulose acetates were prepared from sulfite wood pulps on a semi-commercial scale. They were fully acetylated with a mixture of acetic

acid and acetic anhydride, sulfuric acid being used as a catalyst, and then hydrolyzed to a degree of substitution of $2^{1/2}$.

Absorbance measurements were made with an unmodified Beckman DK-2 recording spectrophotometer.

Chromatographic analyses were carried out by the method of Pridham.⁸ The samples were hydrolyzed in 72% H_2SO_4 for 2 hr. at 20°C. and then in boiling dilute H_2SO_4 for 4 hr. The hydrolyzates were neutralized by ion exchange. The chromatograms were developed in an equilibrated Chromatocab at 33–35°C. for 30–32 hr. with the use of butanol–water as developer. Identification strips were sprayed with aniline phthalate, and then corresponding portions of comparable strips were eluted and analyzed with a color reagent (Fehling's solution and arsenomolybdate) by use of a Beckman D.U. spectrophotometer.

Centrifugation of the 1% acetone solutions was carried out with a Sharples continuous supercentrifuge operating at maximum speed (about 50,000*g*). The flow rate was the fastest obtainable with no liquid head and the smallest feed nozzle (#60).

The rheological measurements were made with a Rao Couette viscometer (Rao Instrument Company, Pratt Station, Brooklyn, U.S.). The viscometer was kept at 25°C. The diameter of the stator was 37 mm. and the annulus gap was 1 mm.

The solubility tests were made in a qualitative way by leaving about 0.2 g. of material in 50 ml. of the appropriate solvent overnight on an oscillating shaker.

Extractions were carried out by leaving 25 g. of acetate in 1 liter of solvent or solvent mixture in 1-qt. sealer jars overnight.

III. EXPERIMENTAL RESULTS

Turbidity Studies on Acetone Solutions of Cellulose Acetates

In the early stages of this investigation, the main interest was in the turbidity–wavelength relationship of cellulose acetate solutions in acetone. The absorbance of solutions of 12% cellulose acetates in acetone was measured over a wavelength range of 300–700 $m\mu$ with a Beckman DK-2 spectrophotometer. Figure 1 shows a selection of typical results from these measurements.

In Figure 1 the logarithm of absorbance is plotted against the logarithm of the wavelength of the light at which the absorbance was measured. Two facts are apparent from these results: (a) the substantial linearity found in all of the many cases investigated, and (b) the range of slopes observed.

The results are in accordance with the relationship established by Heller⁷ for the variation of scattering with wavelength and size of scattering particles.

$$\tau = K \cdot \lambda^{-n} \quad (1)$$

$$\log \tau = \log k - n \log \lambda \quad (2)$$

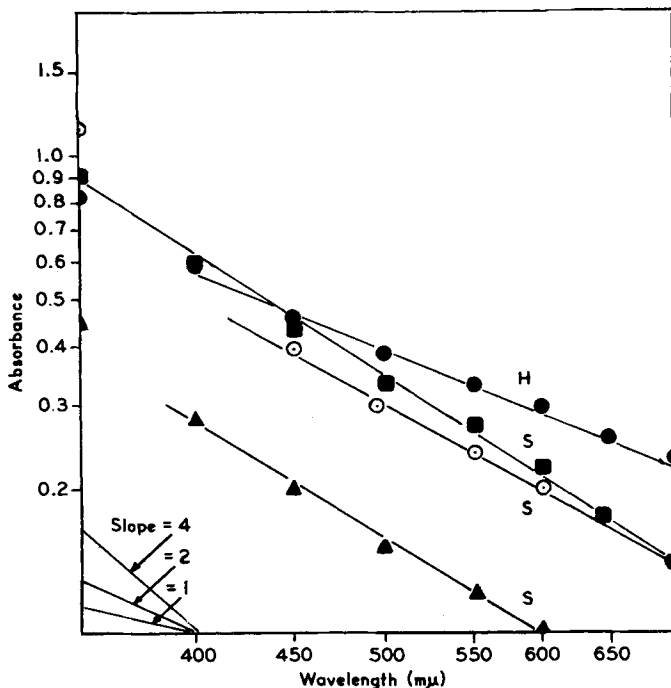


Fig. 1. The absorbance of 12% acetone solutions of cellulose acetates of different origin. (S from softwood pulps, H from hardwood pulps).

where τ is turbidity, λ is wavelength, k is a constant, and n is a size parameter (0 for particle size $\gg \lambda$; 2 for particle size $\sim \lambda$; 4 for particle size $\ll \lambda$).

The fact that turbidity varies with wavelength is in conflict with a technical definition of color and turbidity widely used in the cellulose acetate field, which assumes that turbidity is independent of wavelength. The present results indicate that true color is negligible in the cellulose acetate solutions studied. The increase in absorbance observed when going from 600 to 400 $m\mu$ is explicable on the basis of turbidity, although there is, in some samples, a nonlinearity of the $\log \tau$ versus $\log \lambda$ plot which suggests a small absorbance. Since turbidity is the dominant aspect of absorbance, absorbance and turbidity may be regarded as synonymous in what follows.

The particle sizes suggested by the slopes of the absorbance curves as given in Figure 1 are of the order of 1μ . This led to the conclusion that the material responsible for turbidity occurs as aggregates large enough to sediment from dilute solutions in moderately strong centrifugal fields.

Effect of High Speed Centrifugation of Acetone Solutions of Cellulose Acetates

Accordingly, 1% solutions of various $2\frac{1}{2}$ acetates were centrifuged in a Sharples continuous centrifuge in a field of about 50,000*g*.

The amount of sediment removed by centrifugation was in the range of 4–14%, and varied depending on the source of cellulose acetate. No relationship could be established between the amount of sediment and either the anomalous viscosity or the turbidity of acetone solutions of the cellulose acetates.

The sediments and the acetates isolated from the supernates were examined for the following properties: (a) chemical composition, by hydrolysis and paper chromatography, (b) turbidity of 12% solutions in acetone, (c) rheological properties of these solutions as obtained with a Couette viscometer, (d) solubility in various solvents.

The sugar analyses made of the hydrolyzates indicated a considerable enrichment of xylan and mannan acetates in the sediments. For the sake of clarity the term "xylan acetate" has been used to indicate an acetate containing substantial amounts of xylan. The same simplification applies to "mannan acetate" notwithstanding the fact that mannan has been shown to occur in chains bound with varying amounts of glucose.⁹ These analyses also showed that substantial amounts of pure cellulose acetate were present in the sediment. Some typical results are summarized in Table I.

A false viscosity factor is also included in Table I. This is the result of a convenient industrial evaluation of the rheological behavior defined as

$$\frac{10 \times \log \text{viscosity of 24\% solution of cellulose acetate in acetone}}{\text{specific viscosity of 0.091\% solution of cellulose acetate in 92\% acetic acid}}$$

A low value of the false viscosity factor is desirable.

The removal of nonglucosidic impurities by centrifugation improved the turbidity and false viscosity of solutions of the wood pulp acetates, rendering them comparable to those of the purest cellulose acetate.

TABLE I
Effect of Centrifugation on Composition
and Solution Properties of Cellulose Acetates

Source	Acetate fraction	Xylan, %	Mannan, %	Turbidity (absorbance at 650 m μ)	False viscosity factor
Softwood	Original acetate	1.1	2.0	0.26	145
	Sediment	5.0	10.0	Very high	(350)
	Residue	0.6	1.3	0.16	135
Hardwood	Original acetate	1.5	2.0	0.28	157
	Sediment	10.0	4.0	Very high	Very high
	Residue	0.0	1.0	0.14	127
Purest available acetate		0	0	0.04	127

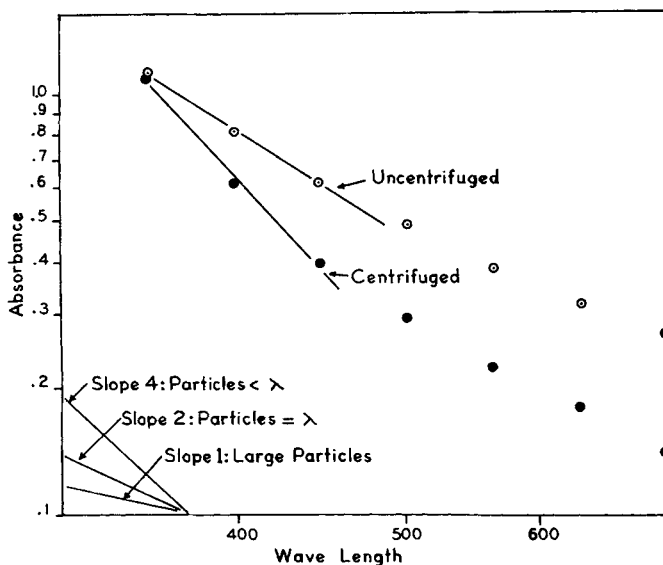


Fig. 2. The effect of centrifugation on the absorbance of 12% solutions of cellulose.

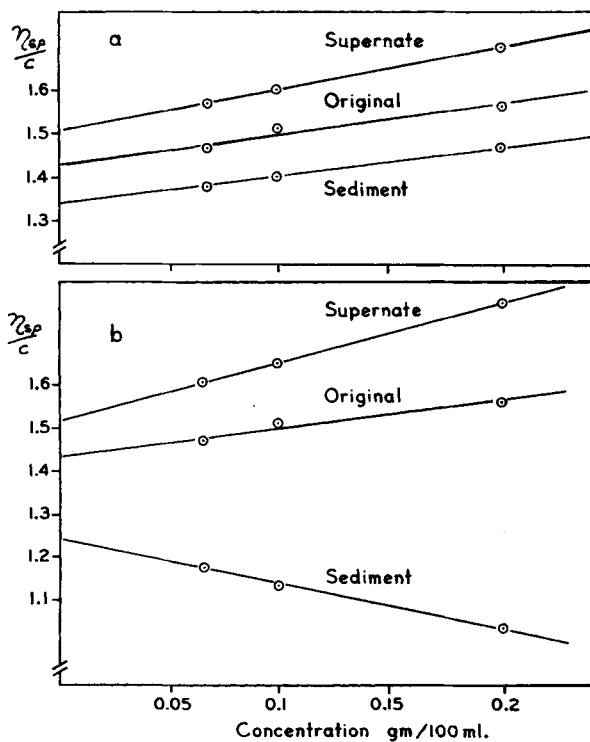


Fig. 3. The reduced viscosities of acetone solutions of fractions obtained by centrifugation of (a) a softwood pulp acetate and (b) a hardwood pulp acetate.

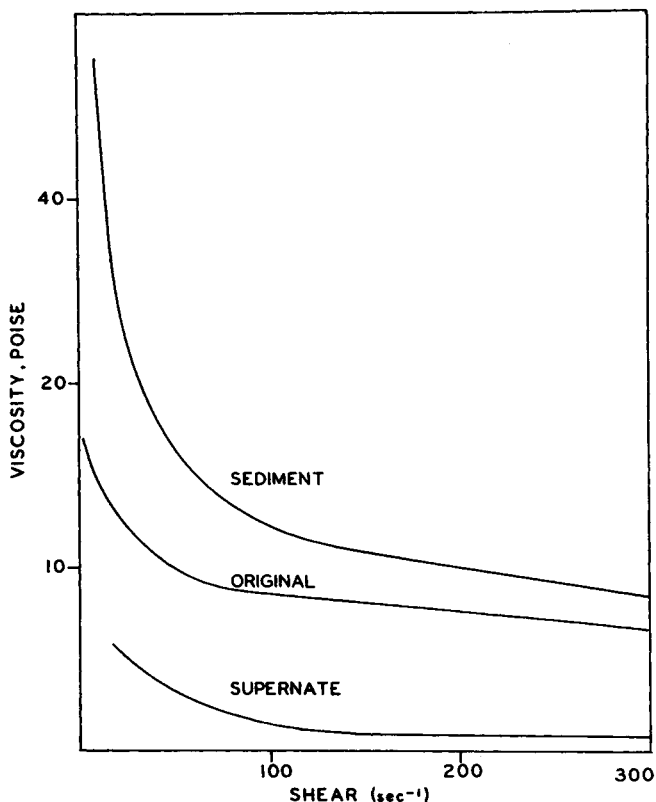


Fig. 4. Viscosity vs. shear rate for 12% acetate solutions of cellulose acetate from softwood pulp. The three curves are for the original material, and the sediment and supernate from centrifugation from acetone at low concentration.

The effect of the removal of sedimentable material on turbidity is even more clearly demonstrated by studies on the absorbance-wavelength relationship. Typical examples of the results obtained with 12% solutions of the original acetates and the acetates isolated from the supernates are given in Figure 2.

This graph shows that the removal of sedimentable material not only reduces the overall level of turbidity but also usually increases the slope of the $\log \tau$ versus $\log \lambda$ plots. This is the result expected from a selective removal of the larger scattering particles.

Attempts to perform similar investigations on 12% solutions of the sediments in acetone resulted in such high turbidity levels that meaningful readings could not be obtained. It was observed that the sediment of hardwood pulp acetates, whose xylan content was higher, was practically insoluble.

The effect of removing sedimentable material on the rheological behavior of acetone solutions was studied both at low and high concentrations.

Figure 3a gives the results of viscosity measurements on dilute acetone

solutions of an uncentrifuged softwood pulp acetate, its sediment, and the acetate isolated from the supernate. These were measured in the conventional way with an Ubbelohde viscometer.

The sedimentable fraction had a lower intrinsic viscosity than the original acetate and its removal raised the intrinsic viscosity of the supernates.

The results of similar investigations on a hardwood pulp acetate are shown in Figure 3*b*.

The results in general agree with those obtained for the softwood pulp acetate. The negative slope of the curve for the sediment obtained from the hardwood pulp acetate is an artifact caused by the poor acetone solubility.

Figure 4 shows the rheological behavior of concentrated solutions of original acetate, sediment, and supernate.

The non-Newtonian flow character of the sediment solution is clearly evident. Its false viscosity factor was estimated to be 350, more than twice that of the original acetate. The improvement in flow behavior of the supernate becomes more evident when one considers that the viscosity of its 12% solution is lower than that of the 12% solution of the original acetate, although its intrinsic viscosity is about 10% higher. Its false viscosity factor of approximately 130 closely approaches that of acetates made from the purest commercially available celluloses.

There were indications that the sediments obtained from hardwood pulp acetates differed in solubility from those obtained from softwood pulp acetates. Solubility investigations were therefore made with solvents covering the entire range of solubility parameters. The behavior of these sediments in different solvents is indicated in Table II.

TABLE II

Solubility parameter*	Solvent	Hardwood pulp acetate sediment	Softwood pulp acetate sediment	Supernate
8.6	Methyl chloride		Insoluble	Swollen
9.05	Ethyl acetate	Insoluble	Insoluble	Very highly swollen
9.15	Benzene	Insoluble	Insoluble	Partly swollen
9.15	M.E.K.	Insoluble	Partly soluble	Slightly swollen
9.3	Chloroform		Partly soluble	Very highly swollen
9.5	Chlorobenzene		Insoluble	Insoluble
9.55	Methyl acetate	Very turbid solution	Slightly swollen	Slightly turbid solution
9.7	Acetone	Turbid solution	Turbid solution	Clear solution
10.0	Dioxane	Very turbid		Very turbid
10.7	Pyridine	Clear solution	Some sediment	Clear solution
—	Morpholine	Clear solution	Clear solution	Clear solution
12.6	Nitromethane	Very turbid	Insoluble	Clear solution
15.2	Methanol	Partly soluble	Insoluble	Insoluble

* Data of Moore.¹⁰

Even from a qualitative point of view, it is apparent that the solubilities of the two sediments differ from each other and from that of the supernate. The xylan-rich sediment from hardwood pulp acetate shows a higher solvent interaction with solvents of high solubility parameter, while the mannan-rich sediment from softwood pulp acetate interacts more with solvents of low solubility parameter.

Removal of Nonglucosidic Polysaccharide Acetates by Solvent Extraction

The differences in solution properties of sediments from dilute cellulose acetate solutions suggested the possibility of removing the impurities responsible for turbidity and false viscosity by selective extraction. Accordingly, cellulose acetates were extracted with solvents which were just outside the limits of solubility parameter within which the cellulose 2¹/₂-acetate is soluble. The most successful of these were chloroform, methyl ethyl ketone and ethyl acetate, which have lower solubility parameters than cellulose 2¹/₂-acetate, and pure methanol and an azeotropic mixture of methanol and nitromethane, whose solubility parameters are higher than that of cellulose 2¹/₂-acetate.

Since these extractions are very sensitive to changes in the degree of substitution, the proportion of extract to residue is not meaningful. The amounts extracted varied from 1 to 10% of the total cellulose acetate, depending on the source of the cellulose and the degree of substitution. The extracts and the residues were studied with respect to chemical composition, turbidity of 12% solutions, and rheological behavior.

The effect of extracting with nonpolar and polar solvents on chemical composition and solution properties is shown in Table III.

The chloroform soluble fraction was enriched in mannan acetate. Its removal improved the false viscosity, but did not affect the turbidity. The methanol extract was enriched in xylan and slightly in mannan. The extraction with nitromethane-methanol reduced both turbidity and false viscosity. Methanol extraction improved only turbidity of the residual acetate. The improvement was comparable to that obtained with the use of nitromethane-methanol. The intrinsic viscosity of the extracted fractions was much lower than that of the original acetate and of the residue. Furthermore, the chloroform extraction also removed some more highly substituted cellulose acetate while the methanol extraction removed some less highly substituted cellulose acetate in addition to the mannan or xylan acetates, respectively.

The effect of the extraction on the turbidity of 12% solutions of cellulose acetate is shown in Figures 5 and 6.

Figure 5 shows that chloroform extraction did not decrease the turbidity. Figure 6, however, indicates that extraction with methanol (which has a more selective action on polar impurities, including xylan acetates) led to a consistent decrease of about 15% in turbidity. The differences in selectivity of methanol and chloroform are greater than is apparent from the figures,

TABLE III
Effect of Extraction with Polar and Nonpolar Solvents on Composition and Solution Properties

Source	Acetate fraction	Extraction with	Xylan, %	Mannan, %	$[\eta]$	False viscosity factor	Turbidity (absorbance) 650 m μ	Original % of
Softwood pulp	Original acetone	Chloroform	1.5	0.7	1.39 (acetone)	146	0.21	100
	Extract		0.2	4.0	0.46	225	Clear	20
	Residue		1.5	0.5	1.40	123	0.23	80
Softwood pulp	Original acetate	Methanol	1.5	0.9	1.76	146	0.32	100
	Extract		6.2	2.6	Acetone-insoluble	145	Insoluble	1
	Residue		1.3	0.8	1.76	145	0.27	99
Softwood pulp	Original acetate	Azeotrope nitromethane-methanol	1.76 MeCl ₂ + ETOH			146	0.32	100
	Extract		0.59 MeCl ₃ + ETOH			145	Insoluble	5.5
	Residue		1.75			145	0.27	94.5

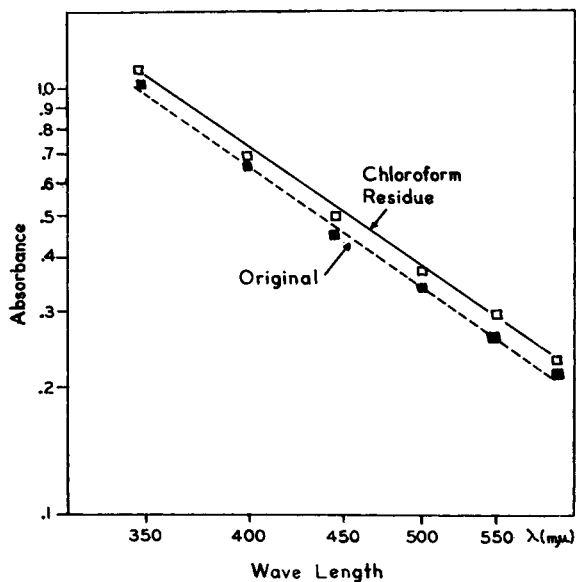


Fig. 5. Absorbance vs. wavelength of 12% acetone solutions of cellulose acetate before and after extraction with chloroform.

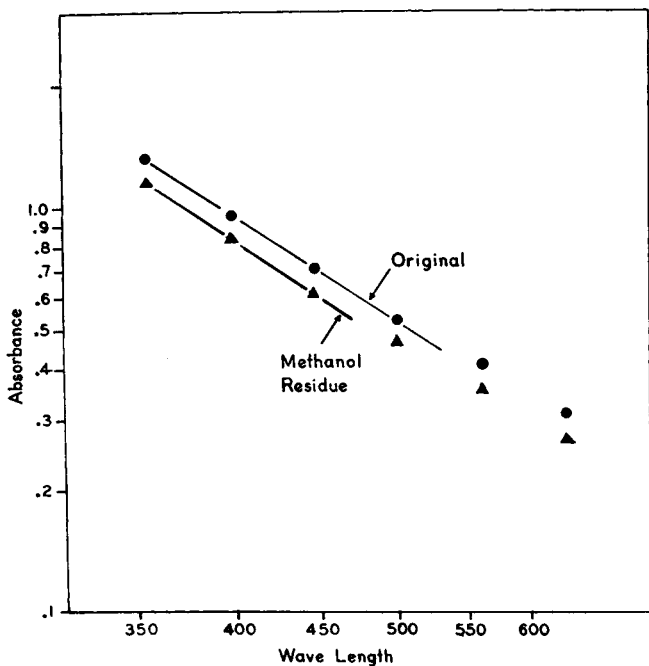


Fig. 6. Absorbance vs. wavelength of 12% acetone solutions of cellulose acetate before and after extraction with methanol.

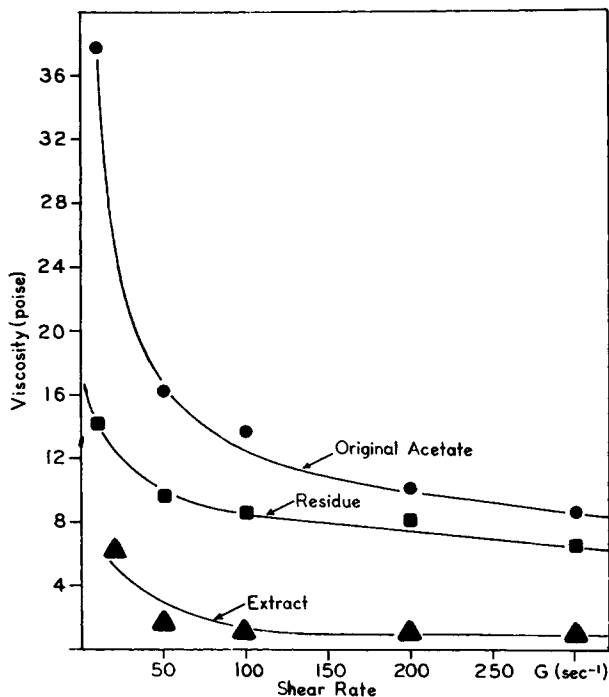


Fig. 7. Viscosity vs. shear rate of 12% acetone solutions of cellulose acetate, extract residue, and unextracted with chloroform.

since CHCl_3 extracted about 20% of the original material, while methanol removed only 1%.

The results of rheological studies on 12% solutions of the original and extracted acetates are shown in Figures 7 and 8.

Figure 7 indicates that chloroform extraction (which selectively removes the more nonpolar impurities, including mannan acetate) reduces the shear dependence of the viscosity. The false viscosity factor was decreased from 145 to an estimated value of 120. Owing to the lower level of viscosity, the highly non-Newtonian flow characteristics of the extract solution are not entirely evident from the curve. The estimated false viscosity factor of the extract is about 225, which is nearly twice as high as that of the original acetate.

Figure 8 shows the effect of extraction with nitromethane-methanol on the rheological properties. The extraction resulted in a slight improvement. This is not surprising, since the extraction removed mannan as well as xylan. Methanol extraction, however, did not alter the rheological behavior.

Solutions of the material extracted with nonpolar solvents were invariably so clear that no turbidity measurements were made on them. The material extracted with polar solvents was insoluble in acetone, so that neither rheological nor optical measurements were possible.

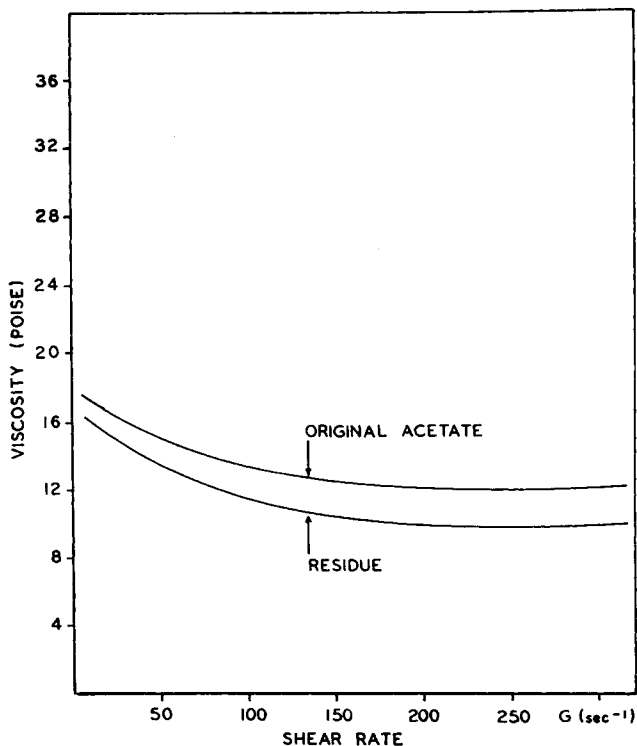


Fig. 8. Viscosity vs. shear rate of 12% acetone solutions of cellulose acetate extracted and unextracted with methanol.

The extraction experiments indicate that nonpolar impurities, such as mannan acetate or fractions of more highly substituted cellulose acetate are responsible for false viscosity, while polar impurities, such as xylan acetate or less highly substituted cellulose acetate fractions, give rise to turbidity.

IV. DISCUSSION

The following hypothesis is advanced to explain these results, and to serve as a basis for further work.

Solvents can be arranged in a sequence according to their solubility parameter. The same applies to polymer solutes. When the difference between the solubility parameters of a solvent-solute system is within a certain limit, solution will take place. If the solubility parameter is just outside the limits, the polymer will not dissolve but will be highly swollen. As the difference becomes greater, the polymer is less and less swollen, and finally the polymer is unaffected by solvents whose solubility parameter is very different from its own.

Roughly speaking, cellulose 2¹/₂-acetate is soluble in a range of solvents whose solubility parameter is between 9.5 and 13. The optimum solubility shifts to lower values of solubility parameter as the degree of substitution

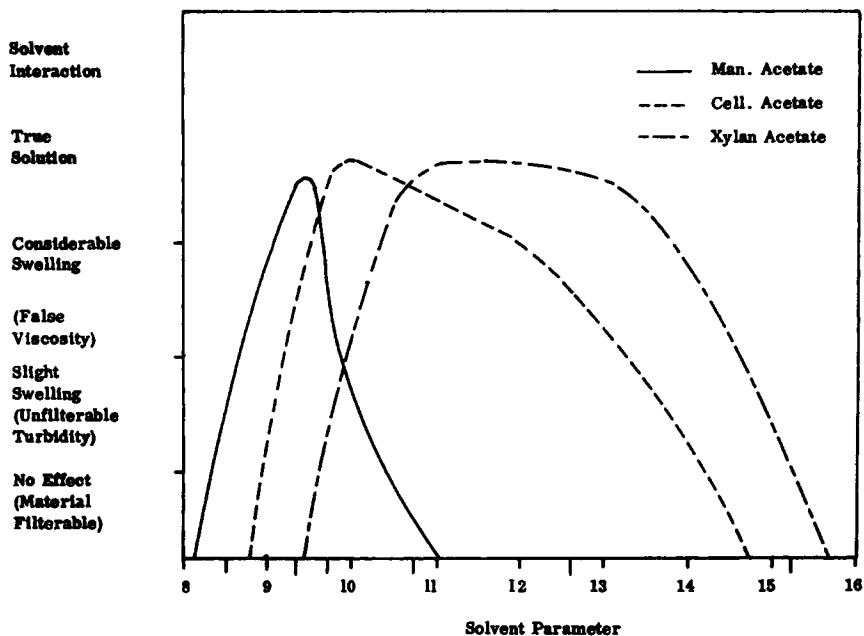


Fig. 9. Schematic representation of solvent interaction of cellulose acetate, mannan acetate, and xylan acetate.

is increased, and the solubility range increases as the molecular weight is reduced. Outside these limits, the behavior tapers from soluble to highly swollen to swollen to inert as is shown schematically in Figure 9. The y axis of this graph is an arbitrarily defined degree of solvent interaction.

Figure 9 also shows the solvent interaction of preparations rich in mannan and xylan because of sedimentation, selective extraction, or by choice of wood species. The mannan acetate is evidently less polar and the xylan acetate is more polar than normal cellulose acetate. The solvent parameter of acetone, the usual solvent of technical importance for cellulose $2^{1/2}$ -acetate, is about 9.7, almost at the lower limit of the solubility range for cellulose $2^{1/2}$ -acetate.

Figure 9 shows further that the xylan acetate will be slightly swollen in acetone, so that it is not readily filterable. However, it is not so highly swollen that its refractive index will approach that of the solvent, and thus it will give considerable turbidity. The relatively mild swelling also explains why no significant increase in viscosity at high concentration is caused by the presence of xylan acetate. Mannan acetates, however, exhibit the reverse characteristics. They are highly swollen and interfere with the flow properties at high concentration. However, they do not appreciably increase the turbidity.

One observation is still unexplained by this hypothesis. The viscosities at high concentrations of both extract and residue are less than that of the original acetate before extraction with nonpolar solvents (see Fig. 7).

This is probably a consequence of polymer incompatibility, which leads to a phase separation when solutions at two polymers, even apparently very similar polymers, are mixed. This effect is not inconsistent with the hypothesis, although it does lead to a slight modification. Thus polymers which by themselves would be reasonably soluble are only highly swollen in the presence of another polymer. Highly swollen polymers are less swollen in the presence of another polymer and so forth.

It has been mentioned that the range of solubility parameter within which a polymer dissolves is reduced as the molecular weight of the polymer is increased. The presence of a different polymer also reduces this solubility range.

Incompatibility also explains why it is possible to achieve the properties of the purest cellulose acetates without removing all the mannan and xylan. It is simply necessary to remove enough of these components to bring the acetate within the limits of compatibility.

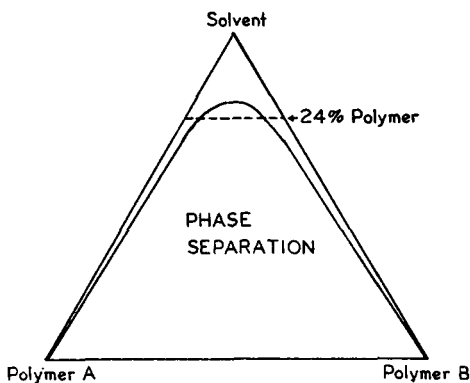


Fig. 10. Diagram showing the effect of incompatibility.

As an example, an acetate containing 1.5% xylose and 2% mannose whose false viscosity was 157 was centrifuged. The false viscosity was reduced to 127, although the product still contained 0.6% xylose and 1% mannose. Now this false viscosity is comparable with that obtained using the purest cellulose, so that the acetate seems capable of supporting over 1% of impurities without any loss in properties. The same argument is probably applicable to turbidity. Figure 10, taken from the reference by Dobry et al.,¹¹ shows the suggested incompatibility clearly. Evidently, from the diagram, the lower the concentration of the solution the more impurities will be tolerable. However, even at concentrations as high as 24%, which is the region of industrial importance, a significant quantity of mannan acetate or xylan acetate may be present before phase separation occurs.

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Résumé

Dés mesures d'absorbance effectuées sur des solutions concentrées d'acétates de cellulose-2¹/₂ dans l'acétone montrent que l'absorbance apparente provient presque entièrement de la turbidité. La taille des particules diffusantes est comparable à la longueur d'onde de la lumière. Certaines fractions sédimentables sont responsables des anomalies de viscosité présentées par les solutions concentrées d'acétate de cellulose ainsi que de leur turbidité. Ces fractions sédimentables sont enrichies en acétate de xylane et de mannane. Les différences de solubilité entre les sédiments riches en acétate de xylane et ceux qui sont riches en acétate de mannane ainsi que les expériences d'extraction par des solvants polaires et nonpolaires montrent que les impuretés les plus polaires, soit les acétates de xylane, sont responsables de la turbidité tandis que les impuretés les moins polaires, soit les acétates de mannane, sont responsables des anomalies de viscosité. Une hypothèse basée sur une interaction avec le solvant et sur l'incompatibilité du polymère a été avancée pour lier ces observations à celles qui ont été faites précédemment.

Zusammenfassung

Absorptionsuntersuchungen an konzentrierten Lösungen von Zellulose-2¹/₂-acetaten in Aceton zeigen, dass die scheinbare Absorption fast völlig durch die Trübigkeit verursacht wird. Die Grösse der streuenden Teilchen ist mit der Wellenlänge des Lichts vergleichbar. Sedimentationsfähige Fraktionen sind sowohl für die anomale Viskosität konzentrierter Lösungen von Zelluloseacetat, als auch für ihre Trübigkeit verantwortlich. Diese sedimentationsfähigen Fraktionen sind mit Xylan- oder Mannanacetat angereichert. Löslichkeitsunterschiede bei an Xylan- oder Mannanacetat reichen Sedimenten und Extraktionsversuche mit polaren und nichtpolaren Lösungsmitteln zeigten, dass stärker polare Verunreinigungen wie Xylanacetat für die Trübigkeit verantwortlich sind, während weniger polare Verunreinigungen wie Mannanacetat für die falsche Viskosität verantwortlich sind. Zur Koordinierung der vorliegenden und früherer Befunde wurde eine auf Lösungsmittelwechselwirkung und Polymernichtverträglichkeit beruhende Hypothese aufgestellt.

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