A PRECISE FRACTIONATION OF CELLULOSE NITRATE

by

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II. INTRODUCTION

The purpose of this study was the development of a fractionation procedure which could be used to obtain reproducible fractions, both in weight and in the average degree of polymerization, from a high-viscosity type cellulose nitrate.

This work was the preliminary investigation necessary to begin the study of the effect of the shape of the differential distribution curve on the physical properties of cellulose nitrate films. In order to accomplish this purpose, it was desirable to have a method by which cellulose nitrate could be separated into a number of fractions whose average degrees of polymerization differed from fraction to fraction while the degree of substitution remained constant.

It was found by a search through the literature that the methods used by other investigators were not applicable to such a study. It was necessary to develop a method which would give reproducible results over a series of fractionations without the tedious refractionation procedures used heretofore. Therefore, the investigation of the conditions and the development of a fractional precipitation method for the fractionation of cellulose nitrate was begun.

III. CONSTITUTION OF CELLULOSE

Cellulose may be termed a natural high polymer, of which the fundamental building unit is an anhydride of glucose. Apparently nature produces this polysaccharide in the form of long-chain molecules by the dehydration and condensation of glucose.

Cellulose is found in all vegetable matter (16) in various forms; for example, as hair in cotton, as bast in flax, and as fibers in wood. These forms of cellulose may be regarded as aggregates of large numbers of glucose anhydride units, arranged in long chains more or less parallel to each other and stabilized by secondary valence forces or by hydrogen bonds resonating between opposite hydroxyl groups. There is a probability that occasional primary valence bonds also exist as cross linkages between the chain molecules.

In a discussion of the chemistry of cellulose it is necessary to consider the microscopic and sub-microscopic structure and its colloidal nature which results from its high-polymeric character. These properties of structure are at least a partial explanation of the heterogeneous course taken by cellulose in its reactions and explain the utility of cellulose for a great variety of purposes.

The generally accepted chemical constitution of cellulose is a linear chain of anhydro-glucose units held together by oxygen bridges between the number one carbon of one unit and the number four carbon of another unit (Fig.1). The chemical reactions of cellulose resemble those of simple sugars. Since all except one of the potential reducing groups of the glucose residues, the one terminating unit of the open chain, are involved in glucosidic linkages between the individual units of the chain, cellulose lacks the reducing power of the simple sugars, and its chief reactions are those involving the hydroxyl groups.

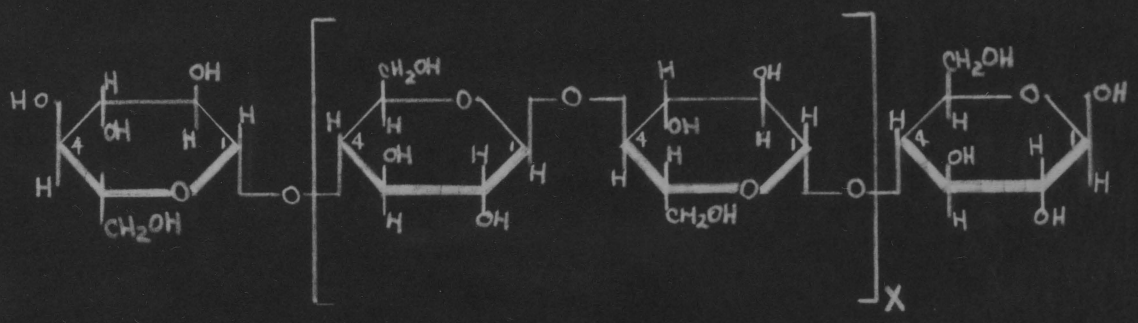


Figure 1. Theoretical configuration of the cellulose molecule. Degree of polymerization (D.P) = X+2. At the left of the drawing is shown a secondary alcohol configuration, the non-reducing end group. At the right is shown the hemiacetal configuation, only one of the several configurations possible for the reducing-end group.

(Taken from "Advancing Fronts in Chemistry", Vol. I., High Polymers. Edited by Twiss. Reinhold Publishing Corporation (1945), p. 79.)

The free hydroxyl groups thus react as in alcohols to form addition compounds, esters and ethers, and on oxidation are converted step-wise into aldehydic and carboxylic groups. In fact, even carefully purified cellulose is found to contain carboxyl groups (102).

Complete hydrolysis of cellulose yields beta-glucose as the end product. By carefully controlled hydrolysis, a number of intermediate products, oligosaccharides consisting of six, four and three anhydro-glucose units, may be obtained before the chains break down to the end product, beta-glucose.

Cellulose possesses, on the average, a high molecular weight. The molecular weight corresponds to the number of anhydro-glucose units of the chain multiplied by the molecular weight of the monomer, a single anhydro-glucose unit, 162. The number of units in a chain molecule is termed the degree of polymerization (D.P.).

MICROSCOPIC STRUCTURE

Cellulose is the chief constituent of the cells which compose the plant tissue. The cells may be observed by microscopic examination of cross sections of plants. These cells appear in various shapes, and when millions of cells combine the structure becomes visible to the unaided eye.

There are cases where a single cell is visible without the aid of a microscope. For example, cotton hairs represent single cells; they may vary in size from 1 to 5 cm. in length and from .0012 to .0040 cm. in thickness. Flax fibers measure 4.3 to 5.3 cm. in length and .0012 to .0026 cm. in width. Ramie fibers measuring up to 26 cm. in length have been reported; the thickness measures from .0040 to .010 cm. Fibers obtained from soft wood have an average length of .3 cm. and a width of .003 to .004 cm. and from hard wood a length of .012 cm. and a width of from .0015 to .0025 cm. (49).

The structure of the cellulose fiber may be studied by means of cross sections of the cellulosic material. This method was used in a study of certain species of wood fibers by Bailey (6). The individual fibers are separated by intercellular material, and adjacent to the intercellular material are the primary wall, the outer, central and inner layers of the secondary wall. The inner layer of the secondary wall surrounds the lumen. Both the primary and secondary walls are composed chiefly of cellulose but also contain, in varying amounts, members of a group of carbohydrates related to cellulose. This group of related carbohydrates was designated as "hemicelluloses" by Schulze (109), and this term has become very general including pentosans,

hexosans, and polyuronides (90).

The wood and cellulose chemists prefer to define "hemicelluloses" as that portion of the plant material which is soluble in cold sodium hydroxide solution of 17-18 per cent by weight. The soluble material obtained by the use of this reagent includes both beta- and gamma-cellulose. These are distinguished by their behavior with dilute acids. The beta-cellulose is insoluble in the acidified solution and is precipitated. Gamma-cellulose is soluble in the acidified solution but may be salted out by the addition of the ammonium salt. This arbitrary classification was originally suggested by Cross and Bevan (16).

The intercellular substance which separates the cells consists of lignin but may also contain tannins, pectins, and numerous other non-cellulosic compounds in small quantities according to the species (125).

SUBMICROSCOPIC STRUCTURE

In advancing to the invisible region of fiber structure, von Naegeli (89) first assumed in 1858 that the fibers which are visible under the microscope are further subdivided into microscopically invisible particles, which he regarded as crystals. His ideas were forgotten until Ambronn in 1911 (5) found that cellulose fiber shows the phenomenon of double refraction. This is an essential characteristic of crystalline substances and was strong support for von Naegeli's concept.

A short time after Ambronn's finding, the development of x-rays proved to be an important tool to research in this field. The use of x-rays began with von Laue's discovery (70) that a crystal behaves as a three-dimensional diffraction grating to x-rays, which indicated regularity of interatomic distances and thus, of internal structure. von Laue's work was followed by the application of x-radiation to cellulose and starch by Debye and Scherrer (20), by Hull (61), and others. The rapid development which followed is characterized by the work of Polanyi (92) and by Weissenberg (93), who furnished the fundamental data according to which the cellulose fiber was regarded as representing a crystal lattice composed of rows of crystals arranged parallel to the fiber axis.

The first attempt to determine the dimensions of the basic cell, or unit of cellulose, was made by Polanyi (92) at this time. The lattice on which the cellulose crystal is built may be ascribed to the monoclinic system with dimensions of the basic cell expressed in Angstrom units as follows (84):

a (Horizontal)	8.35
b (vertical, representing the length of the basic cell, parallel to the fiber axis)	10.3
c (forming the angle with a)	7.95
Angle between "a" and "c"	84 degrees

Sponsler and Dore (113) using the work of Bragg and his collaborators devised a structural arrangement of the glucose units in the basic cell. Although they erroneously chose alternating glucosidic and ether linkages instead of glucosidic linkages only, their work gave great impetus to the studies in the years which followed, notably Meyer and Mark.

In their attempts to place the glucose units in the basic cell, Meyer and Mark chose the dimensions of Polanyi and made use of the beta-form of Haworth's cellobiose model. Combining the various pieces of evidence, Meyer and Mark (83) concluded that, in the basic cell, the cellobiose residues lie parallel to the b axis. This arrangement was modified in accordance with Meyer and Misch's (84) suggestion that the glucose residues point alternately in opposite directions.

IV. THE REACTIONS OF CELLULOSE

Almost all cellulose reactions start with fibrous cellulose which is usually partially crystalline and partially non-crystalline. One of the major problems in the preparation of cellulose derivatives is to make all portions of the cellulose fiber available for reaction. Therefore, the characteristic of swelling which usually preceeds or accompanies most cellulose reactions must be considered.

According to Katz (64), "a solid is said to swell when it takes up a liquid, while at the same time (1) it does not lose its apparent (microscopic) homogeneity, (2) its dimensions are enlarged, and (3) its cohesion is diminished; that is, it becomes soft and flexible."

Swelling should be distinguished from capillary imbibition, such as is shown by a solid having numerous capillary canals. A porous tile will absorb liquids, but it is nonhomogeneous, its dimensions do not change, and its cohesion is not decreased. When the order of magnitude of the capillary tubes becomes very small, there may exist phenomena lying between the extremes of swelling and capillary imbibition. This, in addition to real swelling, is exhibited by cellulose and its derivatives.

Cellulose fibers are porous solids of high molecular weight which are held together by at least four types of bonds, van der Waals', polar, hydrogen bonds, and primary valence bonds, forming minute crystalline and amorphous areas (112). It should be noted that cellulose fibers fulfill all the conditions for complex swelling, capillary imbibition, and other intermediate phenomena.

Cellulose, in its esterification reactions with both organic and inorganic acids, may be regarded as a polyhydric alcohol. It is not always possible to convert all three hydroxyl groups into ester groups,

and esterification may stop with the introduction of from less than one ester group per glucose unit to three ester groups. The hydroxyl groups which react first are those which are exposed on the surface of the chain bundles, and when all of the surface hydroxyl groups have been esterified, the reaction will cease temporarily, unless some measure is taken to make the hydroxyl groups below the surface of the chain bundles accessible to the reactants. Swelling is an effective means of increasing the number of hydroxyl groups which may react. The dehydrating agent used in the esterification is frequently a swelling agent.

Of the three hydroxyl groups available for esterification in each glucose residue, one hydroxyl group is in the primary position, and the other two are in the secondary position. Substitution, then, may occur several different ways. For example, with a degree of substitution of 2, the substitution may occur in positions 6 and 2, in 6 and 3, or in 2 and 3 on the same glucose residue. The substitution may occur in position 6, 3, or 2 on one glucose residue and in all three positions on the adjacent glucose residue. On the basis of the foregoing possibilities of substitution, Spurlin (115) has calculated that a chain of 100 glucose units with an average degree of substitution of 1.5 groups per anhydro-glucose unit can be arranged in some 10^{85} different ways. This fact alone makes it impossible to obtain any substituted cellulose except the tri-ester as a definite homogeneous compound. It would appear that a mono- or di-substituted ester could better be prepared by a carefully controlled partial hydrolysis of the tri-substituted ester. However, hydrolysis also occurs in a heterogeneous manner. The solvents suitable for cellulose are either alkaline or acid, and in such

solvents, the ester groups in all positions are susceptible to cleavage. Moreover, degradation of the cellulose chain itself may also occur by oxidation.

The degree of polymerization governs the rate and the homogeneity of the reaction to some extent. By using a degraded cellulose, a certain degree of substitution may be reached in a shorter time than is required when the cellulose is composed of longer chains of glucose units. The usual method of esterification, the use of acids or their anhydrides in the presence of a dehydrating agent, usually results in considerable degradation of the cellulose. The rate of reaction has considerable influence, for, as in the case of nitration, the reaction is completed in a relatively short time and thus degradation is limited to the actual time of nitration.

PREPARATION OF CELLULOSE NITRATE

Cellulose nitrate may be prepared by subjecting cellulose to the action of nitric acid in the presence of a dehydrating agent whose main function is to take up the water of reaction. For each esterified hydroxyl group, one molecule of water is liberated.

Depending on the conditions of esterification, time, temperature, concentration of acid, etc., various degrees of substitution may be obtained. The completely substituted product is the trinitrate which contains a nitrogen content of 14.14 per cent according to the reaction:

$$C_6H_7O_2(OH)_3 + 3HNO_3 = C_6H_7O_2(ONO_2)_3 + 3H_2O$$

Strong mineral acids are usually used as dehydrating agent, although under certain conditions acetic acid and acetic anhydride (122) are reported to be satisfactory. The most common acid used is sulfuric acid, first used by C. F. Schoenbein in 1846 in Germany.

Cellulose nitrates may be prepared by submerging the cellulose in the form of cotton linters or other material, in a mixture containing nitric and sulfuric acids and water in certain proportions for a certain length of time at a temperature usually below 40 degrees Centigrade. The use of higher temperature, although having a favorable influence on the rate of reaction, would be detrimental, because the acid mixture also exerts hydrolyzing and oxidizing effects on cellulose. The degradation products formed from such side reactions must be removed because their presence would increase the rate of decomposition of the nitrate when stored or exposed to the atmosphere or heat. Even during nitration

at 30 degrees, certain amounts of such impurities are formed. In addition, acid residues in the form of cellulose sulfates or sulfanitrates must also be removed.

To remove degradation products and acid residues, the commercial nitrate is usually treated by boiling in slightly acid water (0.25 to 0.50 per cent acid calculated as sulfuric acid) (19) followed by decanting, and boiling with fresh water. Further treatments consist of pulping by a Jordan mill, and boiling in a dilute sodium carbonate solution, boiling in fresh water, and finally at least three washings with fresh water. For certain uses the nitrate is purified without pulping; thus the fibrous structure is retained.

THE MECHANISM OF THE NITRATION PROCESS USING SULFURIC ACID AS THE CARALYST

Of all the factors governing the process of nitration, the amount of water present exerts an essential influence upon the degree of substitution. The relation between the water content and the nitrogen content of the nitrate was revealed in the investigations of Lunge and Bebie (74). In general, an increase in the water content in the nitration mixture consisting of equal weights of concentrated nitric and sulfuric acids results in decreasing the degree of substitution in the resulting cellulose nitrate. In addition, it was found that with less than about 3.5 per cent of water in the nitration mixture, the reaction proceeds in a heterogeneous manner, some fibers being completely unnitrated (50).

The low degree of substitution and heterogeneous nature of the reaction would indicate that there is a lower limit for the water content as well as a higher limit.

Many investigations have been carried out using different conditions, time of reaction, temperature, percentage of nitric acid, sulfuric acid, and water (7,50). In general, it may be said that the rate of nitration increases with rise in temperature, but this is also accompanied by excessive degradation with a resultant decrease in the yield. The time of reaction is consequently decreased. The final nitrogen content is determined by the composition of the spent acid in contact with the cellulose nitrate rather than the original acid, thus an excess of acid is used in order to maintain the rate of reaction despite the increase in water content and decrease in nitric acid content due to the substitution.

The influence of the sulfuric acid is mainly twofold. In the first place, the sulfuric acid exerts a swelling effect upon the cellulose; and secondly, the sulfuric acid removes the water formed in the reaction by forming a hydrate (51).

Two reasons are suggested for the failure to obtain the theoretical nitrogen content (14.14 per cent) of the trinitrate. First, the reaction is one of esterification and is an equilibrium reaction. This has been demonstrated by leaving three nitrates of different nitrogen contents in two acid mixtures of different compositions for a long period of time. In each case the nitrates of each series, after treatment, contained the same degree of substitution (51). The second reason is that the sulfuric acid also reacts, and some cellulose sulfate is formed which is not converted to nitrate and is removed by the stabilization treatment.

NITRATION USING OTHER CATALYSTS

The replacement of sulfuric acid by phosphoric acid has been studied because products of better stability are obtained. The phosphoric acid exerts less degrading influence on the cellulose and has less tendency to esterify cellulose and to hydrolyze the nitrate than has sulfuric acid. It is therefore possible to prepare a nitrate of higher nitrogen content up to 14.01 per cent nitrogen under certain conditions (52). The resulting nitrate shows a higher viscosity and only a trace of phosphoric acid.

Other work has been done by Dorzens (18) and Brissaud (12) using a mixture of nitric acid, acetic anhydride and chloroform. A nitrate of 13.7 per cent nitrogen was obtained, and the products were found to be insoluble in ether-alcohol. Trogus (123) used a mixture of nitric acid and acetic acid for nitration obtaining products with different nitrogen contents when varying the ratio of the acids to each other.

THEORY AND METHODS OF FRACTIONATION OF CELLULOSE AND CELLULOSE DERIVATIVES

Introduction

In a discussion of the methods used to separate the different degrees of polymerization of cellulose and cellulose derivatives, classification of the methods is essential. The classification may be based on any one of several considerations: the purpose of the fractionation, the material fractionated, or the underlying principle of the method. According to the classification used by Cragg and Hammerschlag (15) the methods have been classified on the basis of the separation principle (see Table I).

TABLE I

CLASSIFICATION OF FRACTIONATION METHODS

	Method	Principle on which Separation is Based
I.	Solubility methods	Solubility decreases with molecular weight
	1. Fractional precipitation (a) By adding of precipitant (b) By cooling	
	2. Fractional solution (a) Solvent of varying composition (b) Varying temperature	
	3. Distribution between two immiscible solvents	Distribution coefficient depends on molecular weight
II.	Rate-of-solution method (diffusion into a single solvent)	Smaller molecules diffuse faster
III.	Ultracentrifuge	Sedimentation velocity increases with molecular weight
IV.	Chromatographic adsorption	Smaller molecules are preferentially adsorbed
V.	Ultrafiltration through graded membranes	Sieving action
VI.	Molecular distillation	Larger molecules are less volatile

Solubility Methods

The solubility methods for fractionating cellulose and cellulose derivatives depend on the greater solubility in a given solvent of the lower-molecular-weight species, and on the fact that the solvent power of the binary liquid mixture, composed of solvent and non-solvent, depends on the proportion of the two liquid constituents. If a precipitant, or non-solvent, is added to a solution of a polymer as in fractional precipitation, or if the polymer is added to the solvent-non-solvent mixture, as in fractional solution, two phases may be obtained at equilibrium if the proportions of the solvent and non-solvent are properly adjusted. The upper layer is a solution of the more soluble fraction of the polymer. The lower layer, or precipitated phase, is either a swollen gel, or a viscous liquid and contains the less soluble fraction of the polymer. The precipitated phase contains the fraction of higher molecular weight. The lower molecular weight material remains in the supernatant liquid.

One of the earliest theories of solubility fractionation was that proposed by Brønsted (13). "He suggested that when only the members of a single homologous polymeric series are considered, the potential energy of the polymer molecules is proportional to the molecular weight. The distribution of the molecules between the two phases is determined by the difference in potential energy, the less mobile large molecules collecting in the phase with the lower potential energy, the precipitated phase, the smaller and more mobile ones in the supernatant liquid." (15) The equation which he derived is

$$\ln \frac{c'}{c''} = \lambda M / RT \qquad (1)$$

where "c'" and "c"" are the concentrations in the two phases at equilibrium, "M" is the molecular weight of the polymer, and "λ" is a constant characteristic of the polymer-solvent system but is independent of the molecular weight.

Theories of Fractional Precipitation

At the present time there are three theories accounting for the fractional precipitation of different molecular-weight species from solution. One of the early theories was that of Schulz (34,35) who further developed the Brønsted theory by considering the distribution of the polymer between the two phases, the solution or supernatant liquid, and the highly swollen gel or precipitate, as being governed by the relative energies of the two phases and the Boltzmann probability for such energies. The second theory is the thermodynamic approach developed by Flory (34,35,37), Gee (39), and Huggins (55,56, 57). Entropies and heats of mixing are calculated for the solution and precipitate phases, and these are used in the thermodynamics of equilibrium between the two phases. The third theory is one proposed by Morey and Tamblyn (85).

Theory of Schulz

The theory of Schulz is based on a Brønsted-Boltzmann expression for the distribution of a substance in two immiscible solvents. Letting "E" represent the energy difference per molecule of the material on passing from the first solvent to the second solvent, and

by "a_1" and "a_2" the activities in the two liquids

$$\frac{a_1}{a_2} = K' e^{-\frac{E}{kT}} \qquad (2)$$

Schulz makes several assumptions in his development. He first assumes that the concentrations may be substituted for the activities. This is questionable at higher concentrations and also when the polymer is aggregated. He further assumes that the immiscible solvents may be replaced in the theory by the solution and the precipitate; the latter is considered as a fluid. The application to high polymers comes in defining "E" as proportional to the number of monomer units in the chain, and the proportionality factor as a linear function of the per cent of precipitant "P" which has been added to the solvent.

$$\frac{c_1}{c_2} = K'' e^{-(A+BP)\left(\frac{M}{kT}\right)} \qquad (3)$$

For a study of this nature, a convenient parameter is the per cent of precipitant just at the moment of precipitation. The saturated state and the values of concentration, precipitant, and temperature which will produce the saturated state make up an easily measured set of parameters. The concentration of the polymer in solution which produces saturation is designated as "C_γ"; the per cent of precipitant corresponding to this state of saturation is designated as "P_γ".

Schulz made one more assumption. He assumed that the concentration of polymer in the precipitated phase "C_2", is constant. This is known to introduce an error, which fortunately is counterbalanced by the error introduced when he replaced the activities by concentrations. Schulz thus obtained the equation:

$$C_\gamma = K e^{-(A+BP_\gamma)\left(\frac{M}{kT}\right)} \qquad (4)$$

in which "K", "A", and "B" are constants. At constant temperature this expression leads to two consequences which may be experimentally tested: (a) for constant molecular weight, "P_γ" is linearly related to log C_γ; (b) with the concentration the same at saturation for each different species precipitated, "P_γ" is linearly related to 1/M.

According to the work of Morey and Tamblyn (85), the first statement is true, the second statement only approximated. It should be noted that the energy difference between solution and gel is made proportional to the molecular weight. Thus, when the equation is applied to the start of precipitation, in the precipitate, the longer the chain, the greater the number of secondary links to other chains. This is the case for large-size particles, but in the initial coalescence only a few secondary cross links are required to establish a nucleus, this number being nearly independent of chain length. The probability of establishing these first links is related to the chain length, but this probability is not to be confused with the number of cross links required for initial coalescence.

Another assumption which has been noted by Flory and Huggins is the neglect of effects due to the entropy of mixing of polymer and solvent.

Thermodynamic Theory

An explanation for the large entropy of mixing was proposed by Meyer (82). He suggested that the deviation is due to the flexibility of the polymer molecules and to the vast differences in size of the solvent and solute molecules. As a model for a solution of a high polymer in a low-molecular solvent he proposed a lattice of $N_1 + nN_2$ sites, to be occupied by N_1 solvent molecules and N_2 polymer molecules, each of the latter consisting of n submolecules of a size comparable to that of

molecules of solvent. Flory (34,35,37) and Huggins (55,56,58,59) developed the thermodynamic approach independently. The approach is a general study of phase relationships from which, as particular cases, can be derived both fractionation by successive precipitation from solution, and fractionation by extraction from a highly swollen gel. An outline of the general theory is as follows: The partial molal free energy of the solvent, $\Delta \bar{F}_1$, and its activity, a_1, are expressed by the fundamental relation:

$$\Delta \bar{F}_1 = RT \ln a_1 = \Delta \bar{H}_1 - T\Delta \bar{S}_1 \qquad (5)$$

and for the polymer:

$$\Delta \bar{F}_2 = RT \ln a_2 = \Delta \bar{H}_2 - T\Delta \bar{S}_2 \qquad (6)$$

To predict a separation of phases requires a knowledge of these partial molal free energies. Thus, the partial molal heats of mixing and partial molal entropy changes on passing from one phase to another, must be calculated. For the heat term those using the thermodynamic approach take the form as given by Scatchard (100), and by differentiating with respect to the mole fraction of solvent or polymer, obtain:

$$\Delta \bar{H}_1 = B V_1 \phi_2^2 \qquad \Delta \bar{H}_2 = B V_2 \phi_1^2 \qquad (7)$$

V_1 and V_2 are the molar volumes, and ϕ_1 and ϕ_2 are the volume fractions which the solvent and polymer occupy in the whole system and B is a constant.

The entropy term is obtained from the Boltzmann definition of

entropy as the logarithm of probability:

$$S = K \ln \phi \tag{8}$$

The problem now becomes one of counting all the different ways in which the polymer and solvent molecules can be arranged. This procedure is difficult and requires assumptions as to the randomness of mixing, the absence of aggregation, the degree of flexibility of the chains, etc. Some of these assumptions have been considered by Flory (38), Alfrey and Doty (4), and by Schuchowitsky (103). The counting method is based on the assumption that the polymer-solvent system may be regarded as an assembly of lattice points or holes into each of which may be placed a solvent molecule or an equal sized polymer segment. The segments of a chain must be placed in neighboring lattice points, although not in a straight line. For cellulose derivatives, it must be assumed that on the average, the monomer units must be placed in a straight line before a kink occurs. By this means, variations in chain flexibility are incorporated into the theory. These entropy calculations result in expressions for the partial molal free energies:

$$\Delta \bar{F}_1 = \frac{RT}{\beta}\left[\frac{\beta B V_1}{RT}\phi_2^2 + \ln \phi_1 + \left(1 - \frac{V_1}{V_2}\right)\phi_2\right] \tag{9}$$

$$\Delta \bar{F}_2 = RT\left[\frac{\beta B V_2}{RT}\phi_1^2 + \ln \phi_2 + \left(1 - \frac{V_2}{V_1}\right)\phi_1\right] \tag{10}$$

Following Huggins, the coefficient "BV_1/RT" is designated as μ. The effect of "β" is to emphasize the heat term at the expense of the entropy term.

The calculation of the amounts of the components which will bring the appearance of a precipitate using the above equations is not simple analytically, but it can be done graphically. The compositions can then be plotted against "$\beta\mu$" or against the per cent of precipitant added to the solution.

Such a plot gives the limiting compositions at which a change in the number of phases takes place. This curve represents the case when the polymer is considered to be of one molecular weight; for each different molecular weight there is a characteristic curve as determined by the ratio V_2/V_1 appearing in the equations expressing the partial molal free energies.

From the work of Morey and Tamblyn (85) it is stated that the concentration, as well as the identity of a species determines the precipitation point, and further, a species of low molecular weight may start precipitating before one of higher molecular weight if the former is present in much greater amounts. Thus, the starting distribution plays a part in determining the heterogeneity of the fractions and necessitates a refractionation when abrupt changes in distribution are present. This effect of low molecular weight species precipitating before a higher one owing to the original distribution, is not to be confused with the true reverse-order (20), which is still found when the species are made to have equal concentration.

Fractionation by extraction may also be predicted by this outline of phase relationships (110).

The Relative Importance of the Entropy Contribution

It has been shown that a large portion of the thermodynamic development has been concerned with the inclusion of entropy effects which were neglected in the theory of Schulz. The size of the error resulting from disregarding the entropy terms must depend on the type of polymer molecule, and polymer solutions may be separated into two classes: (1) relatively uncross-linked polymers with large flexibility at each segment; (2) relatively rigid chains, such as cellulose esters, for which entropy effects are less pronounced and interaction effects are strong. For example, rubber molecules in solution may have such high kinking that the distance between the ends may be one-tenth the extended length; but considering cellulose esters, it appears that the entropy effects must be much smaller. Stein and Doty (119) concluded from a study of cellulose acetate in acetone that "The smaller molecules of cellulose acetate are approximately fully extended in acetone solution, but that the longer ones are bent in gentle waves." From other optical measurements, Doty and Kaufmann (23) conclude that cellulose acetate chains are relatively rigid, and they mention calculations by Simha indicating that such chains in solution have approximately one-half the extended length. Further evidence that interaction effects, rather than entropy effects, are a greater influence on solutions of cellulose esters, is given by the large differences in fractionating behavior obtained by the use of varied types of precipitants (86). Doty, Wagner and Singer (24) have recently showed that association may occur before the visual turbidity point is reached and that such associations may be quite stable. This condition gives a

different statistical counting than an ideally random solution and a lowered entropy contribution.

Schulz's theory should not be expected to hold for polymers with large flexibility at each segment, such as rubber, but when applied to cellulose derivatives (relatively rigid chains), its shortcomings due to the neglect of entropy terms are not particularly significant. Again, the thermodynamic treatment needs a careful consideration of the entropy contribution before it is applied specifically to cellulose derivatives. In the equilibrium rate theory, entropy is not calculated directly; but its effects are not completely ignored, since the probability of collision enters into the calculations.

Precipitation as a Reversible Reaction Considered from the Kinetic Viewpoint

A step common to the three theories is that of precisely defining the state of saturation. The measurable factors which define the saturation state are the per cent of precipitant (P_γ), the temperature (T), the concentration (C_γ) and the molecular weight (M_i) of the dissolved polymer. In practice a measure of this state is best obtained by carrying a little beyond saturation so that the precipitation has progressed enough to give a measurable turbidity. It is therefore necessary to consider the mechanics of the process of aggregations. The initial step consists of two chains coming together and remaining attached until two other chains have formed a similar union. It is assumed that for such a union it is necessary that the chains be joined through only a relatively few junction points, "n" in number, to form an aggregate. The rate at which one chain will be able to find another chain and establish with it the necessary "n" bonds is inversely

proportional to "n", and since the "n" bonds must all be between the same two chains, then the rate is proportional to the chain lengths "M_i" and "M_j" of the pair of molecules uniting. The rate will also be proportional to the number of other chains in solution from which one particular "M_i" can choose a partner. The number of such chains is proportional to the weight concentration of polymer "C_γ" divided by the average molecular weight. The rate of aggregation for a particular chain molecule is

$$(\text{rate})_i = D/n \cdot M_i \cdot M_j \cdot C_\gamma / M_a \qquad (11)$$

where "D" is a constant, including a diffusion coefficient. Thus, the rate for all possible pairs of chains is:

$$(\text{rate})_{\sum i} = D/n \cdot \tilde{M_i} \cdot \tilde{M_j^2} \cdot \tilde{C_\gamma} / \tilde{M_a} \qquad (12)$$

Now the assumption is made that all the different "M" values indicated may be replaced by the number average, "M_a". "D" may be further defined as proportional to the square root of the absolute temperature, and inversely proportional to both the chain length and the viscosity of the solvent, since both factors result in decreased mobility. Since the viscosity depends on the temperature, this would require further evaluation if the theory is tested by temperature experiments. Most data available are taken at some fixed temperature. Therefore,

$$(\text{rate})_{\sum i} = \frac{B T^{1/2} \tilde{M_a} \tilde{C_\gamma}}{n \eta} \qquad (13)$$

where "B" is a constant.

This rate is calculated on the assumption that all bondings are equally effective whether arising from various chain segments or from

end groups. There is evidence that the end groups may, under certain conditions, exert considerable influence. In considering a long chain, the action of the end groups can be differentiated from those groups attached to the inner segments. Highfield (53) showed that solvents for cellulose nitrate contain polar and non-polar groups, and he considered that each was necessary to solvate different parts of the polymer. The marked influence of traces of metallic ions, for example, calcium or magnesium, present in water used for washing newly acetylated cellulose is recognized commercially (124). The increased viscosity ("salt effect") which results has been explained by calcium bridges forming complexes of chains (97). This increased viscosity appears with acetone as solvent but does not appear with acetic acid, according to Lohmann (72). This requirement of particular groups and particular solvating medium has also been found necessary for the reverse-order precipitation (85,86), which is to be discussed later in this study.

Since the size of the linear chain determines the number of inner segments but has nothing to do with the number of ends of the chains, the quantities "M_i" and "M_j" which appear in equations 11, 12, and 13, do not effect the contribution of the end groups to the aggregation rate. The combined rate becomes:

$$\text{Aggregation rate} = \frac{B T^{\frac{1}{2}} C_\gamma M_a + f B T^{k} C_\gamma^{2} M_a^{3}}{n n} \qquad (14)$$

where "f" is a weighing factor which weighs the relative bonding strength or the importance of the end-containing bonds as compared to segment-segment bonds, in adding stability to the embryo aggregate. Thus, "f" varies with the solvent-precipitant system chosen.

The rate of aggregation to the rate of solution is now equated, the latter being due to secondary bonds receiving excess thermal energies:

$$\frac{B T^{\frac{1}{2}} C_\gamma^{\sim} \left(M_a + f/M_a^3 \right)}{n \eta} = e^{-\frac{E_s}{kT}} + f e^{-\frac{E_e}{kT}} \qquad (15)$$

"B" may be further defined to include the additional constants introduced. The weighting factor "f" appears on the right hand side of the equation, since if the end groups are important in forming an aggregate, the breaking of an end-containing bond will be equally important for the disappearance of the aggregate. The terms "E_s" and "E_e" are the dissociation energies of the segment-segment and the end-containing bonds. These energies depend upon the randomness of the collisions of the polymer molecules and the introduction of the precipitant molecules. It is assumed that "E_s" is linear with "P_γ":

$$E_s = s P_\gamma - U_s \qquad (16)$$

where "U_s" is a constant related to the energy of association between segment and solvent. The proportionality factor "s" could be defined in terms of the cohesive densities of the polymer, solvent, and precipitant, but it is not essential to the present development of this theory, and therefore only the dependence of "s" upon concentration shall be presented. For low polymer concentrations the bonds in the embryo aggregate are surrounded by mostly small molecule material. As the concentration is increased, the segments from still other chains form part of the shell of neighbors around the secondary link being considered.

This will in effect aid the precipitation so that it is assumed

$$E_s = S_s P_\gamma (1 + C_\gamma/100) - U_s \qquad (17)$$

and also

$$E_e = S_e P_\gamma (1 + C_\gamma/100) - U_e \qquad (18)$$

where "C_γ" is expressed in grams per 100 grams of solution.

Equations 15, 17, and 18 may now be applied to specific conditions. Considering normal-order precipitation in which the influence of the end groups may be neglected, the weighting factor "f" is assigned a very small value. Then

$$C_\gamma^2 = \frac{n\eta}{BT^{\frac{1}{2}}M_a} e^{-S_s P_\gamma (1 + C_\gamma/100)/kT} e^{U_s/kT} \qquad (19)$$

$$\simeq \frac{n\eta}{BT^{\frac{1}{2}}M_a} e^{-S_s P_\gamma/kT} e^{U_s/kT}$$

for concentrations below ten per cent. This equation predicts: (a) with increasing molecular weight, a decrease in the concentration at which precipitation begins; (b) with increasing amount of precipitant, a decrease in the concentration needed for saturation; (c) for some systems, an increase in the concentration needed for saturation, with increasing temperature. Two other predictions are made, for which the experimental evidence is less known; (d) at a fixed molecular weight, there is a linear relation between log C_γ and P_γ. The actual concentration at each precipitation point must be used; (e) at a fixed value of C_γ, there is a linear relation between log 1/M and P_γ.

Reverse-Order Precipitation

The reverse-order precipitation is particularly adapted to the use of a polymer-solvent-precipitant system in which the end groups are very active. This corresponds in equation 15 to making the weighting factor "f" a large value. In the extreme case, terms not containing "f" are neglected and for low concentrations the equation becomes:

$$C_{\gamma}^{\sim} = \frac{n \eta M_a^3}{B T^{1/2}} e^{u_e/kT} e^{-S_e P_\beta / kT} \qquad (20)$$

With an increase in molecular weight, the concentration required for saturation increases; that is, the shortest chains will precipitate first. Some cases of this have been reported previously (86). Further study (85) has shown that it is not a temperature-dependent phenomenon, but does depend to a great extent on the concentration of the polymer solution used.

The reverse-order effect is associated with the formation of aggregates in the early stages of their growth, and by the use of a very sensitive detecting apparatus is picked up at low concentrations. It is interesting to note that when precipitation is allowed to proceed to the growth of large particles, the longer chains again become more able to precipitate first. Therefore, a fractionation designed to obtain the lower-molecular weight species first must keep the precipitates small.

Equation 20, which predicts the appearance of reverse-order precipitation, does not explain its dependence on concentration. To explain this dependence, it is necessary to connect "E_e" more fully with the state of aggregation. For the bonds which lie in the center of an aggregate, the type of solvation is likely to be different from that

for those bonds which are on the surface. For very small aggregates, where the ratio of volume to surface is small, this difference may produce marked effects in the value of the average solvation and the "E_e" value to be chosen.

It is also possible to find cases where "f" is intermediate in value (see equation 15), and the end and segment bondings both contribute to aggregation. Over a limited range, precipitation can possibly occur without any preference as to molecular weight. One such case has been reported by Battista and Sisson (8).

The Efficiency of Fractionation

The efficiency of fractionation is a prime essential of practical importance, and it should be examined in the course of the development of theories. It is unusual that in such a discussion so much attention has been paid to the concentration while the importance of the choice of the system has not been understood. In one case (54), a number of solvent-precipitant systems for cellulose acetate were examined and the combination chosen was the one which spread out the fractions over the greatest range of per cent precipitant. The advantage is that less precision is required in adding the proper amount of precipitant for approximately equal fractions.

Admitting that the spreading of the fractions over a wide range of precipitant is desirable, this leaves unanswered the obtaining of fractions which are spaced in molecular weight.

As to the use of low concentrations, it must be determined critically whether the gains predicted by approximate theory are sufficient to justify the disadvantages attending such a procedure. The opinion

has been expressed by Morey and Tamblyn (86) that too much emphasis has been placed on the use of low concentration. Spurlin (114) carried out a fractionation of nitrocellulose from a ten per cent acetone solution using n-heptane as the precipitant, and he reported a good degree of molecular weight separation. In connection with this work, it is of interest to note that Spurlin also used a refractionation procedure for fractions of similar viscosity to increase the molecular weight separation, and furthermore, he used a type of nitrocellulose known as "Hercules RS-$\frac{1}{2}$ Second" which has an extremely low viscosity. As reported by Hercules Powder Company in "Nitrocellulose" (47) the viscosity of RS-$\frac{1}{2}$ Second nitrocellulose in a solution composed of 12.2 per cent dry nitrocellulose in a solvent composed of 25 per cent specially denatured No. 1 ethyl alcohol, 20 per cent ethyl acetate, and 55 per cent toluene averages 190 centipoises.

The expressions for denoting efficiency as deduced by Schulz and Flory are more concerned with the volume fraction of the precipitated phase than with the concentration. Efficiency is concerned more with obtaining a large number of small fractions than it is with the overall concentration.

In precipitation, a species is not one pure molecular weight, but it is a band of neighboring sizes which are not distinguishable, and these can be considered to interact. When the molecular weights are far enough apart for low concentrations, these can be considered as acting independently.

Fractional Precipitation

Fractional precipitation procedures are those in which the polymer is completely dissolved in a suitable solvent and then partially precipitated. The precipitated phase, which contains the high molecular weight material, and the supernatant solution are separated by decantation. More of the polymer is then precipitated, and the procedure is repeated. There are two principal methods of precipitation which will be considered. The first method is concerned with the adding of a precipitant under isothermal conditions; the second method pertains to the addition of the precipitant at one temperature and the precipitation occurring at a lower temperature. A combination of these two methods can be used.

In a fractionation the choice of solvent and precipitant is very important. Relative solvent and precipitating powers can be determined by titrating a solution of the polymer in the solvent with the precipitant using the sudden appearance of turbidity as the end point. The larger the amount of precipitant needed to reach the end point for each solvent in a series, the greater is the solvent power of the solvent; or if a series of precipitants is used with a constant solvent, the smaller is the precipitating power of the precipitant.

Theories as to why liquids differ in their solvent and precipitating power have not been completely developed. Gee (40) showed that the solvent power of a binary liquid mixture is intermediate between that of the components if they mix ideally. If the heat of mixing is large, the solvent power of the mixture is greater relative to that of

the components. Erbring (31) found in his work using the saturated monhydric alcohols from methyl to octyl that a direct relationship existed between the precipitating power and the dielectric molecular polarization of the alcohol on the system cellulose acetate in acetone. Since the molecular polarization increases with the molecular weight of the alcohol, the higher alcohols are more effective than the lower ones in precipitating polar substances, such as cellulose derivatives. A more significant relationship is that which exists between the precipitating power and the quantity μ^2/ϵ where μ is the dipole moment and ϵ is the dielectric constant. This relationship has been found to be approximately linear (30,32). Studies have been made by other workers (41,65,76,121).

Fractional Precipitation under Isothermal Conditions

In this method the precipitant is added to the polymer solution in a suitable amount to cause separation into two phases but not enough to cause complete precipitation of the dissolved polymer. The phases are then separated either by decantation directly or by centrifugation followed by decantation. The precipitant is again added to the supernatant liquid until the formation of a precipitate is observed. Separation of the two phases is again accomplished. The concentration of the polymer in the solvent has been considered by many investigators as being a very important factor in obtaining efficient fractionation, but Morey and Tamblyn (85) have expressed the view that the concentration is a minor factor.

A precipitation titration may be used to determine the solvent power of the solvent. The end point of such a titration may be located either

visually or by instrumental means (1,33,41). Viscosity measurements have also been used for this purpose (48,69,75,96,99). The decrease in viscosity upon addition of the non-solvent is explained as due to tighter curling and more compact shape of the polymer molecules in the "poorer" solvent medium. With further addition of non-solvent, the viscosity decreases less rapidly and may become constant or increase slightly. A sudden decrease in viscosity occurs when precipitation begins, producing a sharp break in the "viscometric" titration curve at the end point.

In a preparative method, the fractions are recovered from the precipitated phase either by evaporation of the solvent and drying, or by redissolving in a suitable solvent and precipitation in a non-solvent resulting in the formation of a fibrous or amorphous form which may then be filtered and dried.

In an analytical method, the amount of unprecipitated polymer in the supernatant liquid is determined by evaporating an aliquot sample. The fractions are not isolated since a distribution curve can be obtained from the viscosities of the solution as the precipitant is added (14).

The first paper to be published on fractional precipitation of cellulose nitrate was that of Duclaux and Wollman (29) in 1920. In their procedure, they obtained three fractions from an acetone-water system; these fractions differed in viscosity but not in nitrogen content.

Kumichel (69) in 1928 described the method of locating the precipitating point viscometrically. He found anomalous changes in viscosity on adding a 1:1 acetone-water solution to an acetone solution

of cellulose nitrate. After separation, two fractions were obtained by drying the precipitate and ultrafiltering the supernatant liquid. The uniformity of the fractions could be improved by a repetition of this procedure.

In 1929 Duclaux and Nodzu (27) compared fractional precipitation with other fractionation methods involving diffusion and ultrafiltration. The earlier finding, that fractions differ in molecular weight, but not in the degree of nitration was confirmed.

Beck, Clement, and Riviere (9) in 1930 used a 16 per cent solution of cellulose nitrate in acetone adding varying amounts of 20–80 per cent water–acetone mixture. They obtained four fractions. A continuous procedure was described in which a mixture of cellulose nitrate, acetone, and water was distilled at reduced pressure at room temperature. As the acetone evaporated more rapidly than the water, a composition was soon reached at which precipitation began, and thereafter precipitation proceeded as the distillation proceeded. This method gave eleven fractions.

In 1933 Duclaux and Barbiere (26) showed that there is a limit beyond which the uniformity of a fraction cannot be improved by further fractionation.

In 1934 and 1935 Glikman (42,43,44,45,46) used Duclaux's method in his study of cellulose nitrate fractions. Solvents other than acetone were used. A fractionation by vacuum and ordinary distillation of a cellulose nitrate–acetone–water mixture was also attempted (45).

In 1935 Rogovin and Glaxman (98) used Duclaux's method to separate commercial cellulose nitrate into three fractions but found a lower nitrogen content in the lowest fraction.

Schulz (104) in 1936 used a similar method but carried out the separation at a temperature of 27 degrees Centigrade.

In 1938 Spurlin (114) rejected water as a precipitant because it produces a high Tyndall effect. He used acetone as a solvent and heptane as a precipitant. He made a study of the mechanical properties with molecular weight.

Rath and Dolmetsch (95) also tried a fractional precipitation method using water or ethanol as the precipitant.

In 1940 Jurisch (63) precipitated cellulose nitrate from an acetone solution using water as the precipitant.

In 1941 and 1942 Schulz (106,107) fractionated cellulose nitrate but did not describe his method.

Sugarman (120) in 1942 used a fractional precipitation procedure to obtain ten fractions of cellulose nitrate. He used methyl alcohol as the precipitant.

Jones (62) in 1943 used an original concentration of five grams of cellulose nitrate to one liter of acetone. He used water as the precipitant and obtained ten fractions.

Tasman and Corey (122) separated nitrated pulp into three fractions using acetone as the solvent and water as the precipitant.

A study of the molecular properties of cellulose nitrate was made by Blaker, Badger and Noyes (11). The cellulose nitrate fractions for this work were prepared by using as the solvent a mixture of three parts (by volume) of commercial 95 per cent alcohol and five parts of acetone. The precipitant was ligroin which was added under controlled conditions. The fractions obtained were refractionated by the same procedure.

Fractional Precipitation by Cooling

The precipitation point of a polymer-solvent-precipitant solution is dependent upon the temperature (3,17,36,104,105). This temperature dependence of solubility can be and has been used in carrying out fractionations. Mark (77) states that better separation can be obtained this way than by fractional precipitation under isothermal conditions. The process is somewhat analogous to fractional crystallization in low-molecular chemistry, but the precipitates are usually not crystalline.

Fractional Solution

The solution is placed in contact with a solvent-non-solvent mixture, and the system is allowed to come to equilibrium. After the supernatant liquid is decanted, the residue is treated with a fresh mixture, richer in solvent than the first, and this process is repeated until the polymer has dissolved, or until no more will dissolve. Low-molecular fractions are extracted first, the high-molecular ones last.

Like those involving fractional precipitation, fractional solution procedures can be classified according to whether it is the composition of the extracting mixture or the temperature that is being varied.

Distribution Between Two Immiscible Solvents

In the fractional precipitation and solution methods, the solvent and precipitate are completely miscible. Only the presence of a polymer (under certain conditions) will cause a separation into two

phases. A solvent system which is heterogeneous in the absence of polymer molecules depends on the molecular weight (13,108).

This method has been applied to polyethylene oxide (108) and lignin (73). In the latter application, fractions obtained differed both in viscosity and in methoxyl content.

Although only two applications of this method have been reported, it could be used with any high polymer provided that a suitable solvent system could be found. Schulz and Nordt (108) expressed the opinion that fractional precipitation is preferable because of better efficiency whenever applicable.

Rate of Solution (Diffusion) Methods

The methods described in this section are sometimes classed with fractional solution methods, but they should be treated separately since they are based on a different principle. The separation according to molecular size depends on the difference in the rate of solution or diffusion of the different species. In solubility methods equilibrium conditions should prevail; in diffusion methods the fractions are separated while they are still diffusing. The method involves placing the polymer in contact with a solvent, removing the supernatant solution after a definite interval, replacing it with fresh solvent and repeating the process until the desired number of fractions has been obtained. The smaller molecules concentrate in the first fractions, because they diffuse more rapidly than the large ones which are found in the last fractions.

Application of Diffusion Methods

Diffusion methods have not been applied to cellulose esters except in a few cases. Krueger (68) in 1928 used a method of diffusion in which he let 20 cc. of a solution of nitrocellulose in acetone, methanol, amyl acetate and other solvents diffuse against 60 cc. of pure solvent. After a definite time, four layers could be separated which differed both in molecular weight and in degree of nitration.

In 1929 Duclaux and Nodzu (27) mentioned that nitrocellulose can be fractionated by solution in ethanol.

Ultracentrifugation

An ultracentrifuge is an instrument in which sedimentation in centrifugal fields can be measured quantitatively. The centrifugal fields employed are usually very strong, and the apparatus is a complex and specialized piece of equipment. The best ultracentrifuge in existence is still that of The Svedberg, although several other types have been developed.

An ultracentrifuge can be used to measure sedimentation velocity and sedimentation equilibrium. The latter method is used for molecular-weight determinations on high polymers; the former can be used for molecular-weight determinations, but its chief value is for the measurement of heterogeneity.

From Stokes' law it may be seen that the sedimentation velocity under gravity depends on the size of the particle. The same is true in a centrifugal field, except that the force applied is much greater, and thus, is made large enough to apply to particles of colloidal dimensions. When a strong centrifugal field is applied to a high-polymer solution composed of a single species, the particles will settle at the same rate. The boundary between the solution and particles will move outward from the center of rotation and will remain sharp except for a slight spreading due to diffusion. In a polydispersed system, the particles will settle at different rates according to their respective sizes, and the boundary will spread more and more as it moves down. The amount of spread of the boundary is measured by optical means and is a measure of the heterogeneity of the

sample.

The ultracentrifuge furnishes an analytical method of separation, and as an analytical method it is one of the best available.

One of the main contributors in the use of ultracentrifuge was Kraemer (66,67) who pointed out that cellulose is continuously heterogeneous, that all the members of the homologous polymeric series within a certain range are present. His results are in contradiction to those of Stamm (116,117) who in 1930 reported cellulose as being composed of essentially one species with only a small proportion of smaller particles.

However, the fact remains that the ultracentrifuge is an expensive and highly complex piece of equipment which few laboratories can obtain, and therefore its use has not become widespread.

Chromatographic Adsorption

Chromatographic adsorption is a method for separating mixtures into their components. The method consists of filtering the solution containing the mixture through a column of an adsorbent, developing the chromatogram by washing with pure solvent and then eluting various parts of the column separately to recover the adsorbed material. The separation is based on the principle of preferential adsorption. The species preferentially adsorbed are found in the upper part of the tube, those more poorly adsorbed in the lower part, and the most poorly adsorbed remain in the solution. Elution reverses the process of adsorption; the substance passes from the adsorbed layer into solution again. This can be carried out either by filtering the elutant through the column and collecting the filtrates in a series of containers as the bands are washed out of the container separately, or by dividing the column into bands and eluting each separately. It has been found that the smaller molecules are preferentially adsorbed, and therefore, fractionation of homologous polymeric mixtures is possible.

The first study of this method as applied to the fractionation of high polymers was made in 1936 by Mark and Saito (78) who tested blood charcoal, aluminum oxide, calcium carbonate, and starch as adsorbents and acetone as solvent and dioxane as the elutant. They successfully fractionated cellulose acetate and found their fractions differed in molecular weight but not in acetyl content.

In 1937 Levi and Giera (71) repeated the experiments of Mark and Sato, and they recommended the use of 2:1 ether-alcohol as a solvent for the chromatographic fractionation of cellulose nitrate with blood charcoal as the adsorbent.

Ultrafiltration

Ultrafiltration is the process of separating particles of different sizes by the use of carefully graded cellulose or nitrocellulose membranes. The pore sizes of the membranes are chosen in such a manner that particles up to a certain size can pass through the membranes, but the larger ones cannot. Such a method is satisfactory enough for spherical particles, but in the case of chain-polymeric molecules whose sizes are of colloidal dimensions in one direction, and of molecular dimensions in the other, the long molecules should pass through the pores as easily as the short ones. Other factors such as the coiling up of the chains and internal Brownian movement exert considerable influence on the long molecules.

Ultrafiltration has been used with success for the fractionation of cellulose derivatives by Beck (9,10), Duclaux (27,29), and Kumichel (69). Other investigators consider this method to be too slow, and Meyer (81) considers it as unsatisfactory for long chain polymers.

Molecular Distillation

Molecular distillation has not been used as a method of separation of cellulose derivatives. The method essentially consists of distillation at a very low pressure, .001 to .0001 mm. of mercury. The distance between the distilling pan and the collecting plate is shorter than the mean free path of the evaporating molecules, so that on the average they suffer no collisions in the vapor state. Under these conditions, even slightly volatile substances can be distilled without decomposition. The method of molecular distillation is, however, useful for the purification of a high polymer, that is, the removal of the low molecular weight fraction.

METHODS OF DETERMINATION OF THE MOLECULAR WEIGHT OF CELLULOSE NITRATE

Introduction

The question of how many glucose residues compose the chain molecule of cellulose and its derivatives has been the subject of many investigations; and in the course of these investigations, it has been determined that cellulose or its derivatives can be separated into several fractions, each of which may be shown to have an average chain length different from that of the original. As yet, it has not been possible to separate cellulose or its derivatives into as many fractions as there are chain lengths in the original material. Thus, the chain length of any cellulose preparation represents an average degree of polymerization of a heterogeneous sample. If the polymer is a linear polymer, that is, there is no cross-linking, the average chain length of the aggregate will give its molecular weight.

The methods used for the determination of the average chain length of cellulose nitrate are physical methods and are applicable to the substance in a state of molecular dispersion. The cryoscopic methods of molecular weight determination, boiling point elevations and freezing point depressions, are impractical because the changes are too small to be of any value for calculation. Certain chemical methods such as end-group determinations are useful for cellulose itself but cannot be applied to cellulose nitrate.

Osmotic Pressure Measurements

It was recognized quite early that colloidal solutions, including cellulose derivatives, gave easily measured osmotic pressures. Ostwald (94) pointed out that it is necessary to extrapolate to zero concentration to obtain satisfactory molecular weight determinations. This observation was immediately followed by a series of investigations in many laboratories.

The series of investigations initiated by Duclaux (28) and continued by other coworkers (21,22) showed that the molecular weight is independent of the solvent employed.

The methods employed in the Duclaux laboratory required a relatively long time for a determination, and a different type cell was developed by Herzog and Spurlin (91) to secure rapid attainment of equilibrium.

Staudinger's Viscosity Method

Much of the early work on the correlation of the molecular weights of cellulose derivatives with other properties depended on the application of Staudinger's rule (118) which is defined as

$$\frac{\eta_{sp}}{c} = K_m M \qquad (1)$$

in which η_{sp} is the specific viscosity, c is the concentration, M is the molecular weight, and K_m is a constant. This empirical equation was founded mainly on cryoscopic and end-group determinations with very low molecular weight polymers. The uncertainty in extrapolating these

results to high molecular weight polymers caused the method to be received with considerable doubt.

To determine the value for "K_m" in the above equation, the molecular weight of the cellulose derivative must be determined in some way. The osmotic pressure method or the ultracentrifuge method can be used. The specific viscosity is determined preferably in the same solvent. From the molecular weight and the specific viscosity "K_m" can be calculated.

Staudinger's viscosity rule is based upon a number of suppositions which are not always true. One of the basic assumptions is that the solutions of cellulose and cellulose derivatives contain these materials dispersed into single molecules. Another is that the chain molecules represent stretched-out rod-shaped units which retain their shape in solution. Both assumptions have been criticized (2,60,87,88,111). However, the method permits a convenient means of determining a relative molecular weight and is of practical value.

Modifications of the Viscosity Method

In recent years Kraemer (66) has developed a more reliable method for calculating molecular weights from viscosity measurements. The viscosities are expressed as intrinsic viscosities extrapolated to zero concentration:

$$[\eta] = \left(\frac{\log_e \eta_r}{c} \right)_{c \to 0} \qquad (2)$$

in which "η_r" is the viscosity of the solution relative to that of the solvent and "c" is the concentration in grams of solute per 100 cc. of solution.

Kraemer's method has recently been applied to a study of the molecular heterogeneity of cellulose nitrate (11,25).

The Ultracentrifugel Method

The ultracentrifuge method of determining the particle size of cellulose polymers by observing the phenomena of sedimentation and diffusion supplies a direct method of determining both molecular weight and the degree of heterogeneity of the preparations under investigation.

The ultracentrifuge was developed by Svedberg and co-workers among whom was Kraemer. Kraemer listed the advantages of the ultracentrifugel method (66), but the disadvantages of high cost of equipment and highly skilled technique outweigh the advantages, and consequently, the ultracentrifuge is not widely used.

VI. EXPERIMENTAL PROCEDURES AND RESULTS

Materials Used

The cellulose nitrate was Lot 1379, Type 600-1000 seconds, obtained from Hercules Powder Company, Parlin, New Jersey. The nitrogen content was reported to be 12.07 per cent.

The acetone was chemically pure grade and was obtained from Commercial Solvents Corporation, Peoria, Illinois.

The ethyl acetate was technical grade 85 - 88 per cent ethyl acetate obtained from Commercial Solvents Corporation, Peoria, Illinois.

The n-butyl acetate was technical grade obtained from Eastman Kodak Company, Rochester, New York.

The n-heptane was pure grade 99 mole per cent minimum obtained from Phillips Petroleum Company, Bartlesville, Oklahoma.

The primary purpose of this study of fractionation conditions was to develop a precise method of separating the high-viscosity cellulose nitrate into ten fractions of different average degrees of polymerization. In order that such a method be developed there were several requirements to be met.

It was known that the selection of the solvent and non-solvent could be made from previously reported experimental work. The proper solvent should be non-hygroscopic and should have a fairly low vapor pressure at room temperature. The density of the solvent and non-solvent should be preferably less than that of water. The solvent should form a true solution with cellulose nitrate, and this solution must be water-white. The non-solvent should be miscible with the solvent in all proportions, non-hygroscopic, and should have a low vapor pressure at room temperature. The precipitating power of the non-solvent should be such that a relatively small amount will produce turbidity in a solution of the solvent and cellulose nitrate. Finally, recovery and separation of the solvent and non-solvent are imperative. Therefore, azeotropic mixtures of solvent and non-solvent must be avoided.

The concentration of the cellulose nitrate in the solvent was a factor to be considered, but this could be determined only by experiment.

It was decided to use a fractionation procedure combining the precipitation method with a temperature decrease. This temperature differential was to be determined by experiment.

To obtain separation of the solvent-non-solvent-polymer system into two phases requires a period of standing at the temperature experimentally determined as satisfactory for the formation of a gel phase from which the supernatant liquid can be easily separated. This period of standing may

be chosen arbitrarily according to the attainment of solution-precipitation-equilibrium.

The recovery of the precipitated phase is another factor to be considered. The precipitate can be recovered by: (1) evaporation of the solvent, thus forming a film which may be removed from the flask; and (2) by redissolving it in some solvent which is completely miscible with water and the cellulose nitrate is precipitated out in a fibrous or amorphous form. Previous work by Jones (62) indicated that the latter method is satisfactory for the cellulose nitrate fractions.

It should be noted that selections of conditions, solvent and non-solvent must lead to a procedure of separation in which the results obtained may be reproduced.

A study of the literature indicated that a solvent often used was acetone, and although it did not fulfill all the requirements, it was chosen. The choice of a non-solvent was based on the work of Spurlin (114) and was n-heptane.

The first experiments run indicated the choices of solvent and non-solvent were satisfactory, and it was also found that a solution of cellulose nitrate in acetone could not exceed 2.5 to 3.0 per cent if a viscous solution were to be avoided.

In the first experiments a solution of acetone containing 2.5 per cent cellulose nitrate was prepared by dissolving 20.5 grams of oven-dry cellulose nitrate in one liter of acetone. Samples consisting of 200 cc. of this solution were measured into Erlenmeyer flasks. The n-heptane was added from a 50 ml. buret until a slight turbidity persisted after complete mixing. Gentle agitation was maintained during the addition of the n-heptane to prevent localized precipitation.

A series of experiments was run to determine the proper temperature differential to use. The series included samples to which the non-solvent was added at the first temperature given, and the system was allowed to stand overnight at the second temperature given. The series of experiments included samples run at 27 degrees - 15 degrees, 25 degrees - 15 degrees, 21 degrees - 15 degrees, 18 degrees - 18 degrees, 15 degrees - 21 degrees, 15 degrees - 24 degrees, and 15 degrees - 27 degrees. From this series of experiments it was decided that a temperature drop of from 10 to 12 degrees was sufficient to produce a hard precipitate from which the supernatant liquid could be decanted without difficulty.

Other investigators have reported the use of optical means in determining the turbidity necessary to give a precipitate (1,33,41). It was decided that the use of an optical instrument might provide a more accurate means of determining the precipitation point.

A Hellige nephelometer was first used to determine the proper turbidity to give a precipitate. Later a Klett-Summerson potentiometric colorimeter was used to continue the study. From Table I, in which results of several series of experiments are given, it is seen that there is no correlation (1) between the amount of heptane added and the colorimeter reading; (2) between the amount of heptane added and the percent of precipitate obtained; (3) between the colorimeter reading and the percent of the precipitate obtained. The conditions used in these experiments were: a 200 cc. sample of acetone solution containing 2.5 per cent by weight cellulose nitrate; the addition of n-heptane at 27 degrees and subsequent cooling to 15 degrees and standing for a period of 21 hours.

It was thought that with the addition of n-heptane the formation of aggregates was so rapid that solution equilibrium could not be attained,

Table I

Titrations Using Klett-Summerson Potentiometric Colorimeter

cc. of Heptane added	Colorimeter reading	% Precipitate obtained
114.5	42	77.2
115.5	41	74.3
117.5	40.5	75.2
117.5	40	89.5
115	38.5	45.4
115	40.5	43.5
115.5	38	44.9
114	37	30.8
115	40.5	41.4
115	42	45.4
116	40.5	45.4
113	33	40.5
114.5	40	46.5
115	34.5	48.2
115	36	50.0
117	42	56.4
114	26	29.0
114	29	33.2
115	28	35.5
116	—	38.9
114	31	42.1
115	33	43.7
115	34.5	45.5
115	30	38.6
115.5	34	49.4
116.5	38	53.2
110	24	16.0
110	25	11.3
110	26	25.6
110	27	18.5
110	27	28.5

Samples consisted of 200 cc. of acetone containing 2.5 per cent by weight cellulose nitrate. n-Heptane was added at 27 degrees. Samples were allowed to stand for 21 hours at 15 degrees Centigrade. Colorimeter was set at zero reading for distilled water.

and the precipitate thus might contain occluded material of short chain lengths.

In order to decrease the rate of addition of the heptane and the subsequent disturbing of the solution equilibrium, it was decided to use a mixture of acetone and heptane (25-75 by volume) as the precipitant. The results of several series of experiments using the diluted precipitant are given in Table II. A study of these results indicated that some variable was entering into the procedure in such a manner as to prevent reproducible results from being obtained. In one series of experiments the addition of 220 cc. of the acetone-heptane precipitant produced a precipitate of 25 per cent. In a similar run, the precipitate obtained with the same amount of precipitant was 38.3 per cent. The uncontrolled factor was believed to be the effect of moisture absorption by the acetone. These experiments were run during a period of high relative humidity, and the acetone used might have been exposed to the air sufficiently to allow the absorption of water vapor. The presence of a small amount of water in acetone enhances the solvent power of the acetone. Therefore, to minimize the effect of this absorbed moisture, it was decided to add an arbitrary amount of distilled water to the acetone. Thus, enough distilled water was added to the acetone to increase the moisture content in one series of experiments to 2.5 per cent, in another series of experiments to 5 per cent. The results of these experiments are given in Tables III and IV.

It was found that in all samples the precipitates were highly solvated gels, and decantation was difficult. The percentage of the cellulose nitrate obtained was much greater than the desired ten per cent. Therefore, it was decided that the proper solvent for such a fractionation procedure was not acetone, nor acetone containing 2.5 per cent or 5 per cent additional

Table II

Results Obtained Using an Acetone-Heptane Mixture as Precipitant

cc. of Mixture added	Colorimeter Reading	% Precipitate Obtained
225	25	36.5
230	33	50.0
200	13	0
205	14	0
210	16	0
215	18	0
216	16.5	0
217	15.5	0
218	16	16.8
219	17	22.3
220	27	25.0
217	24	31.3
217.5	25.5	33.8
218	26	33.8
218	28.5	37.3
218.5	27	37.1
219	28	37.7
219.5	26	29.7
220	28	38.3

Sample consisted of 200 cc. of acetone containing 2.5% cellulose nitrate. Precipitant mixture (acetone-heptane 25 - 75) was added at 27 degrees, and sample was allowed to stand for 21 hours at 15 degrees Centigrade.

Table III

Results Obtained Using Acetone Containing 2.5% Water Added as Solvent

cc. n-Heptane Added	% Precipitate Obtained
92	27.2
95	67.
100	78.
105	83.
107	84.
109	87.6

Samples consisted of 200 cc. of solution. n-Heptane was added at 27 degrees. Sample was allowed to stand for 21 hours at 15 degrees Centigrade.

Table IV

Results Obtained Using Acetone Containing 5.0% Water Added as Solvent

cc. n-Heptane Added	% Precipitate Obtained
87	83.3
87	83.7
88	85.6
89	87.1
90.6	87.5

Samples consisted of 200 cc. of solution. n-Heptane was added at 30 degrees. Sample was allowed to stand for 21 hours at 15 degrees Centigrade.

distilled water, and a search for a more satisfactory solvent was begun.

Several solvents were used in test tube experiments including α and β -picolines, nitromethane and nitropropane. None of these was satisfactory.

It was known that the alkyl acetates were widely used as solvents for cellulose nitrate in lacquers, paints and plastics. These esters are not completely miscible with water in all proportions, and their boiling points increase rapidly. Again the separation and recovery of the solvent was considered. The ethyl ester boils at 77 degrees, the propyl ester at 101.5 degrees, and the butyl ester at 126.5 degrees.

The solvent used cannot have a boiling point above 100 degrees because cellulose nitrate decomposes rapidly at elevated temperatures. This fact eliminated butyl acetate. If n-heptane were used as the precipitant, propyl acetate could not be used due to the small difference in respective boiling points. Thus, the only choice was ethyl acetate. Methyl acetate was not considered due to its high volatility and solubility in water.

Due to the scope of operations in this procedure, it was necessary to secure the ethyl acetate in large quantities. Therefore, commercial grade ethyl acetate (85 to 88 per cent) was selected.

A small quantity of technical grade ethyl acetate (99.5 per cent) was available, and a series of experiments was begun to determine whether the temperature differential and concentration should be changed. In the first tests, the precipitated phase was formed as a hard gel and contained a very small amount of solvent. The rapidity of the separation was such that long-time standing was not necessary to obtain two separate phases. This separation occurred at room temperature. These facts indicated that the

procedure might be developed to eliminate the long-time standing at a lower temperature. These results are given in Table V. It was at this point that volume measurements were abandoned in favor of weight measurements. The difficulty of transferring a measured amount from a graduated cylinder into a flask became evident, due to the viscosity of the solution, and the volatility of the solvent was noticeable.

Subsequent experiments (Table VI) showed that the results were not consistent. Some unknown factor was still present and its effect was variable.

The formation of the precipitate had been found to be quite rapid; that is, upon addition of the precipitant in sufficient quantity to cause precipitation, aggregation of the chains into visible particles occurred almost instantly, and these particles settled to the bottom of the flask in a short time. It was questionable whether this precipitation was occurring under equilibrium or near equilibrium conditions. The formation of a precipitate in fractional precipitation should occur slowly in order to decrease the probability of occlusion of short chains in the fast-growing particle.

A series of experiments was designed statistically to determine whether precipitation at 25 degrees isothermally was more satisfactory than the addition of the precipitant at 25 degrees, followed by heating the sample to 50 degrees and allowing it to cool to 25 degrees and stand for 20 hours. This series of experiments was carried out over a period of two days using two replications each day. Samples were prepared containing four different concentrations of non-solvent. The solvent used was ethyl acetate (87-88 per cent, commercial grade); the non-solvent was n-heptane.

Table V

Preliminary Experiments Using Ethyl Acetate as Solvent

cc. n-Heptane Added	% Precipitate Obtained
186	76.8
187	82.2
188	79.3
189	78.3
190	80.0

Samples consisted of 200 cc. of ethyl acetate (technical grade) containing 2.5 per cent cellulose nitrate. n-Heptane was added at 30 degrees. Samples were allowed to stand for 21 hours at 15 degrees Centigrade.

Table VI

Experiments With Ethyl Acetate as Solvent Under Isothermal Conditions

Gm. n-Heptane Added	% Precipitate Obtained
134.0	0
135.0	5.2
135.0	5.8
136.0	3.8
137.0	6.5
137.0	18.2
138.0	32.2
138.0	35.3

Samples consisted of 181.1 grams of ethyl acetate (technical grade) containing 2.5 per cent cellulose nitrate. n-Heptane was added at 30 degrees. Samples were allowed to stand 21 hours at 30 degrees Centigrade.

Treatment I consisted of the addition of n-heptane to a 2.5 per cent solution of cellulose nitrate in ethyl acetate (solution weight 90.5 grams) at 25 degrees, and the solution-non-solvent system was allowed to stand for 20 hours. The supernatant liquid was decanted, the precipitate redissolved in acetone, reprecipitated in water and dried.

Treatment II consisted of the addition of n-heptane to a 2.5 per cent solution of cellulose nitrate in ethyl acetate (solution weight 90.5 grams) at 25 degrees, and the solution-non-solvent system was heated to 55 degrees, then cooled and allowed to stand for 20 hours. The supernatant liquid was decanted, the precipitate redissolved in acetone, reprecipitated in water and dried.

The amounts of non-solvent added are designated as:

C_1 - the addition of 67.0 grams of n-heptane.

C_2 - the addition of 67.5 grams of n-heptane.

C_3 - the addition of 68.0 grams of n-heptane.

C_4 - the addition of 68.5 grams of n-heptane.

The samples were randomized within each batch as to the order taken and treatment given. The weights of the precipitates obtained are given in grams in Table VII, and calculations follow the Analysis of Variance Table.

The benefits derived from the experiment may be listed as follows:

1. The greatest variability is between days, though not significant.
2. The next greatest variability is between treatments, though also not significant.
3. The effect of concentration was smaller than the error term.
4. Neither treatment was significantly different, but also neither treatment gives satisfactory reproducible results.

Table VII

Experiment as Set-Up

Day 1

	Treatment I		Treatment II	
	Batch I	Batch II	Batch I	Batch II
C_1	No ppt.	No ppt.	No ppt.	No ppt.
C_2	.229	.279	1.582	.134
C_3	.136	.372	1.542	1.811
C_4	.101	.217	.392	.532
Total	.466	.868	3.516	2.477

Day 2

	Treatment I		Treatment II	
	Batch III	Batch IV	Batch III	Batch IV
C_1	No ppt.	No ppt.	No ppt.	No ppt.
C_2	.168	.169	.212	.231
C_3	.382	.198	.225	.022
C_4	.037	.413	.523	.096
Total	.587	.780	.960	.349

Two-Way Table

	C_2	C_3	C_4	Totals
T_I	.845	1.088	.768	2.701
T_{II}	2.159	3.600	1.543	7.302
Total	3.004	4.688	2.311	10.003

Analysis of Variance for Two-Way Table

Sources of Variance	d/f	ss	ms
Treatments	1	.882	.882
Concentrations	2	.374	.187
Treats. X Cons.	2	.198	.099
Total	5	1.454	

Analysis of Variance Table

Sources of Variance	d/f	ss	ms
Between Treatments	1	.882	.882
Between Concentrations	2	.374	.187
Between Days	1	.901	.901
Between Batches	2	.0483	.0242
Treats. X Cons.	2	.198	.099
Residual (Error)	15	3.233	.215
Total	23	5.636	

Using the F test:

For treatments $\frac{.882}{.215} = 4.10$ n.s. at 5% level.

For days $\frac{.901}{.215} = 4.19$ n.s. at 5% level.

Calculations

Calculation of Correction Factor

$$C = \frac{\sum x^2}{24} = \frac{(10.003)^2}{24} = 4.169$$

Difference Between Treatments

$$\frac{(2.701)^2 + (7.302)^2}{12} - C = .882$$

Difference Between Concentrations

$$\frac{(3.004)^2 + (4.688)^2 + (2.311)^2}{8} - C = .374$$

Difference Between Days

$$\frac{(7.327)^2 + (2.676)^2}{12} - C = .901$$

Interaction Treatments x Concentrations
From Two-Way Table:

$$\text{Total ss} = \frac{(.845)^2 + (2.159)^2 + \cdots + (1.543)^2}{} - C$$

Total ss = 1.454

Treats. x Cons. = 1.454 - (.882) - (.374) = .198

Total Sum of Squares

$$(.229)^2 + (.136)^2 + \cdots + (.096)^2 - C = 5.636$$

The conclusions reached were that neither treatment under the conditions was satisfactory, and the variability from day to day was an important factor to consider in developing future procedures. It was thought that the uncontrolled variable might be the rate at which the individual chains aggregate to form a particle of sufficient mass to precipitate out from the solution. One means of approaching the critical point in a precipitation titration would be to add the precipitant very slowly while stirring the solution rapidly. This method might be satisfactory, but it would necessitate addition by volume. Another method of approaching the critical point under near-equilibrium conditions would be the use of the temperature decrease after the addition of the precipitant.

The latter method was satisfactory for the earlier experiments using acetone; therefore, it was applied to the ethyl acetate solution.

A series of experiments was begun utilizing the addition of the precipitant, n-heptane, at 25 degrees and allowing the samples to stand at 15 degrees for a period of 20 hours. The results obtained, as shown in Table VIII, were more satisfactory than previous results. The fractions obtained by the addition of 132.5 grams and 133.0 grams n-heptane, respectively, were highly solvated gels and difficult to decant.

The cellulose nitrate being used in this investigation is a high-viscosity type and therefore contains a preponderance of high-molecular weight material. The average degree of polymerization should be slightly lower for a fraction consisting of 15 to 17 per cent than for a fraction consisting of 10 per cent of the original weight. Since the average degree of polymerization will be only slightly decreased, and the larger sized fraction can be more easily separated, it was decided to adjust the procedure to remove 16 to 17 per cent in the first fraction and to decrease

Table VIII

Results Obtained Using Temperature Differential

Grams of Heptane Added	% Precipitate Obtained
130	0
131	0
132.0	0
132.5	8.8
133.0	12.8
133.5	17.4
133.7	18.0
134.0	18.1
134.0	18.9
134.5	19.3

Samples consisted of 181.1 grams of ethyl acetate containing 2.5% by weight cellulose nitrate. n-Heptane was added at 25 degrees. Samples were allowed to stand for 20 hours at 15 degrees Centigrade.

the percentage of the subsequent fractions to compensate for this increase.

It was determined from a plot of the results that with the addition of 133.3 grams of n-heptane to 181.1 grams of ethyl acetate solution, a precipitate consisting of 16 to 17 per cent should be obtained.

In Table IX the results of twenty-three determinations obtained for the first fraction are given. The average is 17.0 per cent.

The supernatant liquid from the first fractions was weighed into 500 ml. flasks and to these samples were added varying amounts of n-heptane according to the data given in Table X. From a study of the values given, it may be seen that there is considerable variation in the size of the second fraction. The size of the fraction was arbitrarily set at eight per cent. This corresponded to the addition of about 3.0 grams of n-heptane to each 250 grams of supernatant liquid present. Table XI shows the results obtained by the procedure. The large amount of variance found indicated that a time cycle of 20 hours was not sufficient time for the precipitation of the first fraction to occur completely, that is, for the attainment of equilibrium between the solvent phase and the precipitated phase.

Up to this time all work had been concentrated on establishing the procedure for the first and second fractions. No information had been obtained for the further separation of subsequent fractions. It was decided to attempt to discover some information about these fractions, and at the same time to further investigate a time-cycle of 45 hours as compared with a 21 hour cycle.

It was decided to run the two sets of experiments simultaneously using two samples in each time-cycle procedure. Each sample consisted of 18.1 grams of dry cellulose nitrate dissolved in 706.4 grams of commercial

Table IX

Series of Determinations of First Fraction

	X	(X-$\bar{X}$)	(X-$\bar{X}$)^2
Batch I	17.1	.1	.01
	16.5	- .5	.25
	17.8	.8	.64
	18.0	1.0	1.00
Batch II	16.4	- .6	.36
	16.1	- .9	.81
	17.0	.0	.0
	16.4	- .6	.36
Batch III	16.4	- .6	.36
	17.7	.7	.49
	14.9	-2.1	4.41
	17.4	.4	.16
Batch IV	17.3	.3	.09
	17.5	.5	.25
	17.9	.9	.81
	17.2	.2	.04
Batch V	17.3	.3	.09
	18.0	1.0	1.00
	16.9	- .1	.01
Batch VI	16.1	- .9	.81
	16.1	- .9	.81
	16.5	.5	.25
	18.1	1.1	1.21
$\bar{X}$ =	17.0		14.22

$$\sigma = \sqrt{\frac{14.22}{23}} = .786$$

Table X

Determinations of Second Fractions

	Gm. n-Heptane Added	% Precipitate Obtained
Batch I	1.2	2.77
	1.7	3.12
	2.2	5.92
Batch II	1.7	2.93
	2.2	4.38
	2.7	5.77
	3.2	11.60
Batch III	2.0	3.32
	2.5	4.77
	3.0	6.48
	3.5	12.20

Samples consisted of 250 grams of supernatant liquid from batch indicated. n-Heptane was added at 25 degrees. Samples were allowed to stand at 15 degrees for 20 hours.

Table XI

Determinations of Second Fractions

	Gm. n-Heptane Added	% Precipitate Obtained
Batch IV & V	3.0	6.3
	3.0	6.8
	3.0	7.0
	3.0	8.0
	3.0	6.1
Batch VI	3.0	9.8
	3.0	8.6
	3.0	11.2
	3.0	10.5

Samples consisted of 250 grams of supernatant liquid from the batch indicated. n-Heptane was added at 25 degrees. Samples were allowed to stand for 20 hours at 15 degrees Centigrade.

ethyl acetate giving a solution of 724.5 grams. The n-heptane was added at 25 degrees Centigrade. After the addition of the n-heptane, the samples were agitated until uniform mixing was obtained. The weight of n-heptane added to the original solution was 533.2 grams; the sample was four times the 181.1 gram sample previously used, and the weight of n-heptane was also a multiple of four times the 133.3 grams used. The additions of n-heptane to subsequent fractions was based on "grams of n-heptane per 250 grams of supernatant liquid", and was to be varied as was necessary. The time-cycle was set at 21 hours; that is, the time the samples were allowed to stand at 15 degrees Centigrade was to be 21 hours. The results are given in Table XII.

The procedure set up for the 45 hour cycle was very similar. The amount of n-heptane added to the original solution was decreased to 532.8 grams, and each sample was allowed to stand at 15 degrees Centigrade for 45 hours. The results are given in Table XIII.

From a study of the results obtained from these two different time cycle runs, it was found that a decrease of .4 gram in the amount of n-heptane added to the original solution and an increase of 24 hours in the time of standing resulted in a considerable decrease in the size of the first fraction obtained, 15.5 per cent as compared to 18.5 per cent obtained in the 21 hour cycle run. In both procedures the precipitating power of the n-heptane on the supernatant liquid increased to a maximum at approximately 50 per cent of the original material removed and then decreased rapidly.

After the removal of the third or fourth fractions in both procedures it was noticed that the supernatant liquid was almost water-white. There was no visible difference between the 21 hour and the 45 hour samples in

Table XII

Complete Run Using a 21 Hour Cycle, Run No. 1

Fraction	Sample	Wgt. of Soln. or Supernatant Liquid	Gm. Heptane per 250 gms.	Gms. Heptane Added	Wgt. of ppt. Obtained	% ppt. Obtained	Average Percentage
1	(1)	724.5	183.3	533.2	3.326	18.4	
	(2)	724.5	183.3	533.2	3.382	18.6	18.5
2	(1)	1182.9	2.0	9.5	1.063	5.9	
	(2)	1178.0	2.0	9.4	0.850	4.7	5.3
3	(1)	1170.7	2.0	9.4	2.371	13.1	
	(2)	1166.9	2.0	9.4	2.044	11.3	12.2
4	(1)	1140.7	2.0	9.1	2.735	15.1	
	(2)	1142.4	2.0	9.1	2.949	16.3	15.7
5	(1)	1109.1	2.0	8.8	1.811	10.0	
	(2)	1107.9	2.0	8.8	1.647	9.1	9.6
6	(1)	1093.5	2.0	8.7	1.216	6.7	
	(2)	1092.1	2.0	8.7	1.338	7.4	7.1
7	(1)	1085.8	2.0	8.7	0.883	4.9	
	(2)	1082.7	2.0	8.7	0.852	4.7	4.8
8	(1)	1083.8	2.0	8.7	0.651	3.6	
	(2)	1080.2	2.0	8.7	0.730	4.0	3.8

9	(1)	1084.3	3.0	13.0	0.778	4.3	
	(2)	1080.2	3.0	13.0	0.813	4.5	4.4
10	(1)	1089.0	3.0	13.0	0.559	3.1	
	(2)	1084.1	3.0	13.0	0.584	3.2	3.2
11	(1)	1094.9	4.0	17.5	0.537	3.0	
	(2)	1090.0	4.0	17.5	0.530	2.9	3.0
12	(1)	1106.9	7.0	29.8	0.582	3.2	
	(2)	1101.7	7.0	29.8	0.608	3.4	3.3

13 Added 520 cc. of n-heptane to each sample of supernatant liquid from Fraction 12. After standing for 21 hours, no precipitate was formed.

Total recovered by precipitation 91.2

Table XIII

Complete Run Using a 45 Hour Cycle, Run No. 2

Fraction	Sample	Wgt. of Soln. or Supernatant Liquid	Gm. Heptane per 250 gms.	Gms. Heptane Added	Wgt. of ppt. Obtained	% ppt. Obtained	Average Percentage
1	(1)	724.5	182.7	532.8	2.748	15.2	
	(2)	724.5	182.7	532.8	2.859	15.8	15.5
2	(1)	1193.4	2.0	9.5	1.080	6.0	
	(2)	1193.7	2.0	9.5	1.210	6.7	6.4
3	(1)	1178.5	2.0	9.4	2.252	12.4	
	(2)	1177.4	2.0	9.4	2.389	13.2	12.8
4	(1)	1148.0	2.0	9.2	2.544	14.0	
	(2)	1146.3	2.0	9.2	2.565	14.2	14.1
5	(1)	1119.3	2.0	8.9	2.010	11.1	
	(2)	1115.1	2.0	8.9	1.924	10.6	10.9
6	(1)	1099.1	2.5	11.0	1.592	8.8	
	(2)	1096.8	2.5	11.0	1.273	7.0	7.9
7	(1)	1090.1	5.0	21.8	1.859	10.3	
	(2)	1091.1	5.0	21.8	1.860	10.3	10.3
8	(1)	1092.5	7.0	30.6	1.383	7.7	
	(2)	1094.2	7.0	30.6	1.362	7.5	7.6

9	(1)	1110.9	8.5	37.7	0.788	4.4	
	(2)	1112.7	8.5	37.7	0.795	4.4	4.4

10 Added 500 cc. of heptane to each sample of supernatant liquid from Fraction 9. After standing 45 hours, no precipitate was formed.

Total recovered by precipitation 89.5

this respect.

Finally, there were no visible effects of degradation sufficient to appreciably change the degree of substitution of the cellulose nitrate. Such degradation would have been evidenced as the fractionation proceeded by the yellowing of the supernatant liquid and further would have been shown by a significant change in nitrogen content.

It was then decided to set up a procedure whereby the first and second fractions would be separated after a 45 hour standing period and the remaining fractions separated after a 21 hour standing period.

The solutions were made up as previously given, each sample consisting of 18.1 grams of dry cellulose nitrate dissolved in 706.4 grams of commercial ethyl acetate giving a solution of 724.5 grams. To the solution was added 532.8 grams of n-heptane at 25 degrees Centigrade. The solution-non-solvent system was then agitated to insure complete mixing before being placed at 15 degrees Centigrade for a period of 45 hours. After standing, the supernatant liquid was decanted and warmed to 25 degrees before the addition of more n-heptane for the next fraction. The precipitate was redissolved in acetone and reprecipitated into distilled water; the water and cellulose nitrate fraction were filtered and the fraction was dried in a 55 degree Centigrade convection oven. The fractions were left in the convection oven for several hours, usually overnight, and dried at 100 degrees for one hour before being cooled in a desiccator and weighed. The additions of n-heptane to the supernatant liquid for the second fraction and subsequent fractions were based on the weight of the supernatant liquid. This weight changed from fraction to fraction, and therefore the addition was calculated as "grams of n-heptane per 250 grams of supernatant liquid present." For example, in Table XIV, in which the results from Run No. 3

Table XIV

Fractionation Procedure Utilizing 45 Hour and 21 Hour Cycles, Run No. 3*

Fraction	Sample	Wgt. of Soln. or Supernatant Liquid	Gm. Heptane per 250 gms.	Gms. Heptane Added	Wgt. of ppt. Obtained	% ppt. Obtained	Average Percentage
1	(1)	724.5	182.9	532.8	2.793	15.4	
	(2)	724.5	182.9	532.8	2.736	15.1	15.3
2	(1)	1196.8	2.3	11.0	1.129	6.3	
	(2)	1196.5	2.3	11.0	1.300	7.2	6.8
3	(1)	1184.2	1.3	6.1	1.351	7.4	
	(2)	1180.6	1.3	6.1	1.189	6.6	7.0
4	(1)	1165.2	1.3	6.1	2.140	11.8	
	(2)	1164.0	1.3	6.1	2.008	11.1	11.5
5	(1)	1136.6	1.9	8.6	2.467	13.6	
	(2)	1136.9	1.9	8.6	2.599	14.4	14.0
6	(1)	1110.3	2.0	8.8	1.500	8.3	
	(2)	1108.3	2.0	8.8	1.316	7.3	7.8
7	(1)	1100.1	3.7	16.3	1.923	10.7	
	(2)	1097.9	3.7	16.3	2.017	11.2	10.9
8	(1)	1094.9	5.8	25.5	1.680	9.3	
	(2)	1092.5	5.8	25.5	1.711	9.5	9.4

9	(1)	1105.0	—	500 cc.	0.732	4.1	
	(2)	1102.6	—	500 cc.	0.351	1.9	3.0
					Total recovered by precipitation		85.7

* Fraction 1 and 2 were decanted after standing 45 hours at 15 degrees Centigrade. Fraction 3 and remaining fractions were decanted after standing 21 hours at 15 degrees Centigrade.

are given, the supernatant liquid remaining from the first fraction is 1196.8 grams. The calculation is $\frac{1196.8}{250} = 4.78$

4.78×2.3 grams per 250 grams = 11.0 grams of n-heptane.

An average of the two weights for the supernatant liquid was used.

In Tables XV and XVI are given two more runs which were made to determine whether the procedure was reproducible. The fractions obtained by addition of n-heptane were in fibrous form. The last fraction, "Residue", was recovered by the complete removal of the ethyl acetate under reduced pressure.

In order to determine the accuracy of this fractionation procedure and to determine the spread of the fraction percentages, the cumulative weight fraction percentages were plotted against the cumulative weight of n-heptane added, based as before on the grams of n-heptane per 250 grams of solution. A curve was plotted for each sample in the three runs, and from these curves were taken the cumulative percentages of cellulose nitrate which would be obtained as a result of the addition of certain arbitrary weights of n-heptane. These weight fraction percentages are given in Table XVII, and a plot of the average curve is presented in Figure 1A.

To determine the degree of polymerization of the fractions obtained, the cellulose nitrate from both samples of a fraction were dissolved in acetone, reprecipitated by pouring into distilled water, filtered and dried in the convection oven.

A sample of approximately .0500 gram of cellulose nitrate was placed in a small weighing bottle, dried for one hour at 100 degrees Centigrade, cooled in a desiccator and weighed accurately. The sample was then transferred to a large Pyrex test tube, to which was added 50 ml. of n-butyl

Table XV

Fractionation Procedure Utilizing 45 Hour and 21 Hour Cycles, Run No. 4*

Fraction	Sample	Wgt. of Soln.or Supernatant Liquid	Gm. Heptane per 250 gms.	Gms. Heptane Added	Wgt. of ppt. Obtained	% ppt. Obtained	Average Percentage
1	(1)	724.5	182.9	532.8	2.900	16.0	
	(2)	724.5	182.9	532.8	2.682	14.8	15.4
2	(1)	1196.5	2.7	12.9	1.319	7.3	
	(2)	1196.8	2.7	12.9	1.487	8.2	7.8
3	(1)	1183.4	1.4	6.6	1.498	8.2	
	(2)	1180.7	1.4	6.6	1.628	9.0	8.6
4	(1)	1163.1	1.0	4.5	1.733	9.6	
	(2)	1158.9	1.0	4.5	1.599	8.8	9.2
5	(1)	1137.5	1.2	5.5	1.273	7.1	
	(2)	1136.5	1.2	5.5	1.287	7.1	7.1
6	(1)	1123.0	2.0	9.0	2.207	12.2	
	(2)	1121.3	2.0	9.0	2.235	12.4	12.3
7	(1)	1102.4	3.0	13.2	1.732	9.6	
	(2)	1104.7	3.0	13.2	1.697	9.4	9.5
8	(1)	1095.4	4.6	20.2	1.697	9.4	
	(2)	1092.7	4.6	20.2	1.713	9.4	9.4

9	(1)	1098.7	—	500 cc.	0.506	2.8	
	(2)	1095.9	—	500 cc.	0.830	4.6	3.7
10	(1)	Residue (Evaporated all solvent and filtered n-heptane)			1.924	10.6	
	(2)	Residue (Evaporated all solvent and filtered n-heptane)			1.930	10.6	10.6
						Total Recovered	93.6

* Fraction 1 and 2 were decanted after standing 45 hours at 15 degrees Centigrade. Fraction 3 and remaining fractions were decanted after standing 21 hours at 15 degrees Centigrade.

Table XVI

Fractionation Procedure Utilizing 45 Hour and 21 Hour Cycles, Run No. 5*

Fraction	Sample	Wgt. of Soln. or Supernatant Liquid	Gm. Heptane per 250 gms.	Gms. Heptane Added	Wgt. of ppt. Obtained	% ppt. Obtained	Average Percentage
1	(1)	724.5	182.9	532.8	2.566	14.5	
	(2)	724.5	182.9	532.8	2.609	14.8	14.65
2	(1)	1196.6	2.7	12.9	1.341	7.6	
	(2)	1196.4	2.7	12.9	1.270	7.2	7.4
3	(1)	1183.8	1.4	6.6	2.441	13.8	
	(2)	1184.7	1.4	6.6	2.460	13.9	13.85
4	(1)	1149.6	1.0	4.6	1.517	8.6	
	(2)	1150.9	1.0	4.6	1.514	8.6	8.6
5	(1)	1128.7	1.2	5.4	1.483	8.4	
	(2)	1130.0	1.2	5.4	1.576	8.9	8.65
6	(1)	1111.6	2.0	8.9	1.526	8.6	
	(2)	1111.7	2.0	8.9	1.621	9.2	8.8
7	(1)	1098.6	3.0	13.2	1.837	10.4	
	(2)	1097.5	3.0	13.2	1.655	9.4	9.9
8	(1)	1089.7	4.6	20.0	1.613	9.1	
	(2)	1090.8	4.6	20.0	1.625	9.2	9.15

9	(1)	1093.5	—	500 cc.	.341	1.93	
	(2)	1094.2	—	500 cc.	.018	.10	1.0
10	(1)	Residue (Evaporated all solvent and filtered n-heptane)			1.868	10.6	
	(2)	Residue (Evaporated all solvent and filtered n-heptane)			1.818	10.2	10.4
						Total Recovered	92.4

* Fraction 1 and 2 were decanted after standing 45 hours at 15 degrees Centigrade. Fraction 3 and remaining fractions were decanted after standing 21 hours at 15 degrees Centigrade.

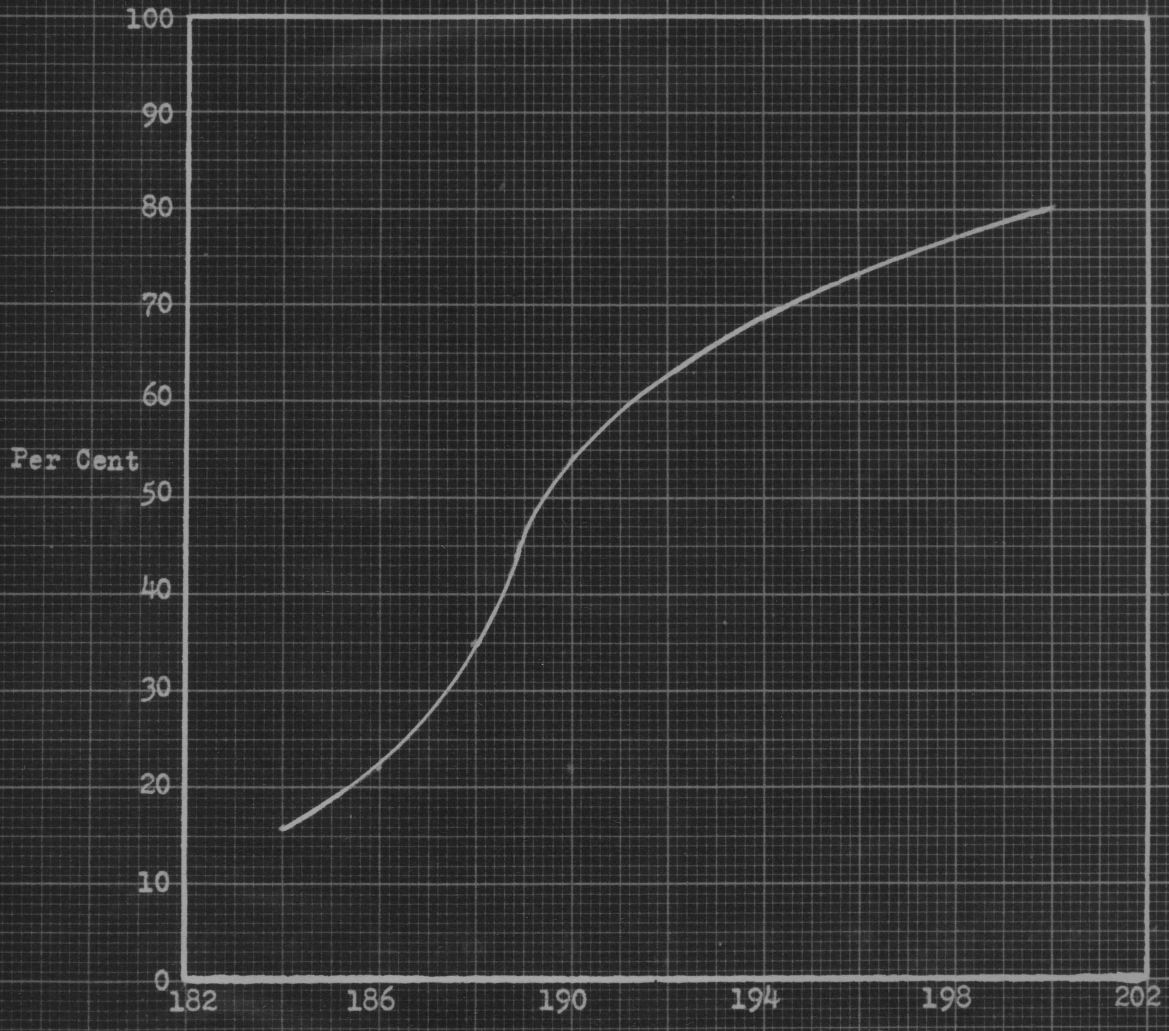
Table XVII

Weight of Fraction per Weight of Heptane Added

Gm. n-Heptane per 250 gms. Solution	Run No. 3		Run No. 4		Run No. 5	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
183.7	15.4	15.1	16.0	14.8	14.5	14.8
186.0	22.0	22.0	21.5	21.0	22.0	21.5
188.0	35.0	35.0	33.5	34.0	36.0	36.0
190.0	54.0	54.0	49.5	49.5	53.0	52.5
192.0	62.0	62.5	60.5	60.5	61.5	62.0
194.0	67.5	68.0	67.5	67.5	68.0	68.5
196.0	72.5	72.5	72.0	72.0	73.5	73.5
198.0	76.0	76.0	76.0	76.5	77.5	77.5
200.0	79.0	79.5	—	—	—	—

Figure 1A

Weight of n-Heptane versus Average Cumulative Per Cent



Average values from Runs No. 3, 4, and 5.

acetate (technical grade). The test tube was stoppered with a cork which had been previously extracted with n-butyl acetate to remove soluble fats and waxes. After the test tube had been well shaken, it was allowed to stand overnight.

The test tube and Ostwald viscometer were suspended in a water bath, maintained at 20.0 ± .1 degrees Centigrade for at least 30 mimutes before the transfer of five milliliters of the solution into the viscometer. The time required for the meniscus of the solution to pass from the top mark to the bottom mark on the pipet was recorded. Five successive readings, agreeing with .2 second, were taken. The determination of the degree of polymerization (D.P.) of the first fraction of Run No. 3 is given as an example of these calculations.

Sample Calculation

Weight of sample 0.0508 grams

Volume of butyl acetate 50 ml.

Viscosity of solvent 57.7 sec.

Viscosity of solution 105.4 sec.

Value of $K_m(120) = 14 \times 10^{-4}$

$$N_{sp} = \frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}} - 1$$

Substituting into Staudinger's equation

$$\frac{N_{sp}}{c} = K_m \cdot P$$

where "c" is concentration in grams per liter and "P" is the degree of polymerization.

$$P = \frac{N_{sp}}{c \cdot K_m}$$

$$P = \frac{\frac{105.4}{57.7} - 1}{\frac{.0508}{50} \times 1000 \times 14 \times 10^{-4}}$$

$$P = 581$$

The results of viscosity determinations for Run No. 3, 4 and 5 are given in Table XVIII.

The determinations of the nitrogen content of the original cellulose nitrate and of the fractions obtained from Run No. 3 were made using the duPont nitrometer equipped with a Universal reading tube. Duplicate determinations were made. These results, as given in Table XIX, show that fractionation according to the degree of polymerization, not degree of substitution, was accomplished.

Table XVIII

Degrees of Polymerization of Fractions for Runs No. 3, 4 and 5

Fraction	Run No. 3		Run No. 4		Run No. 5	
	D.P.	% in Fraction	D.P.	% in Fraction	D.P.	% in Fraction
1	581	15.3	593	15.4	572	14.65
2	560	6.8	568	7.8	545	7.4
3	540	7.0	532	8.6	551	13.85
4	511	11.5	530	9.2	516	8.6
5	480	14.0	480	7.1	465	8.65
6	416	7.8	440	12.3	410	8.8
7	353	10.9	391	9.5	288	9.9
8	249	9.4	292	9.4	288	9.15
9	127	3.0	152	3.7	152	1.0
Residue	—	—	123	10.6	124	10.4
Total		85.6		93.6		92.4
Average D.P.	454		429		424	
Standard Deviation			154.6		150.9	

Average Degree of Polymerization of Original Cellulose Nitrate 420

Table XIX

Nitrogen Determinations on Run No. 3

Fraction	Per Cent Nitrogen	Per Cent Nitrogen
1	12.00	11.95
2	12.00	12.03
3	12.05	12.00
4	11.97	11.95
5	11.92	11.92
6	12.01	12.00
7	11.98	11.92
8	11.80	11.82
9	Not enough material for samples	
Original Cellulose Nitrate	12.14	12.12

VII. DISCUSSION OF RESULTS

It is difficult in a fractionation procedure to obtain results which may be reproduced. Previous investigators have been willing to use a fractionation procedure which gave variable results, and after determining the average degree of polymerization of the fractions, combine those fractions having the same average degree of polymerization.

The method which has been developed is unique in that it combines fractional precipitation with fractionation by cooling in such a manner that reproducible results within a range may be obtained. This is shown by the results given in Tables IX, XIII, XIV, XV and XVI. The results as given in Tables XIV, XV and XVI indicate that the range of reproducibility varied from fraction to fraction, gradually increasing until approximately 50 per cent of the original material had been removed from the solvent-non-solvent system, then decreasing again. The total amount obtained by the addition of n-heptane was about 83 per cent of the original weight.

Another fraction consisting of 10 - 11 per cent was still soluble in excess n-heptane and was recovered by complete evaporation of the solvent and filtering the suspension remaining.

The fibrous form of the original cellulose nitrate was retained by all fractions except the last fraction.

An integral distribution curve showing the distribution of the chain lengths obtained by fractionation may be plotted by graphing the degree of polymerization (D.P.) versus the cumulative weight per cent of the total cellulose nitrate recovered. (See Table XX) Table XXI was prepared to show the range of variance of the degrees of polymerization shown by the three runs whose cumulative percentages and D.P.'s are given in Table XX. Curves representing Runs No. 3, 4 and 5 are given in Figure 2. The

Table XX

Degree of Polymerization versus Cumulative Percentage

Run No. 3		Run No. 4		Run No. 5	
D.P.	%	D.P.	%	D.P.	%
581	15.3	593	15.4	572	14.65
560	22.1	568	23.2	545	22.05
540	29.1	532	31.8	551	35.9
511	40.6	530	41.0	516	44.5
480	54.6	480	48.1	465	53.15
416	62.4	440	60.4	410	62.05
353	73.3	391	69.9	288	71.85
249	82.6	292	79.3	288	81.0
127	85.6	152	83.0	152	82.0
--	—	123	93.6	124	92.4

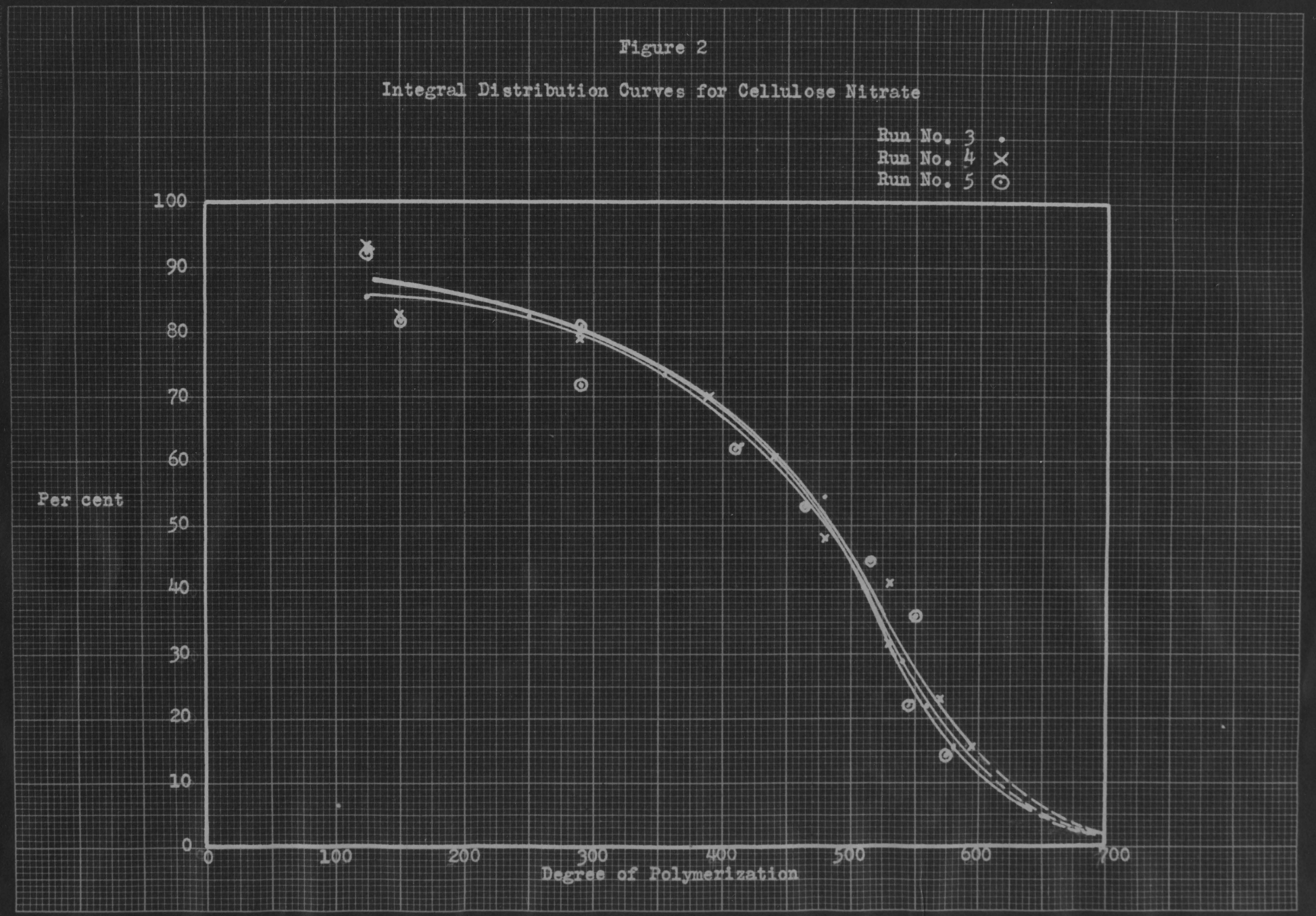
Table XXI

The Range of Degrees of Polymerizations

%	Run No. 3 D.P.	Run No. 4 D.P.	Run No. 5 D.P.	Average D.P.
10	—	—	—	—
20	570	560	575	568
30	535	545	540	540
40	510	520	510	513
50	480	485	480	482
60	435	445	445	442
70	380	385	390	385
80	280	290	295	290
90	—	—	—	—

Figure 2

Integral Distribution Curves for Cellulose Nitrate



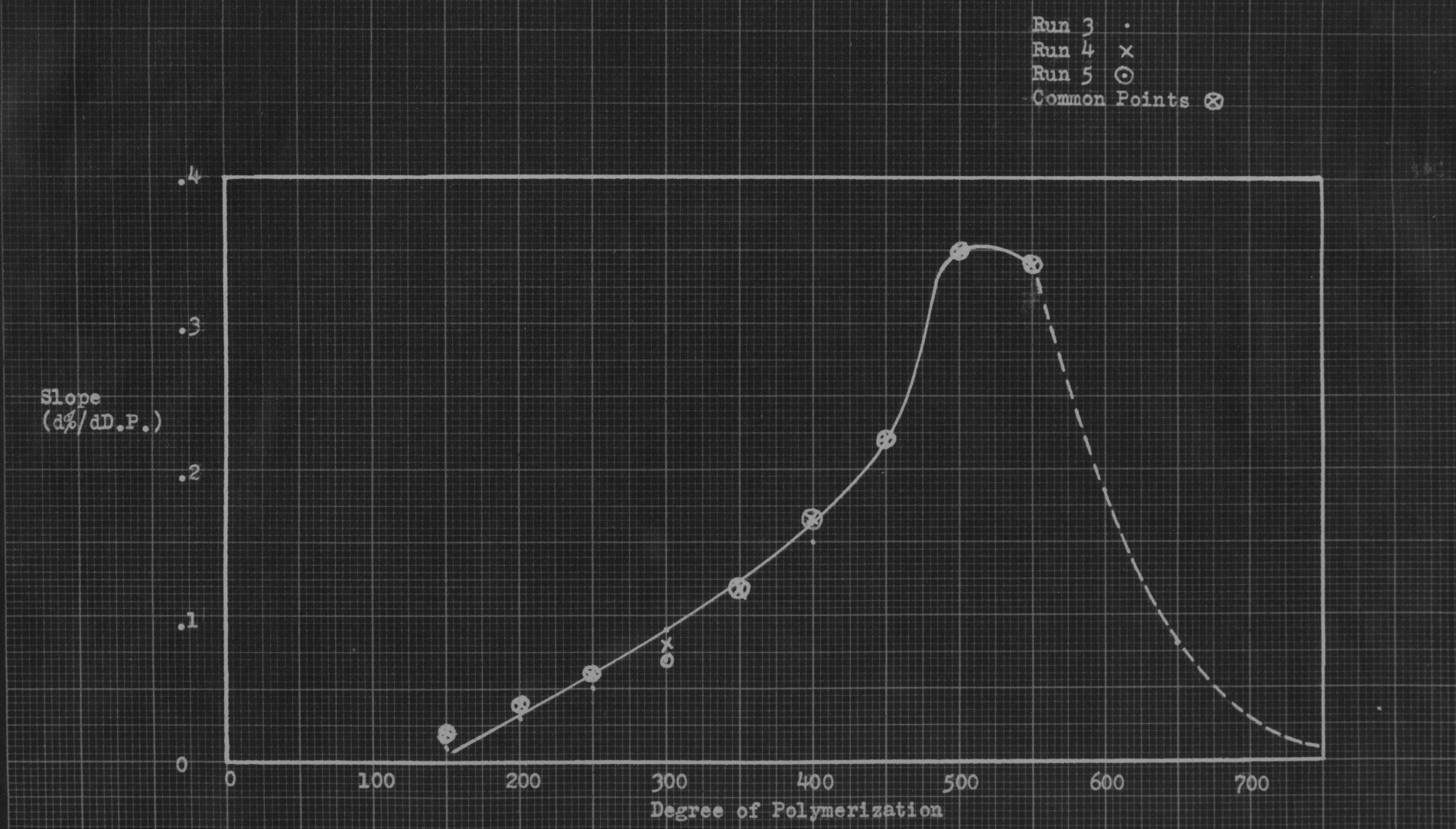
integral curves can be differentiated graphically by taking the tangent to the curve at various points. If the slopes of these tangent lines are plotted against the degree of polymerization, the differential distribution curve is obtained. The distribution curves obtained from the integral curves for Runs No. 3, 4 and 5 are given in Figure 3.

In the differential distribution curve, any point represents the percentage of the sample with a degree of polymerization in an infinitesimally small range of degree of polymerization. The shape of the differential distribution curve is an indication of the heterogeneity of the sample with respect to the degree of polymerization. Thus, the shape of the differential curves indicates that the sample contains a preponderance of one range of D.P. material, the range being 500 to 600 D.P. units.

From a study of the curves it can be seen that the procedure, as developed, gives results which can be reproduced within a satisfactory range.

Figure 3

Differential Distribution Curves for Cellulose Nitrate



VIII. CONCLUSIONS

It has been shown that a precise, reproducible fractionation procedure, combining both fractional precipitation and fractionation by cooling, has produced fractionation of a high viscosity cellulose nitrate into ten fractions.

The solvent-non-solvent system which was satisfactory, was ethyl acetate (commercial grade) as the solvent and n-heptane (pure grade) as the non-solvent.

It is realized that a more precise fractionation might be accomplished by the use of another solvent-non-solvent system, but in the light of previous work, the method of separation as developed in this work can be considered as a precise method.

IX. SUGGESTIONS FOR FUTURE STUDY

It is suggested that a study be made of solvents and non-solvents in an attempt to increase the efficiency of the fractionation procedure, and to discover other systems which can be used in a procedure requiring reproducibility.

It would be interesting to have a comparison of results from osmotic measurements and viscosity determinations using cellulose nitrate fractions obtained from a low viscosity material by a procedure similar to the one developed in this work.

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