THE SOLVATION OF CELLULOSE NITRATE

by

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I. ACKNOWLEDGEMENT

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II. INTRODUCTION

Quantitative data concerning the state of solvation of cellulose derivatives dispersed in solvent-non solvent systems is rather limited. Since such derivatives possess a high commercial importance largely because of their ability to be dispersed and regenerated from solvent-non solvent systems by manipulation of the solution phase of the system, such data are highly desirable from the purely practical viewpoint. Likewise, from the purely theoretical viewpoint, such data are desirable in the investigation of problems involving fractional precipitation techniques, studies in film and filament formation and in the elucidation of a number of similar basic phenomena of current interest.

Specifically, the aim of this investigation is to study, quantitatively, the changes in solvation of a sample of cellulose nitrate in an acetone-water solvent-non solvent system as the composition of the liquid phase is varied over a range from solvent rich to solvent poor.

III. LITERATURE REVIEW

A. Cellulose

1. Chemical Structure and Reactions

Cellulose is a natural high polymer consisting of a number of beta anhydro d-glucose monomer units linked together in a linear manner by a 1-4 oxygen bridge [37], [72]. Its currently accepted structural configuration, representing the result of more than a century of research on the behavior of cellulose and its compounds is shown in Figure 1 [73].

As may be seen from the structural formula, cellulose has a high molecular weight and since it is a linear molecule, the molecular weight is obtained by multiplying the number of beta anhydro d-glucose units in the chain molecule by 162, the weight of one glucose anhydride unit ($C_6H_{10}O_5$). The number of such units per chain is termed the degree of polymerization. However, since in cellulose, the number of beta anhydro d-glucose units may vary over a considerable range, any given sample of cellulose is heterogeneous with respect to chain length. Thus the term D. P. or degree of polymerization refers to the average number of glucose anhydride units in the molecule rather than to the absolute number as in the case of low molecular

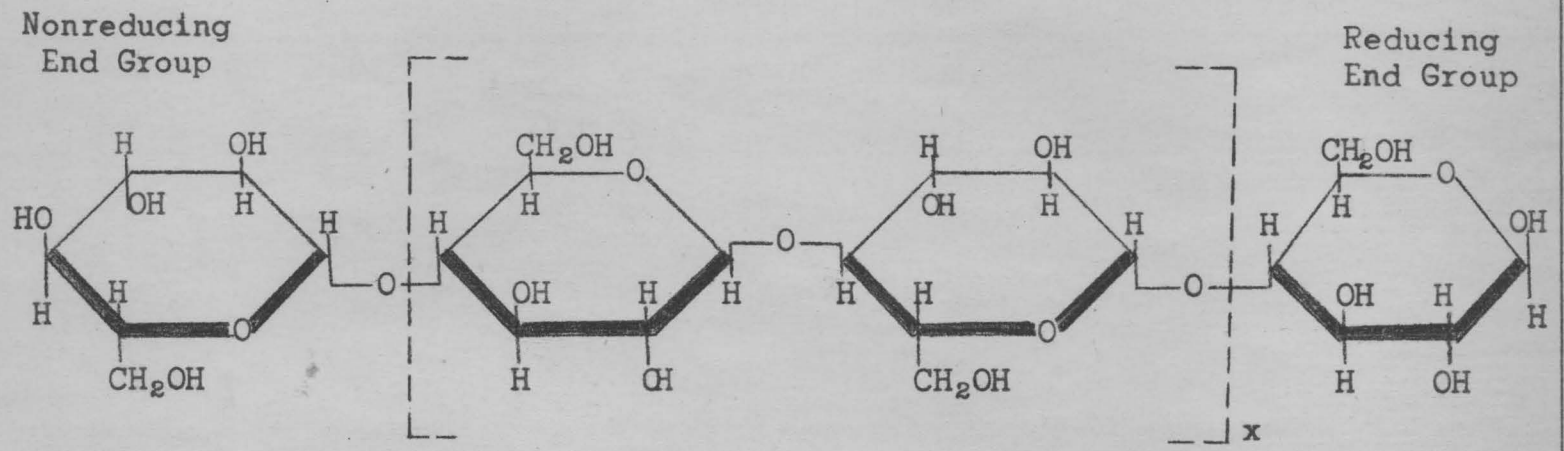

Figure 1.

Theoretical Configuration of the Cellulose Molecule

$D.P. = 2x + 2$

From "The Chemistry of Large Molecules", edited by R. E. Burk and O. Grummit. Interscience Publishers. New York (1943). p. 250.

weight compounds. A sample of commercially useful cellulose will contain from 50 to 5000 glucose units between the beginning and terminal end of the chain; thus x in Figure 1 would have a value of from 25 to 2500.

Chemical and physical methods have been used to establish the structural configuration of cellulose. An almost quantitative yield of glucose resulting from acid hydrolysis of cellulose confirms the six carbon monomer unit as the fundamental building block of the polymer. The presence of three hydroxyl groups per monomer unit is confirmed by nitration, acetylation and other chemical reactions. The position of these groups in the 2, 3 and 6 carbon atoms is established by methylation of the cellulose followed by acid hydrolysis. The hydroxyl group on carbon 6 is primary; those on carbons 2 and 3 are secondary. Since the pyranose ring structure of glucose is involved, therefore carbon number 5 must be involved in ring formation and the C_6 monomer units must be joined through a 1-4 oxygen bridge. The presence of a beta-glucosidic linkage, but no evidence of an alpha linkage, is verified by optical rotation of cellulose derivatives and x-ray data.

It can be seen from the structural formula that while one terminal glucose unit contains an extra hydroxyl unit on carbon number 4, the opposite terminal unit of the chain contains a reducing hemiacetal group on carbon

number 1. Thus both terminal glucose units differ from those in the chain body proper.

The reactions of cellulose are very similar to those exhibited by the simple sugars. However, its chief reactions are those characteristic of the hydroxyl groups since all but one of the potential reducing groups of the glucose units are involved in glucosidic linkages between the monomer units of the chain and therefore cellulose lacks the pronounced reducing power characteristic of monosaccharides in general. The more important reactions are summarized in Table I [74]. The reactions are divided into two general classes: those involving the hydroxyl groups, and those involving the degradation of the cellulose chain.

TABLE I

REACTIONS OF CELLULOSE

I. Reactions Involving Hydroxyl Groups

A. Esterification

1. Esterification Agents

(a) Acids: HNO_3, H_2SO_4, HCOOH

(b) Acid anhydrides: $[(R\text{-}C{=}O)_2O]$ and catalyst (H_2SO_4 or salts such as magnesium perchlorate.)

(c) Acid chlorides: $[(R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl)]$ or acid anhydrides $[(R\text{-}C{=}O)_2O]$ in basic medium

(pyridine, NaOH, etc.)

Acetic anhydride in pyridine gives acetylation with very little degradation

Acid chloride (such as p-toluenesulfonyl chloride) plus alkali cellulose gives sulfonic acid esters; alkyl chloroformates in the presence of alkali give cellulose alkyl carbonates

Note: Halogenated esters are difficult to prepare; for example, the trichloroacetate is best prepared by chlorination of the acetate or the monochoroacetate

2. Xanthation with caustic and CS_2.
3. Mixed Esters
   (a) Nitrate-acetate, acetate-butyrate, acetate-propionate
   (b) Sulfuric acid half ester
   (c) Mixed ester-half-acetal derivative

B. Etherification

1. Etherifying Agents
   (a) Alkylating agent: (such as $(CH_3)_2SO_4$, alkyl halide or aralkyl halide) in the presence of strong alkali

Ethylene chlorohydrin to give hydroxy

ethyl cellulose

Sodium chloroacetate to give sodium cellulose glycolate, for example, $[C_6H_7O_2(OH)_n(OCH_2COONa)_{3-n}]_x$

Triphenylmethyl chloride (trityl chloride); it is difficult to etherify any but primary OH

(b) Olefin oxides (such as ethylene oxide) to give hydroxyalkyl ethers

(c) Diazomethane on the xanthate to give partially methylated cellulose

(d) Aldehydes and methylene sulfate to give acetals

2. Mixed Ether Derivatives

(a) Ether-esters

(b) Esterified half-acetals

(c) Sodium-ether derivatives

C. Addition Compounds

1. With alkalies

2. With acids

3. With salts

D. Replacement of Hydroxyl Group by Halogens, Amino Group, etc.

E. Replacement of Hydrogen in Hydroxyl Group by Metals

F. Oxidation of Hydroxyl Groups

II. Degradation Reactions

A. Hydrolysis of the 1,4-Glucoside Linkage

B. Oxidation

C. Decomposition by Heat and Light

2. Crystalline Structure

The importance of considering the microscopic and submicroscopic morphology of the cellulose fiber in an investigation of this nature can not be overemphasized. The literature covering this subject is voluminous and rather comprehensive surveys of this aspect of cellulose chemistry are to be found in almost any text on cellulose chemistry. The reader is referred to [16], [38], [75], [89] and especially to the extensive review of the literature on this subject contained in [27].

The earliest investigations established that cellulose fibers were anisotropic, however no definite theory concerning the fiber structure was proposed until 1858 when Nageli advanced his micelle theory [68], [69]. He postulated that all cellulose fibers were built up of submicroscopic, anisotropic crystalline particles which he called micelles.

Gilsen, in 1893, used polarized light to first experimentally demonstrate that cellulose was crystalline

[20]. This was confirmed for the first time by x-ray analysis in 1913 by Nishikawa and Ono [71]. Nishikawa noted the sharpness of the pattern and correctly reasoned that any substance which gave a fiber pattern consisted of a definite structure arranged parallel to the fiber axis. Ambronn in 1916 predicted that if cellulose was a crystalline material, it should give a characteristic, sharp x-ray diagram with the newly developed technique of Debye and Scherrer [1]. However, Scherrer, on the basis of this suggestion investigated cellulose with x-rays but reported an amorphous pattern [83]. He repeated this work using ramie fibers and obtained a definite crystalline pattern [103]. Meanwhile Hall had independently obtained x-ray diagrams of cellulose fibers [40].

Herzog and Jancke in 1920 began an investigation designed to check the correctness of Scherrer's preliminary report that cellulose was amorphous [84]. The results of their study were of great value. They proved that cellulose had a definite crystalline pattern which was the same regardless of the source of the cellulose. This substantiated earlier work regarding the chemical identity of cellulose. Herzog further postulated that the crystalline pattern was caused by the continuous repetition of beta-anhydro-glucose units being present in a regular pattern.

He stated that the amorphous pattern background present in x-ray diagrams was probably dependent upon another factor.

Polanyi, in 1921, calculated the first unit cell dimensions as 7.9 x 8.45 x 10.2A° [78]. The 10.2A° dimension corresponds to the vertical dimension along the fiber axis, while the 7.9 and 8.45A° are the horizontal dimensions which form an angle of 84° with each other. From these dimensions Polanyi calculated that a unit cell could accomodate four glucose residues.

Although Polanyi, in his original paper, pointed out that x-ray data were consistent with the concept of long chains common to many cell units, most cellulose workers up to 1926 considered the cellulose molecule to be the $C_6H_{10}O_5$ unit [42] despite the fact that such a concept was not compatible with x-ray interpretations. It was during this period, however, that advances in the field of sugar chemistry, particularly by Haworth, Irvine, Hirst and others, succeeded in making clear the true configuration of the glucose unit. At the same time the Braggs contributed [72] greatly to the knowledge of the size and shape of atoms and molecules. This fundamental knowledge, combined with advances in x-ray technique enabled a more correct analysis of x-ray patterns which were in turn checked by construction of molecular models to demonstrate a three-dimensional

picture of the x-ray interpretation. The first model constructed was that of Sponsler and Dore.

Sponsler, in 1926, advanced the new concept that the cellulose building unit consisted of glucose units connected in chains lying parallel to the fiber axis rather than the independent glucose unit previously conceived [95]. This paper pointed out, for the first time, that the unit cell, deduced from x-ray data, was only a part of the cellulose molecule. The unit cell dimensions were assumed to be 6.10 x 5.40 x 10.25A°, with the cellulose chains being 6.10 x 5.40A° apart. This permitted two $C_6H_{10}O_5$ units within the 10.25A° dimension (fiber axis) and four $C_6H_{10}O_5$ units within the unit cell. Later, Sponsler and Dore constructed three dimensional models based on newly published data on atomic radii, interatomic distances and the chemical constitution of sugars. They concluded that the ring structure for glucose postulated by Haworth [25] was in closest agreement with the x-ray data, and that the glucose units were united in chains of indefinite length. They adopted an alternating 1-1, 4-4 linkage instead of the 1-4 linkage of cellobiose favored by Haworth and used the beta structure in their models. The axes of the unit cell finally adopted by Sponsler and Dore were a = 10.8, b = 12.2, and c = 10.25A° [70]. The distance 10.25A°

represented a recurrency period along the fiber axis of two glucose units and was dependent upon the chemical structure of the cellulose molecule.

The model of Sponsler and Dore did not agree with the chemical evidence of Haworth, however. He postulated a recurrent 1-4 linkage between the glucose monomer units. Meyer and Mark [57][59] in 1928 showed that a model could be constructed which was in agreement with both chemical and x-ray data. To accomplish this they used the unit cell dimensions given by Polanyi in 1921 [79] and the beta form of Haworth's cellobiose formula to fit the glucose units in a basic unit cell. The distance between carbon atoms was 1.54A° between carbon and oxygen atoms, 1.35A° and the length of the cellobiose unit, therefore, 10.3A°. Such a model was compatible with x-ray data which indicated a diagonal screw axis with repeat patterns every 10.3A° since the bottom half of the cellobiose unit was rotated 180° in the model. In addition, this arrangement permitted the 1-4 linkage in agreement with chemical evidence. The glucose units of the cell lie in the ab plane of the unit cell and the axes of the cellobiose units run parallel to the b axis of the cell with each corner and the center of every cell being occupied by a cellulose chain. Two glucose units at each corner of the cell are shared by four neighboring unit cells leaving two glucose units per unit

cell for the eight corners, which together with the two in the center gives a total of four glucose units per unit cell. This cell is merely the geometrical pattern or arrangement of the glucose units which repeats itself in all directions. It should not be confused with the cellulose molecule or micelle. A picture of the model cell is shown in Figure 2.

The important feature of this cell is the basic concept of long cellulose chains, composed of glucose units bound by primary valence bonds, which run parallel to the b axis of the unit cell and which are stabilized laterally by secondary valences.

Again referring to Figure 2, it is evident that the glucose units are held together by 1-4 glucosidic linkages along the b axis. Along the a axis the glucose rings are separated by a distance of 2.5A°. In most other organic crystals two oxygen atoms of different molecules do not approach each other closer than about 3.0A° provided only van der Waal's forces are acting between them. This suggests that stronger forces are acting, and it is reasonable to assume that a hydrogen bond is established between the two oxygen atoms. This would explain the comparatively tight packing in the ab plane in the direction of the a axis, and at the same time offer an explanation for

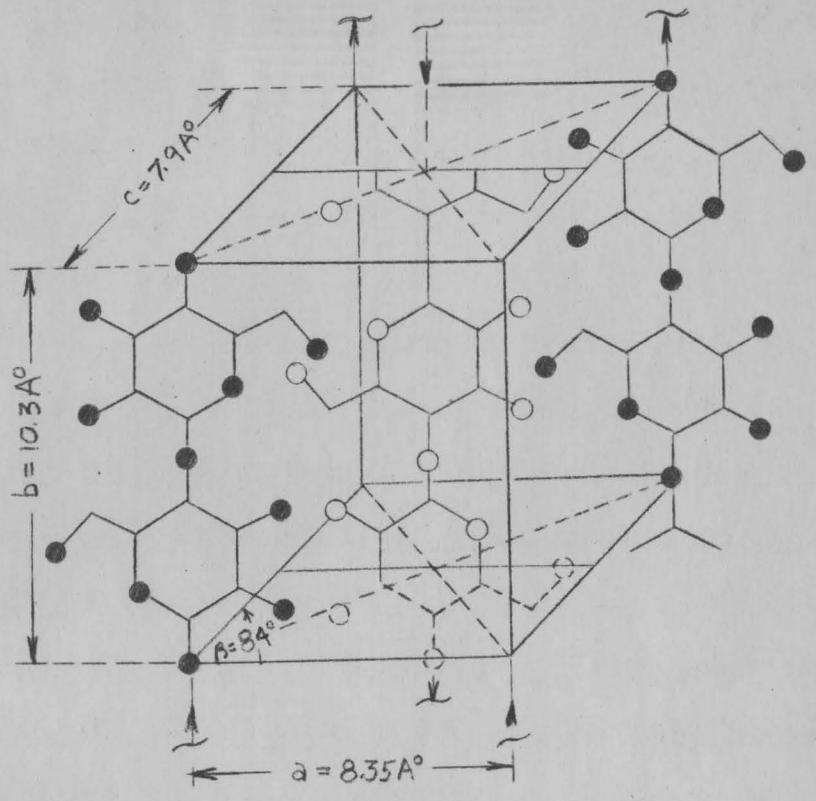

Figure 2. Unit Cell of Native Cellulose
(Meyer and co-workers)

From "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York (1943). p. 211.

the fact that swelling agents disrupt this bond to form swelling compounds. Along the c axis the nearest distance of atomic centers is about 3.1A°. This corresponds closely to the distance to be expected if van der Waal's forces hold the lattice together in this direction. As pointed out by Mark [48], cellulose may be regarded as a combination of a chain lattice and a layer lattice. The strongest forces are the main valence chains along the b axis, but the hydrogen bond nets along the a axis (ab plane) are also comparatively strong. Perpendicular to the ab plane, however, weaker van der Waal's forces are acting and the spacing between the atoms in this direction is large. Thus, cellulose chains are at different distances and are held together by three different kinds of forces in three different directions in space [90].

3. Micellar Structure

Although the establishing of the unit cell concept was of fundamental importance in cellulose chemistry, the cellulose fiber itself is not a single crystal; it is a crystalline aggregate consisting of small crystal areas (crystallites) separated by amorphous or intercrystalline areas. The term crystallite does not define the size, shape or nature of the boundary between the crystalline areas; the term micelle is used to designate a definite concept of the crystallite.

Unfortunately, all of the chemical data which measure the average size of the micelle or macromolecule as it exists in solution depend upon the disruption of the original fiber in some manner, and, since it is not definitely known what happens during the solution process, it is difficult to extrapolate the results back to untreated fibers. This situation has prompted much speculation regarding the nature of the crystallite and has resulted in numerous theories concerning the most probable state of affairs.

A botanist, Nageli, [68][69] advanced the first of these theories--the micellar theory--in 1858. He postulated that all cellulose fibers were built up of submicroscopic, anisotropic crystalline particles called micelles. He based his concept upon polarized light and upon swelling studies and considered micelles to be discrete particles between which water entered to produce swelling. Although this idea was not generally accepted at the time, in 1913 x-ray analysis indicted the presence of amorphous and crystalline regions in the cellulose fiber and Nageli's original concepts were revived and developed into the so-called brick micelle theory. This theory implies an arrangement of the micelles similar to bricks in a wall, each micelle overlapping its neighbor and being bound to it by intermicellar (tertiary) forces. An amorphous matrix

was assumed to exist between the micelles. This concept is shown in Figure 3(a).

As investigation continued ultracentrifugal, viscosity and other related physiochemical data indicated that the molecular cellulose chain was more than ten times longer than the estimated size of a micelle. Consequently, a new concept of the cellulose crystallite evolved--the continuous structure theory--which was in direct contrast to the micellar theory. According to this theory it was not necessary to assume chains broken into small brick-like micelles to form individual crystals. Instead it was proposed that the crystalline regularity of the chains was probably interrupted at regions where the chains were not sufficiently close or regular to form a crystal lattice. Such regions would produce x-ray diagrams indicative of amorphous regions separating well-defined crystallites. The physical properties of native fibers are better explained on the basis of such a continuous structure concept. Figure 3(b) shows the essential features of this theory.

While the characteristics of native fibers were best explained on the continuous structure postulates, the x-ray data and observations of wet tensile strengths of rayon were best explained by the micellar theory.

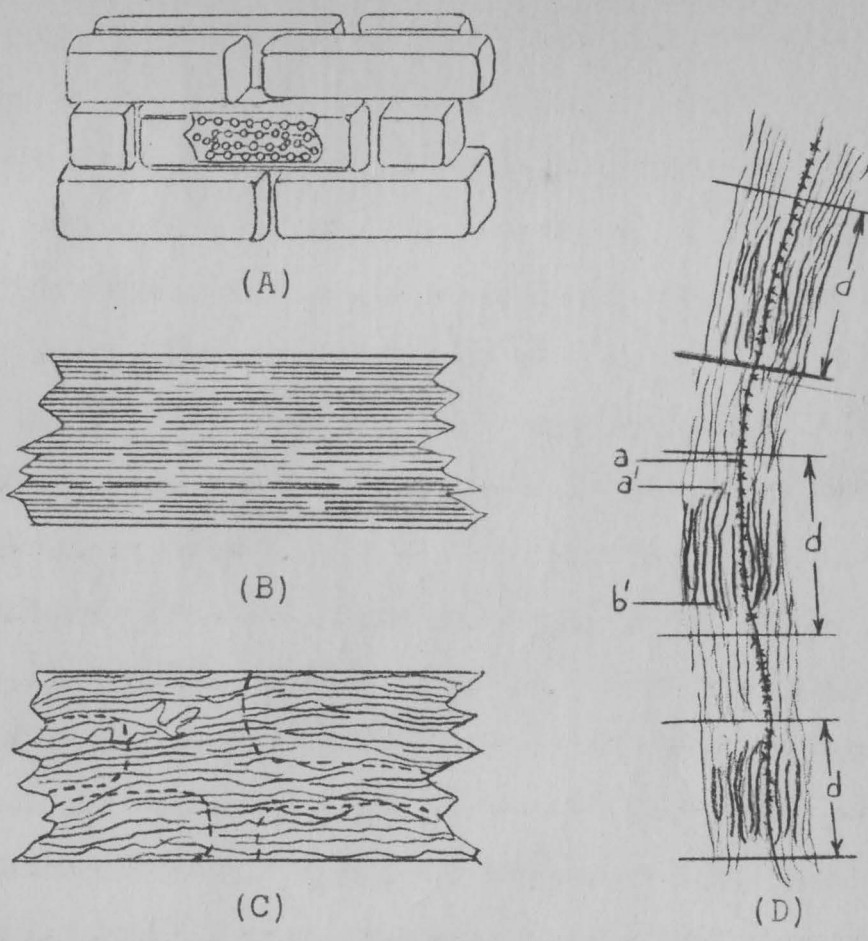

Figure 3. Schematic Representation of Several Possible Crystallite Structures of Cellulose. (Mark)

(A) Micellar theory (Seifriz).
(B) Continuous structure.
(C) Fringe micellar theory.
(D) How main valence chains pass through more than one micelle (fringe micellar theory).

a, a', b'. Molecule ends inside the crystallized region of one micelle.
c. Molecule end outside the crystallized region.
d. Length of crystallized region.

From "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York (1949). p. 216.

Accordingly an attempt was made [91] to effect a compromise between the two concepts. This resulted in the evaluation of the secondary structure theory. It is based principally on the inability to explain the physical properties of a single crystal on the basis of the unit cell arrangement of ions or molecules and the forces bonding them together. Zwicky [104][105] theorized that superimposed upon the unit cell lattice is another lattice on a much larger scale, which consists of crevices or cracks giving the crystal a second structure. The principal crevice run parallel to the cellulose chains and are partly occupied by amorphous materials. There are several points in favor of this hypothesis; it is consistent with the low tensile strength and diffusion through single crystals; it is in agreement with data on the dispersion and modification of cellulose which are difficult to explain on the basis of a micellar theory, since modification and degradation are known to proceed gradually and not in uniform steps. Such a structure would give many long fibril-like fragments when the fiber is disintegrated.

As studies with regenerated cellulose and synthetic high polymeric substances continued, still another concept of micellar structure evolved from the accumulation of new evidence. This is the micellar network or fringe micellar

theory. It is a compromise between an extreme micellar structure and the extreme chain or continuous structure. It is generally accepted today as the most feasible theory particularly with respect to explaining most satisfactorily the behavior of regenerated fibers. Despite its less satisfactory application to native fibers, the theory at present is the most acceptable one. According to this theory the crystalline areas are not clearly separated from each other by a distinct micellar surface, but rather by an area of partially parallel but disorganized chains [87]. This concept is pictured in Figures 3(c) and 3(d). Long crystalline particles are postulated whose outer form is irregular, and defined, especially at the ends, by projecting, irregularly arranged, primary valence chains which may pass through several micelles and thus tie them together. Such an arrangement permits a net-like structure of chains which are both crystalline and amorphous. The crystalline areas are formed by a three dimensional branching of glucose units which have rotated about the oxygen bridge so as to form a crystallite. The amorphous cell wall is an entity in itself. Eventually a more or less coherent mass (structure) of chain bundles is built up. Somewhere in this process still another more or less coherent unit is built up from a group of these chain

bundles to form a submicroscopic fibril. Additional fibrillae form in a similar fashion and a macrofibril is formed. In this process of structure formation a capillary system is concurrently formed. The spaces surrounding the submicroscopic fibrillae form the microcapillary system and the space surrounding the macro fibrillae forms the macrocapillary system. These capillary systems are interconnected and the activity of chemical agents, dyes, etc., is dependent upon their ability to penetrate through and into the capillary systems. A sketch of a cross section of a typical cellulose fiber is shown in Figure 4.

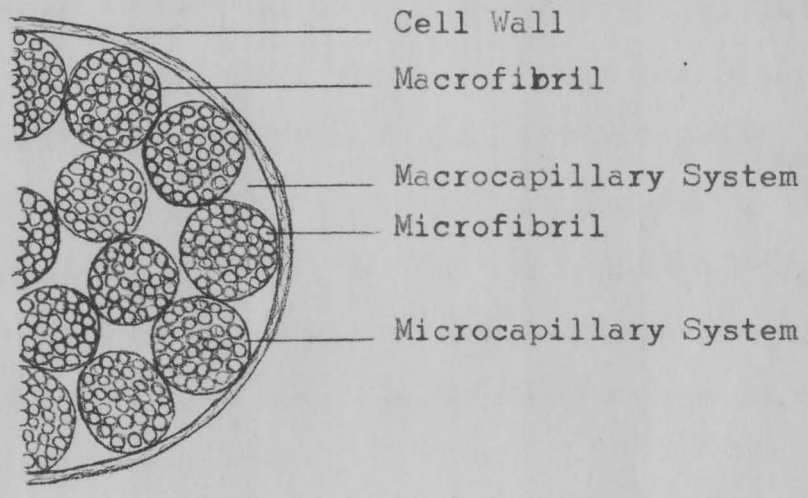

Figure 4. Cross Section of Cellulose Fiber

From Mathew's "Textile Fibers", edited by H. R. Mausersberger. 5th Edition. John Wiley and Sons, Inc., New York. p. 123.

IV. CELLULOSE NITRATE

Cellulose nitrate was discovered by Braconnot in France in 1832 [7]. It was C. F. Schonbein, however, who first prepared it on a commercial basis by using a mixture of sulfuric acid and nitric acid in Germany in 1846, and he is therefore generally credited with its discovery. It is the only inorganic ester of cellulose of commercial importance. It was first used in explosives but soon found uses in plastics (celluloid), synthetic fibers and lacquers. Today it is used extensively in the manufacture of plastics and quick drying lacquers.

Cellulose nitrate is more frequently called nitrocellulose, and the process of esterification is often referred to as nitration. Both terms are incorrect. Cellulose nitrate is an $RONO_2$ type ester of nitric acid and not an RNO_2 type nitro compound.

The ester may be prepared by subjecting cellulose to the action of nitric acid in the presence of a dehydrating agent. The reaction liberates one mole of water for each hydroxyl group esterified. Assuming complete nitration the following equation may be written:

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

Theoretically three "cellulose nitrates" may be prepared; the

trinitrate (14.14%N); the dinitrate (11.11%N); and the mononitrate (6.76%N). The conditions of esterification may be controlled so as to react one, two, or three of the active hydroxyl groups and therefore any desired nitrogen content may be obtained.

Commercially, however, it is impossible to produce the trinitrate ester, the upper nitrogen limit being between 13.5 and 13.8 per cent. Beyond this range the ester becomes insoluble in commercially available solvents. Likewise, below about 10.5 per cent nitrogen it is difficultly soluble and has less desirable physical properties [26].

Except for the trinitrate, the esters do not represent stoichiometric compounds, but rather cellulose chains with the nitrate ester groups substituted in random fashion along the entire length of the chain. Earlier views that cellulose nitrate is a mixture of unnitrated cellulose and mono-, di-, and trinitrate esters of cellulose are erroneous since it has been found impossible to separate these compounds by fractionation [5].

According to present theory nitration is a homogeneous or permutoidal type reaction, wherein the nitrating reagents penetrate uniformly into the cellulose fiber nitrating all the chains at approximately the same time. Therefore, the nitrate groups become rather uniformly distributed along the chain with little likelihood of any

chain being completely nitrated preferentially [2]. This theory is further verified by the fact that upon fractionation of a given sample of cellulose nitrate, certain physical properties are found to vary considerably with different fractions, but the nitrogen content remains relatively the same. This means that cellulose nitrates are homogeneous with respect to nitrogen content and heterogeneous with respect to chain length [4]. Cellulose nitrate is a generic term referring to a family of compounds whose molecules though very similar in chemical properties may differ in size and composition.

The average degree of polymerization and the nitrogen content determine the uses to which a given sample of cellulose nitrate can be put. The degree of polymerization is controlled by the nature of the cellulose, nitration conditions, and treatment of the product after nitration; the degree of esterification only by the nitrating conditions. For explosives the nitrogen content varies from 12.5 to 13.5 per cent; for films and lacquers, from 11.2 to 12.3 per cent; and for plastics, from 10.7 to 12.2 per cent. The average degree of polymerization is lowest for lacquer grades and highest for explosive grades, varying from approximately 170 to 3500 [21][80].

The average number (n) of nitrate groups per glucose unit can be calculated from the relationship,

$$n = \frac{162N}{1400 - 45N}$$

where N is the percentage of nitrogen determined by analysis [17]. There is no method for determining the distribution of the nitrate groups, either along the cellulose chain, or between the second, third, or sixth positions of the glucose units. An attempt has been made [67] to determine the distribution of the nitrate groups in the individual glucose units by replacing the primary nitrate groups with iodine by reaction with sodium iodide. Data obtained in this manner indicate that at least one half of the nitrate groups of low nitrogen content esters (2.5 - 9%N) are in the primary position. This method is unsatisfactory for highly nitrated compounds.

V. SOLVATION OF CELLULOSE

A. Physical Aspects

1. Solvability

"The literature on solutions of cellulose and its derivatives is exceedingly voluminous, but both the theoretical views and the existing copious experimental material lack uniformity and, indeed, are often contradictory.... For instance, opinions still differ as to the state of dispersion in cellulose solutions and solutions of high-molecular substances in general.... The approach to this subject (dispersion of cellulose) is limited because it deals with systems characterized by pronounced reciprocal action between solvent and the solute and also mutually between the dissolved particles. It is always difficult to account theoretically for the action of such forces and inferences as to the size and state of the dispersed particles drawn from the results of physiochemical experimental tests should therefore be accepted with the utmost reserve. This applies in particular to the relatively concentrated solutions used in actual practice..."[28]

The preceeding quotation is not intended to serve as an apology for the present state of knowledge concerning the subject for it would be presumptuous to assume that one is required; rather the quotation is intended to emphasize the only valid premise which can serve as an acceptable basis for such a discussion at the present time.

The term "cellulose" does not denote a homogeneous chemical compound but includes a variety of organic or artifical objects. While these are built up of chain molecules of similar nature the average length and distribution of chains and particularly the supermolecular (micelle) structure may be entirely different in different specimens. In addition the size and percentage of the crystalline regions and the degree of perfection of their lattice order are also complicating factors.

The methods by which cellulose can be dispersed to a solution are divided into two classes--direct and indirect dispersion methods [29]. In the latter method the cellulose is first converted into a derivative by substitution of one or several of the hydroxyl groups and the derivative is then dispersed in a suitable solvent (e.g. cellulose nitrate in acetone, methylcellulose in chloroform). At any rate a chemical reaction between the cellulose derivative and the dispersing medium is postulated

prior to solution. Although such a situation implies that, as a result of a secondary reaction, there must be a certain degree of decomposition of the chain molecules, it has been found in certain instances that chain decomposition is not an indispensable condition for the process of dissolving. Many cellulose preparations can be dissolved and precipitated repeatedly without displaying serious signs of disintegration [30]. In nearly all cases, however, an intermicellar reaction precedes solution indicating that solution is dependent upon this process.

2. Monomolecular vs. Polymolecular Dispersion

a. Evidence for Polymolecular Dispersion

Accepting the fringe micellar theory to account for fiber structure, it is necessary to assume that the methods of solvation accomplish the break down of the structure to a solution without necessarily disintegrating the chain molecules. The processes involved are not directly evident. The simplest case would be if the dispersion progressed to the extent that individual chain molecules of the fiber were dispersed and floated free in the solution as independent particles. Such a situation necessitates complete dissociation of the fiber and here differences of opinion and theoretical difficulties arise. Since the existence of individual micellae (i.e. lattice ordered particle) for the

solid fiber condition has been refuted, this concept is not acceptable. Imagining the dispersion of polymolecular particles out of the fiber entails the assumption of either the simultaneous disintegration of chains at certain places [85], or at least the disruption of certain chain sections previously held together in a lattice order. This idea cannot explain why the lattice order should be ruptured at certain selective places and, at the same time, be maintained at other equivalent places. Figure 5 shows how Schramek imagines the formation of separate polymolecular particles, while chains disintegrate, when a fiber is converted to cellulose xanthate upon being dissolved. Schramek, therefore, assumes that the xanthation reaction brought about by the solution and causing conversion only in the intermicellar amorphous regions is heterogeneous. Therefore, the dispersed particles would have the character of "fringe micellae." O. Faust [19] proposes a similar theory.

Others favoring the concept of a dispersion of polymolecular particles are J. W. McBain and D. A. Scott [56] and Th. Lieser and his associates [46]. Lieser contends that there is a heterogeneous chemical reaction brought about by solution which affects only the surface and not the interior of the crystalline regions, thus producing polymolecular particles in the nature of an

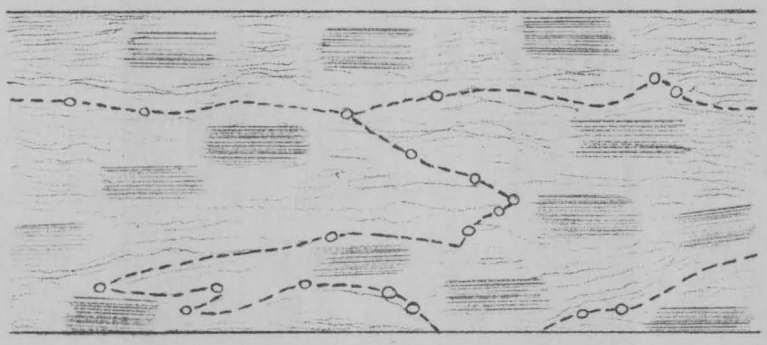

Figure 5. Diagram of Dispersion of a Xanthated Fiber.
(W. Schramek)

-----: Places of cleavage.
ooooo: Oxidizable primary valence bridges in the cellulose molecules.
Faint lines: Sections of disturbed lattice order.

From:
"Physics and Chemistry of Cellulose Fibres", P. H. Hermans.
Elsevier Publishing Co., Inc., Netherlands (1949). p. 47.

island unaffected by the reaction. He does not favor the idea of disintegration of chains but in view of the present fringe micellar concept he cannot explain how the particles are torn out of their association within the fiber without disintegration of the chains. His notion appears applicable only in those instances where only a portion of the reactive hydroxyl groups take part in the reaction, and he is forced to assume molecular dispersion whenever a stoichiometrically comprehensive reaction occurs. Lieser has advanced further experimental arguments in support of his theory [47] and holds that the states of dispersion in solutions of cellulose and its derivatives must vary considerably according to circumstances.

Recently much work has been done in studying the properties of films as functions of the particular solvent and concentration from which they were produced. G. G. Jones and F. D. Miles [41], G. Centola [9], J. Desmaroux and M. Mathieu [13] [49], A. V. Blom [6], E. Heuser and H. Y. Charbonnier [39] have all noted variations in film properties and have attributed them to differences in dispersity.

b. Evidence for Monomolecular Dispersion

The present consensus is that, when extremely dilute solutions are considered, most solvents give rise to

monomolecular dispersion except for experimentally recognizable special cases. For any except low concentrations more complicated processes are involved. First, from a purely kinetic-statistical viewpoint, in a concentrated solution there is less probability of a molecule's being surrounded only by molecules of solvent (i.e. being "free") than there will be in a very dilute solution. In the concentrated solution there are more likely to be chain fragments as well as solvent molecules attached to the various places along a given chain. Thus the chains cannot be considered "free and moving independently of each other" [60] since there are effects of forces between molecules arising at the places of contact.

Secondly, the cellulose derivative, being an incompletely substituted polyhydric alcohol may associate in the fashion characteristic of substances containing hydroxyl groupings.

In the third place, there may be binding of the solvent molecules to the chain molecules, i.e. solvation. In concentrated solutions there will be an increased probability of two adjacent chains setting up attractive forces between themselves by competing for the solvent molecule.

Thus there is the possibility of many kinds of mechanical interlinking and interaction between the

dissolved chain molecules. Therefore, the presence of molecules temporarily interlinked and reciprocally oriented in a certain way must be assumed even in dilute solutions and especially in polar liquids. In any case it should be kept in mind that in both low-molecular and high-molecular substances, these phenomena are dependent upon internal equilibrium. Persistent groups of assembled molecules are not formed, but rather the process is one of repeated formation and dissolution [61]. Moreover, the average particle size is variable, depending on such things as temperature and concentration [31]. Also, there is the chance in chain type molecules of a single chain's being involved in a number of associations and group formations, so that one molecule may be involved in several associations. Thus, to a certain degree, all dissolved molecules might be considered as taking part in the formation of a kind of network of associations pervading the entire solution [62].

In discussing the possible dispersion states of cellulose and its derivatives the views of H. Staudinger should not be overlooked [98] [99]. According to him, the process of solution either for high-molecular or low-molecular substances is the same. Recent investigations and particularly thermodynamic data substantiate his views [58]. His well-known viscosity law is based on the premise

of a molecular dispersion and is subject to the restriction of being applicable only to very dilute solutions. In such solutions Staudinger postulates the interaction, association or agglomeration among "free" chains will be at a minimum.

There is also another factor--the so-called "time effect"--to be considered in discussing dispersion of macromolecular substances. It is, for instance, possible that in macroscopic dissolution, aggregates of several molecules (i.e. polymolecular particles) may initially go into solution and only later disintegrate gradually in the solution. Such an occurrence would be manifested by a time-lag in the transition from concentrated to more dilute solutions. R. O. Herzog and B. Lange [34] were able to show by observing the depolarization of Tyndall light that, after the solution of a number of cellulose derivatives and other macromolecular substances, there was a time lag before before complete equilibrium occurred. The depolarization angle measured indicated a diminution of particle size. Similarly, M. Mathieu [50] claimed that more than a week elapsed after the preparation of a dilute solution of cellulose nitrate in acetone before a state of equilibrium was obtained. During this period the viscosity of the solution and the crystallinity of films produced from it by evaporation of the solvent continued to change. This was

interpreted as further signs of delayed dispersion. There are many other references in the literature [32] for the case of delayed dispersion.

At present the most striking evidence in favor of the idea of monomolecular dispersion is as follows:

(1) The osmotically determined molecular weights and specific viscosity of very dilute solutions are dependent only in a very slight degree upon the temperature and the solvent. If there were marked associative agglomerations, this dependence should be more marked.

(2) The molecular weight determined osmotically and viscosimetrically usually remains unchanged despite the introduction of foreign groups into the molecule (e.g. by acetylation, methylation, etc.), that is, what H. Staudinger calls "polymer-analogous conversions." This was confirmed by E. O. Kraemer by use of an ultra-centrifuge.

(3) Many cellulose derivatives in solution can be spread to monomolecular films on a surface.

In summary of the preceeding views discussed in this section it may be said that extremely dilute solutions of cellulose and its derivatives consist of molecular dispersions. The exceptions to this general rule are incompletely substituted cellulose derivatives containing free hydroxyl groups in certain solvents. In concentrated

solutions it is assumed that interlinking and interaction occurs between the molecules although the exact nature and effect of this action remain unsettled questions. The chains appear to have definite reactive centers which take part in the interlinking processes. This makes possible solutions with a structure. The liquid character of the solution is maintained by the associated chain aggregate's being in equilibrium with the nonassociated molecules so that the points of cohesion are permanently changeable. The total number of association bonds is, for the present regarded as a function of concentration, temperature and the nature of the solvent.

B. Chemical Aspects of Solution

As stated previously (page 36), chemical reaction plays a part in all known processes for the solution of cellulose. In either the direct or indirect dispersion process a compound is always primarily formed with the solvent; either there is substitution of the hydroxyl groups or else a molecular (addition) compound formed, which afterwards dissolves. This has been proved by Alf of Ekenstamm [18] and by Hess and Ulmann [36] with solutions of cellulose and mineral acids. Likewise, the primary formation of compounds when dispersing in concentrated salt solutions [43] and in tetra-alkyl ammonium bases [94] was

proved by x-ray diagrams.

It is possible to conclude, therefore, that an intra-micellar reaction always precedes the process of dissolution. Although there have been instances where solution occurred despite outright proof of a stoichiometrical reaction having previously occurred, in all such cases doubt existed as to whether the case of the crystalline regions had really remained unaffected or whether the amount of new compound formed was too small to be manifested in the x-ray pattern. Numerous investigations have shown that a new diagram does not become perceptible until extensive conversion of the original compound into the new one has taken place [35].

In support of this theory Miles [63] and Mathieu [51] [81] were able to prove that intramicellar reaction takes place dispite incomplete nitration of cellulose (with as yet no preceptible "nitrate diagram"). There are many verifications of this concept in the literature [10] [11] [81]. That intramicellar swelling should be a necessary prerequisite to solution is easily explainable. The cohesion between chain molecules in the crystalline regions of the unchanged cellulose is very strong since there is hydrogen bonding. No "ordinary" solvent exists which is capable or overcoming the cohesive forces and

dispersion cannot take place without the contributive energy of a chemical reaction. Although every intramicellar exhaustive reaction does not entail dispersion, the converse is true.

Whether or not solution occurs depends also upon intramicellar swelling. It is interesting to note that for this to happen the composition of the surrounding solution must more often than not be different from the optimum composition for the formation of the primary compound. Thus, according to Alf of Ekenstamm [18] in order to dissolve hydrate cellulose in phosphoric acid, it must first be saturated with 11.6 N acid (formation of the compound) and then be dissolved in a 14 N acid (swelling). It is not possible to dissolve direct in the latter acid.

A prerequisite to intramicellar swelling is that it occurs with a positive heat effect [33]. It has been shown by x-ray spectrography that when cellulose nitrate is dissolved in acetone, a compound is formed prior to swelling and solution. These facts point toward the primary separation of all the chain molecules. A summary of x-ray behavior during formation and solution of cellulose derivatives including the theories relating to the subject has been published by W. A. Sisson [92].

1. Swelling--The Dissolution of the Micellar System

The initial phase of swelling is usually governed entirely by factors of energy. The molecules of the dispersing or swelling agent first press forward along the amorphous regions forcing the chain molecules apart. In this process if energy conditions at this point do not permit the junction points of maximum cohesive strength to be overcome the process stops at these points. In such cases the liquid acts as a swelling rather than a dispersing agent and the situation is referred to as a case of limited swelling, as for example in cellulose-water systems. Since the crystalline regions are left intact there is no change in the x-ray pattern and this process is also termed intercrystalline or intermicellar swelling.

The concept of intermicellar and intramicellar penetration of solvent may be interpreted by reference to Figure 6. In this diagram an oriented adsorption of the first layer of bound solvent molecules on the chains is assumed. Such an oriented adsorption is explained as being due to the chains containing polar groups to which the solvent molecules attach themselves, either by induced polarization or because of self-contained solvent dipoles. This attachment occurs in an oriented fashion and with a positive heat effect. The oriented adsorption results in a diminution of the partial entropy of the solvent, since

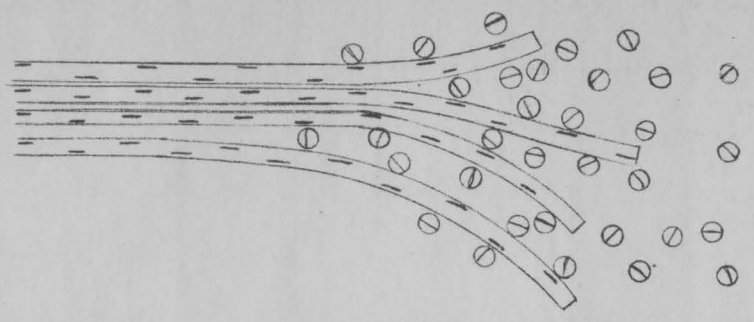

Figure 6(a)

Solution of a Micellar System. Intermicellar Swelling.

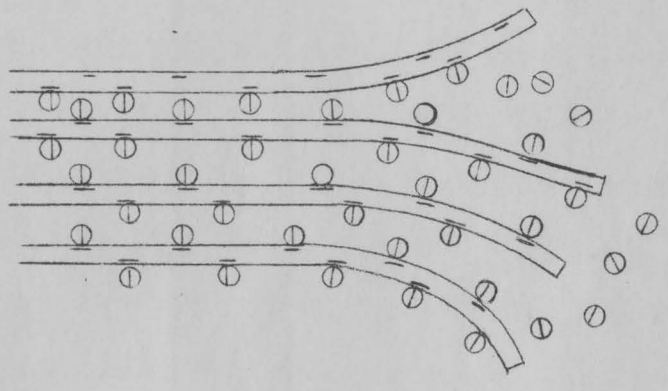

Figure 6(b)

Solution of a Micellar System. Intramicellar Swelling.

From:
"Physics and Chemistry of Cellulose Fibres", P. H. Hermans. Elsevier Publishing Co., Inc., Netherlands (1949). p. 63.

the thermodynamic probability of the aligned molecules is less than that of their random state in the pure liquid. G. V. Schultze [86] has shown the actual probability of this decrease in entropy of the solvent in the initial stage of swelling in the nitrocellulose-acetone system. Provided the affinity of the solvent for the macromolecular components (i.e. the free energy change) is great enough, the process continues and the solvent molecules penetrate further into the crystalline regions causing intracrystalline or intramicellar swelling.

One of two possibilities now occurs; either a stoichiometrical number of solvent molecules penetrates into the lattice and swelling ceases (Figure 6(b)) or there is unlimited penetration by solvent molecules leading to the complete dissolution of the micellar system. In the first case an addition compound is formed between the macromolecular substance and the solvent. Examples of this are cellulose in concentrated sodium hydroxide, nitric acid, perchloric acid, hydrazine and other substances. It is thought that in such cases further swelling depends often entirely upon entropy, with the possible ultimate dissolution of the new addition compound whose heat of solution is far less than that of the original cellulose crystallites. In this respect it has been noted in a few well authenticated

cases, that, after the strongly exothermic absorption of initial doses of swelling agent by the original substance, all further swelling and solution is endothermic. E. Calvet and co-workers [8], in studying the nitrocellulose-acetone system, found that after approximately six moles of acetone per C_6 group were absorbed with considerable positive heat effect (23 kcal), appreciable cooling followed as the absorption of acetone proceeded until 18.5 kcal were reabsorbed by the system up to infinite dilution (and solution).

In support of this, M. Mathieu [53] has shown by radiography, that with six moles of acetone per C_6 unit, the formation of a coordinative addition nitrocellulose-acetone compound is completed. Its composition corresponds to approximately 50 per cent nitrocellulose, the point at which G. V. Schultze, in his thermodynamic analysis of the system likewise found discontinuity in the character of solvent binding.

VI. EXPERIMENTAL

Three major experimental techniques were attempted during this investigation. These were as follows:

(1) The isolation of a cellulose nitrate gel and its analysis by physico-chemical methods.

(2) The analysis of the acetone-water-cellulose nitrate system by measurement of its dielectric properties.

(3) The analysis of the system by means of refractive index studies.

A. Gel Isolation and Analysis

This phase of the investigation was suggested by the work of Miller [64] who initiated the study of the solvation of cellulose nitrate at this laboratory. Using a dilution ratio titration technique [12], with water as the precipitating agent, he titrated a solution of cellulose nitrate dispersed in acetone. The end point of the titration was marked by the appearance of turbidity in the solution which indicated the precipitation of cellulose nitrate. By measuring the change in the electrical nature of the system upon the addition of portions of precipitating agent, Miller attempted to correlate what was thought to be a change in dielectric constant with the solvation of the cellulose.

Sharpe [88], in subsequent work, using the same technique demonstrated that the property actually measured was the electrical permeability of the system rather than a dielectric property. However, since the work up to this point had been concerned only with measurements on the solution phase of the system it was decided to begin an investigation of the precipitated gel phase in an effort to secure additional data.

As in previous work, 5 per cent solutions of cellulose nitrate having an average D. P. of 75 were prepared using acetone as the solvent. These solutions were titrated with water until the addition of more water caused no further precipitation of cellulose nitrate. The titrations were carried out in centrifuge bottles and the samples were then centrifuged for fifteen minutes and the supernatant liquid decanted. After the gel had been weighed, analysis of the sorbed film was attempted by distillation. In the initial experiments dehydrite tubes were used to absorb the water in the distillate but proved unsatisfactory because the absorbent was very quickly reduced to a slurry. This condition could not be remedied either by the use of multiple absorbent tubes or by the application of heat to the initial portion of the tubes. It was finally decided to use a cold trap to catch the

distillate whose composition was then determined by a specific gravity measurement.

A series of runs indicated that reproducible results could not be obtained by the procedure mainly because it was impossible to precipitate a firm, uniform gel with material of such a D. P. Numerous filter aids were tried without success. In view of this factor, along with the inherent difficulties of handling such a system, it was decided to abandon this approach and to concentrate entirely on dielectric measurements which, under further study, had shown definite promise.

B. Dielectric Analysis

During the time the above experiments were being carried out on the gel phase, Sharpe [88] had continued the investigation of the solution phase and had demonstrated that the electrical permeability of the system was an apparent function of the state of solvation of the system. He also proved conclusively that such measurements were extremely sensitive to any ionic impurities present. There was, however, no basis for assuming that the electrical permeability was related to the dielectric constant, since, by definition, the latter is a ratio of electrical capacitances. At this point it was decided to modify the instrument used by Miller and Sharpe so as to actually measure the dielectric constant of the system and thus study it as a function of solvation.

Attention Patron:

Page 54 omitted from numbering

In order to measure dielectric constant it was necessary to replace the coil-type measuring cell of the original instrument with some sort of condenser-type cell. After trying several types, it was finally decided that the most satisfactory cell was one essentially similar to that used by Testerman in his work on dielectric relaxation [100].

The incorporation of such a cell into the instrument also necessitated a major change in experimental technique since the volume of solution which could be handled was limited to 50 ml. by the volume of the measuring cell. The cell, in turn, could not be made larger since the electrical components of the instrument required a very small capacitance and this factor limited the size of the cell unconditionally. Thus, the dilution ratio titration technique was no longer feasible since that procedure involved the handling of volumes up to 130 ml. in the measuring cell during precipitant addition.

The work of Moore [65], in his studies on cellulose nitrate-solvent interaction, suggested a new method of approach. He studied the swelling of cellulose nitrate in binary mixtures of solvents and non solvent (hexane) containing various concentrations of solvent up to that at which solution occurred. By making up a series of solutions of varying composition to which was added sufficient cellulose nitrate to maintain a constant ratio of cellulose

to solution, he was able to estimate the composition of the liquid and absorption of solvent by cellulose nitrate from a dielectric measurement using only a 3 ml. sample.

Preliminary tests showed that a ratio of 0.2 gram of cellulose nitrate to 10 grams of solvent-non solvent solution could be used satisfactorily for the investigation. This was the same ratio used by Moore and by using a multiple of this proportion, it was possible to arrive at the quantities of material which could be handled most conveniently with the equipment available. This was approximately 6.5 grams of cellulose nitrate to 325 grams of solvent-non solvent solution.

The object of the study was to obtain solvation data in the region where there was either none, or a negligible quantity of dissolved cellulose nitrate present in solution. Therefore, a preliminary investigation was made to determine the composition of the solvent-non solvent solution possessing the optimum swelling-minimum dissolving power for the cellulose nitrate.

Twenty samples of 0.2 gram of cellulose nitrate were weighed into test tubes and 10 grams of solvent-non solvent solution whose composition varied by increments of 5 per cent within the range 0 to 100 per cent solvent was added. The tubes were stoppered securely, shaken for one hour and placed over night in the constant temperature box at 25°C.

The samples were examined to determine the solution in which optimum swelling-minimum solution had occurred. Tests for the presence of dissolved cellulose were made using 5 ml. portions of the supernatant liquid to which non solvent was added to precipitate any dissolved cellulose nitrate. Precipitation was indicated by the presence of turbidity in the solutions. It was found that a solution containing 65 per cent solvent and 35 per cent non solvent possessed the desired optimum swelling-minimum solution properties.

Since a resonance type apparatus was to be used to measure the dielectric constant it was imperative that the conductivity of the solutions be minimized as much as possible. Therefore, it was necessary to subject the cellulose nitrate to a vigorous purification procedure [10] since it had been stabilized by washing with sodium carbonate. After purification the cellulose nitrate was dried and stored in vacuum desiccators over sulfuric acid until use.

The acetone and distilled water used to make up the solvent-non solvent solutions were known to be free of ionic impurities and for the sake of accuracy and convenience these solutions were made up in 5000 gram batches and kept as stock solutions. Solutions of 10, 20, 30, 40, 50, 55, 60, 65, 70, and 75 per cent solvent were used for

dielectric measurements although it was realized that solution of the cellulose was appreciable beyond the 65 per cent range previously mentioned. It was found by experimentation, however, that apparently an appreciable quantity of cellulose nitrate could be dissolved in a sample of pure acetone without causing a detectable difference in the dielectric constant of the pure solvent.

The instrument was calibrated as in the previous manner [64] [88] and a series of measurements were attempted. Analysis of the data, however, gave completely anomalous results which were attributed to two principal sources of error, one of which apparently was the fact that the calculation depended upon isolation of the gel phase. It was now possible, by using cellulose nitrate with an average D. P. of 392 to precipitate a firm, hard gel. It also seemed possible to separate excess solvent-non solvent from the gel by an arrangement based on filtration by centrifugation. However, there was a large discrepancy among the gel weights of a given sample although the samples were treated identically in every respect. It was finally concluded that there was always a random amount of excess solvent-non solvent trapped within the gel interstices that could not be removed except by ultrafiltration or ultracentrifuge units.

The second source of error lay in the fact that the instrument was not capable of measuring accurately enough the very small differences in solvent-non solvent composition which occurred during solvation. This introduced such a large percentage error into the measurement that the instrument could not be used for further work unless a precision condenser was installed. A commercial precision condenser with the capacitance range required by the circuit was not available and an attempt to construct one was unsuccessful. An attempt to use another dielectric instrument employing a Hartley type oscillator circuit into which a General Radio Precision Condenser was incorporated was also unsuccessful and in view of the complexity of electronic problems being encountered it was decided to abandon dielectric measurements as a technique of investigation.

C. Refractive Index Analysis

Although no reliable data had been obtained in preceding work, it was evident that a method capable of extremely high accuracy was required to measure the very small differences in solvent-non solvent composition which occurred during solvation. Measurements of refractive index are among the easiest and most accurate measurements in physical chemistry. A Bausch and Lomb immersion or

dipping refractometer, capable of measuring the refractive index to 0.00003 [22], was available, and it was decided to use this instrument for further investigation.

In order to achieve maximum accuracy with this instrument the temperature of the liquid being analyzed was controlled within $\pm 0.1^{\circ}C$ by means of a water bath. To avoid loss of solvent by evaporation, the solution was placed in a metal cup which fitted securely about the prism. This entire assembly was placed in the water bath and at least ten minutes was allowed to attain temperature equilibrium before measurements were made.

The refractive index was not measured directly by the instrument. A grazing or critical ray of light formed a border line between the light and dark parts of the field of view. The micrometer eye piece of the instrument was equipped with an accurately ruled scale and vernier arrangement which permitted estimation of the position of the dark border to a small fraction of a scale division [23]. The scale reading was then converted to the refractive index by reference to a table of data which accompanied the instrument [24].

The refractive index of acetone is 1.3591 at a wave length of 589 mμ (sodium D line) and $20^{\circ}C$; the refractive index of water is 1.3330 under the same conditions [45].

The difference in refractive index of the two components of the system was, therefore, 0.0261--a magnitude capable of accurate measurement by the dipping refractometer.

In order to be certain that the change in refractive index reflected an actual change in solution composition caused by solvation, and was not caused by the presence of dissolved cellulose nitrate in solution, a preliminary experiment was made to determine the quantity of cellulose nitrate actually being dissolved in solution. It was logical to expect some solution to occur in the solvent-rich solutions and it was necessary to determine to what extent this occurred and to evaluate its effect on the refractive index.

A 0.96 per cent cellulose nitrate solution was prepared by dissolving 3.0 grams of test cellulose nitrate in 150 grams of acetone. This concentration was chosen because it represented the ratio of solute to solution (0.2 to 10.0) that was to be used in actual measurements and it was also expected that the solution represented a much higher concentration of dissolved cellulose nitrate than would ever be encountered in actual measurements. A 0.5 per cent cellulose nitrate was also prepared by dissolving 0.5 gram in 100 grams of acetone. This concentration was believed to be much higher than would be encountered in experimental work also, however, it was desirable to

compare changes in refractive index at various concentrations of dissolved solute. It was assumed that the differences in refractive index between the pure solvent and the cellulose nitrate solutions must be caused only by the presence of the dissolved particles since the possibility of a change in composition by sorption was excluded in that only pure solvent was present initially. The results of these tests are summarized in Table II and will be discussed below in conjunction with the second portion of this preliminary experiment.

In the second part of the preliminary experiment the quantity of cellulose nitrate dissolved in the solvent-non solvent solutions used in an actual run was determined. Solutions which were analyzed for dissolved material were in the solvent-rich region of the system and consisted of 55, 60, and 65 per cent solvent. It was in these solutions that the highest concentration of dissolved material should be found. The analysis was made by carefully weighing a portion of the solvent-non solvent solution into a glass stoppered weighing bottle which had previously been dried to a constant weight. The bottles containing the solution were then placed in an oven at 105°C until, after being reheated and cooled in a desiccator several times, they again attained a constant weight. The gain in weight

over the original tare weight of the bottle represented the weight of cellulose nitrate which had been present in solution. Blanks, consisting of a portion of the original solvent-non solvent solution, were run with each analysis, however, they showed no detectable residue.

As shown in Table II, a concentration of cellulose nitrate of 0.96 per cent caused a difference of 0.00167 between the refractive index of the pure solvent and the refractive index of the cellulose nitrate solution. A concentration of 0.50 per cent caused a difference of 0.00051. The actual concentration of dissolved cellulose nitrate found by analysis of experimental solutions used was 0.004, 0.006 and 0.010 per cent cellulose nitrate from solutions consisting of 55, 60 and 65 per cent solvent respectively. Therefore, the highest concentration of dissolved cellulose nitrate encountered under actual experimental conditions was approximately 90 times less than the concentration required to change the refractive index 0.002 and approximately 50 times less than the concentration which caused a change of 0.0005 in the reading. Therefore, it was decided that it was a valid assumption to regard the entire solvent-non solvent system of interest in this investigation as a two component system; that is to regard as negligible any dissolved cellulose nitrate in the system.

As a result of the preliminary experiment it was also decided to change the ratio of cellulose nitrate to solvent-non solvent solution from 0.2 to 10.0 to a ratio of 0.2 to 5.0 in order to secure a difference in solvent-non solvent composition during solvation which was capable of more accurate measurement.

TABLE II

A. THE EFFECT OF DISSOLVED CELLULOSE NITRATE ON REFRACTIVE INDEX

	Refractive Index 25°C	
Per Cent Solution	0.96	0.50
Pure Solvent	1.35511	1.35511
Solvent plus Cellulose Nitrate	1.35678	1.35562
Difference	0.00167	0.00051

B. THE DETERMINATION OF ACTUAL AMOUNTS OF CELLULOSE NITRATE DISSOLVED -- RUN I

	Per Cent Solvent in Solution		
	55	60	65
Weight Sample, gms.	24.1599	24.2691	20.3004
Weight Cellulose Nitrate Dissolved, gms.	0.0010	0.0015	0.0025
Per Cent Cellulose Nitrate Dissolved	0.004	0.006	0.010

Inasmuch as the preliminary experiment established that the dipping refractometer was applicable to the problem, a calibration curve was made which related the refractive index and the percentage composition of the solvent-non solvent solutions. Calibration solutions containing a known weight of solvent and non solvent were prepared using an analytical balance. The refractive index of each solution was determined immediately, and by plotting composition against the refractive index of the solution, a calibration curve was prepared. Scales were chosen so that the refractive index could be read to the fourth and estimated to the nearest tenth of a per cent. Data for the calibration curve are contained in Table III.

TABLE III

DATA FOR CALIBRATION OF

BAUSCH AND LOMB IMMERSION REFRACTOMETER

Acetone		Refractive Index
Weight %	Mole %	25 ± 0.1°C
4.99	1.60	1.33513
10.03	3.33	1.33877
14.94	5.16	1.34207
19.80	7.11	1.34526
24.77	9.26	1.34858
29.86	11.65	1.35169
34.91	14.25	1.35425
39.93	17.08	1.35649
44.79	20.09	1.35836
49.89	23.58	1.35988
54.85	27.35	1.36113
60.00	31.74	1.36192
64.84	36.37	1.36242

An outline of the experimental technique used in making a run is as follows:

(1) Samples of 6.5 grams of dry cellulose nitrate were weighed into metal weighing cans using a small beam balance.

(2) The cans containing the samples were then accurately weighed on an analytical balance after which the cellulose nitrate was transferred from the cans into clean, dry, 500 ml. Erlenmeyer flasks. The flasks, which were marked "Series A" and numbered one through ten, were fitted with rubber stoppers wrapped with tin foil to prevent contact between the solvent and rubber. The cans were weighed again and the difference in weight recorded as the weight of cellulose nitrate sample.

(3) Another set of Erlenmeyer flasks, identical to those above, except designated as "Series B", was used to handle the solvent-non solvent solutions. For the refractive index work, as with the dielectric studies, the solvent-non solvent solutions were prepared in 5000 gram quantities and stored as stock solutions. Ten stock solutions, containing 10, 20, 30, 35, 40, 45, 50, 55, 60 and 65 per cent solvent by weight, were prepared. The stock solution was transferred to the 500 ml. Erlenmeyer flasks marked "Series B". A sufficient volume of solution was

taken so that an excess was available after the required portion of solvent-non solvent was added to the cellulose nitrate. The excess portion of the solution was used for the analysis of the original fraction of solvent-non solvent present.

(4) The weight of solvent-non solvent solution required by the weight of cellulose nitrate sample was calculated on the basis of 0.2 gram cellulose nitrate to 5 grams of solvent-non solvent, and this weight of solution was added to the sample flask using a beam type balance accurate to $\pm$0.1 gram.

A series of runs was also made up using a ratio of 0.2 gram cellulose nitrate to 2.5 grams of solvent-non solvent. This was done to secure data which were to be used in conjunction with the data obtained in the 0.2 to 5 ratio.

(5) The flasks were placed on a mechanical shaker and shaken for a period of one hour at a temperature of 25 $\pm$ 2.0°C. All flasks were kept at this temperature until analyzed. It was found that the solutions attained equilibrium upon shaking and standing over night, so all analyses were made within 24 hours after addition of the solvent solution in order to avoid extended degradation of the cellulose nitrate.

(6) Measurement of refractive index was done by placing a small quantity of the solution in a cup which fitted securely about the prism of the instrument. This portion of the refractometer was then placed in a water bath at 25 ± 0.1°C and ten minutes was allowed for temperature equilibrium to be attained before measurements were made. The method of manipulation of the instrument and of calculating the refractive index and composition of the solvent-non solvent solution was the same as previously described.

The solutions used for analysis of the original fractions of solvent and non solvent present were portions of solution which remained after the required weight of solvent-non solvent was added to the cellulose nitrate samples. These solutions were analyzed without further treatment. However, the analyses of the solvent-non solvent solution to determine the final fractions of solvent and non solvent present after solvation were made on portions of the solution which were decanted from the cellulose nitrate and filtered into the sample cup. The filtration step was necessary to remove small particles of cellulose nitrate from the supernatant solution in order that they would not affect the measurement.

VII. MATERIALS

In the Gel Isolation and Analysis work the cellulose nitrate used was RS type ½-second, Lot 6226, obtained from the Hercules Powder Company, Parlin, New Jersey, having a reported nitrogen content of 12 per cent. Its average D. P. was 75.

The work on Dielectric and Refractive Index Analysis was carried out with cellulose nitrate, type 600-1000 seconds, Lot 1379, obtained from the Hercules Powder Company, Parlin, New Jersey, having a reported nitrogen content of 12 per cent. Its average D. P. was 392.

In all experiments the acetone used was C. P. grade supplied by the Commercial Solvents Corporation, Peoria, Illinois.

The distilled water was prepared by the chemistry department's stock room still and had a negligible conductivity.

VIII. DATA

Data obtained in the investigation are compiled in Tables IV to XVII. These data are based on cellulose nitrate having a nitrogen content of 12 per cent whose molecular weight was 263.7 calculated as follows:

Let x = the number of nitrate groups per C_6 unit.

Then $C_6H_{10}O_5 - x(OH) + x(NO_3)$ = molecular weight of the cellulose nitrate,

and xN = weight of nitrogen present,

where N = atomic weight of nitrogen.

Therefore, $\frac{xN}{C_6H_{10}O_5-x(OH)+x(NO_3)} \times 100 = 12\%$

$$\frac{14x}{162 - 17x + 62x} \times 100 = 12\%$$

$$1400x = 1944 + 540x$$

$$860x = 1944$$

$x = 2.26$ nitrate groups per C_6 unit.

Therefore molecular weight of cellulose nitrate =

$$162 - 2.26 \times 17 + 2.26 \times 62 =$$

$$162 - 38.42 + 140.12 =$$

$$263.7$$

TABLE IV

SUMMARY OF DATA -- RUN NUMBER II

RATIO OF CELLULOSE NITRATE/SOLVENT-NON SOLVENT = 0.2/5

Soln. No.	Cellulose Nitrate		Solvent-Non Solvent	Acetone				Acetone		Water	
	Grams	Moles	Grams	Initial Wt. %	Final Wt. %	Initial Mole %	Final Mole%	Initial Grams	Initial Moles	Initial Grams	Initial Moles
1	6.4426	0.02443	161.1	9.9	9.3	3.3	3.2	15.95	0.2746	145.15	8.0639
2	6.7059	.02543	162.7	20.4	19.5	7.4	7.0	33.19	.5715	129.51	7.1950
3	6.4698	.02453	161.8	29.9	28.7	11.7	11.1	48.38	.8330	113.42	6.3011
4	6.4956	.02463	162.4	34.9	33.5	14.3	13.7	56.68	.9759	105.72	5.8733
5	6.6912	.02537	166.8	39.6	38.5	16.9	16.3	66.05	1.1372	100.75	5.5972
6	6.5002	.02465	162.5	44.7	43.2	20.0	19.0	72.64	1.2507	89.86	4.9922
7	6.4365	.02441	160.9	49.4	48.3	23.4	22.4	79.48	1.3685	81.42	4.5233
8	6.4632	.02451	161.6	54.6	52.8	27.0	25.7	88.23	1.5191	73.37	4.0761
9	6.6154	.02509	165.4	59.4	57.9	31.4	30.0	98.25	1.6916	67.15	3.7306
10	6.7550	.02562	168.9	63.8	62.4	35.3	34.1	107.76	1.8554	61.14	3.3967

TABLE V

SUMMARY OF DATA -- RUN NUMBER III

Soln. No.	Cellulose Nitrate		Solvent-Non Solvent	Acetone				Acetone		Water	
	Grams	Moles	Grams	Initial Wt. %	Final Wt. %	Initial Mole %	Final Mole%	Initial Grams	Initial Moles	Initial Grams	Initial Moles
1	6.6085	0.02506	82.6	9.9	8.8	3.3	3.0	8.18	0.1408	74.42	4.1344
2	6.6143	.02508	82.7	20.4	18.8	7.4	6.7	16.87	.2905	65.83	3.6572
3	6.7665	.02566	84.6	29.9	27.3	11.7	10.7	25.30	.4356	59.30	3.2944
4	6.5499	.02484	81.9	35.0	32.4	14.4	13.1	28.67	.4936	53.23	2.9572
5	6.4907	.02461	81.2	39.6	37.0	16.9	15.4	32.16	.5537	49.04	2.7244
6	6.3641	.02413	79.6	44.6	41.9	20.0	18.3	35.50	.6112	44.10	2.4500
7	6.2921	.02386	78.7	49.4	46.7	23.4	21.4	38.88	.6694	39.82	2.2122
8	6.4300	.02438	80.4	54.4	51.7	26.8	24.8	43.74	.7531	36.66	2.0367
9	6.7719	.02568	84.7	59.3	56.7	31.3	28.8	50.23	.8648	34.47	1.9150
10	6.3093	.02393	78.9	63.5	61.8	35.0	33.6	50.10	.8626	28.80	1.6000

TABLE VI

SUMMARY OF DATA -- RUN NUMBER IV

RATIO OF CELLULOSE NITRATE/SOLVENT-NON SOLVENT = 0.2/5

Soln. No.	Cellulose Nitrate		Solvent-Non Solvent	Acetone				Acetone		Water	
	Grams	Moles	Grams	Initial Wt. %	Final Wt. %	Initial Mole %	Final Mole %	Initial Grams	Initial Moles	Initial Grams	Initial Moles
1	6.5110	0.02469	162.8	9.9	9.3	3.3	3.2	16.12	0.2775	146.68	8.1489
2	6.4578	.02449	161.5	20.5	19.6	7.5	7.0	33.11	.5701	128.39	7.1328
3	6.3918	.02424	159.8	29.9	28.7	11.7	11.1	47.78	.8227	112.02	6.2233
4	6.3713	.02416	159.3	35.1	33.7	14.4	13.8	55.91	.9626	103.39	5.7439
5	6.4926	.02462	162.3	39.7	38.6	17.0	16.3	64.43	1.1093	97.87	5.4372
6	6.7098	.02544	167.8	44.7	43.5	20.0	19.3	75.01	1.2915	92.79	5.1550
7	6.5754	.02494	164.9	50.0	48.4	23.8	22.5	82.45	1.4196	82.45	4.5806
8	6.5774	.02494	164.4	54.8	53.3	27.2	26.0	90.09	1.5511	74.31	4.1283
9	6.5373	.02479	163.4	59.3	58.5	31.3	30.5	96.90	1.6684	66.50	3.6944
10	5.6370	.02138	140.9	64.2	63.0	35.6	34.8	90.46	1.5575	50.44	2.8022

TABLE VII

SUMMARY OF DATA -- RUN NUMBER V

RATIO OF CELLULOSE NITRATE/SOLVENT-NON SOLVENT = 0.2/2.5

Soln. No.	Cellulose Nitrate		Non Solvent	Acetone				Acetone		Water	
	Grams	Moles	Grams	Initial Wt. %	Final Wt. %	Initial Mole %	Final Mole %	Initial Grams	Initial Moles	Initial Grams	Initial Moles
1	2.9788	0.01130	37.2	9.9	8.5	3.3	2.9	3.68	0.0634	33.52	1.8622
2	2.7718	.01051	34.7	20.4	18.3	7.4	6.5	7.08	.1219	27.62	1.5344
3	2.8862	.01095	36.1	29.8	27.8	11.7	10.6	10.76	.1853	25.34	1.4078
4	2.9563	.01121	37.0	34.9	32.5	14.3	13.2	12.91	.2223	24.09	1.3383
5	3.0829	.01169	38.9	39.7	37.3	17.0	15.5	15.44	.2658	23.46	1.3033
6	2.8887	.01095	36.1	44.6	42.2	20.0	18.4	16.10	.2777	20.00	1.1111
7	2.9328	.01112	36.7	50.0	47.0	23.8	21.5	18.35	.3159	18.35	1.0194
8	3.0735	.01166	38.4	54.6	52.0	27.0	25.1	20.97	.3611	17.43	0.9683
9	3.1796	.01206	39.8	59.3	56.9	31.3	29.0	23.60	.4063	16.20	.9000
10	2.8602	.01085	35.8	64.2	62.4	35.6	34.1	22.98	.3957	12.82	.7122

TABLE VIII

SUMMARY OF DATA -- RUN NUMBER VI

RATIO OF CELLULOSE NITRATE/SOLVENT-NON SOLVENT = 0.2/5

Soln. No.	Cellulose Nitrate		Solvent-Non Solvent	Acetone				Acetone		Water	
	Grams	Moles	Grams	Initial Wt. %	Final Wt. %	Initial Mole %	Final Mole %	Initial Grams	Initial Moles	Initial Grams	Initial Moles
1	3.0184	0.01145	75.5	9.9	9.2	3.3	3.1	7.47	0.1286	68.03	3.7794
2	3.0550	.01159	76.4	20.4	19.5	7.4	7.0	15.59	.2684	60.81	3.3783
3	3.0380	.01152	76.0	29.8	28.7	11.6	11.1	22.65	.3900	53.35	2.9639
4	2.8512	.01081	71.3	34.9	33.5	14.3	13.7	24.88	.4284	46.42	2.5789
5	3.0274	.01148	75.7	39.6	38.5	17.0	16.2	29.98	.5162	45.72	2.5400
6	2.9833	.01131	74.6	44.7	43.5	20.0	19.3	33.35	.5742	41.25	2.2917
7	2.7612	.01047	69.0	49.6	48.4	23.4	22.5	34.22	.5892	37.78	1.9322
8	3.2580	.01235	81.5	54.6	53.2	27.0	25.9	44.50	.7662	37.00	2.0556
9	3.0533	.01158	76.3	59.3	58.2	31.3	30.3	45.25	.7791	31.05	1.7250
10	2.6691	.01020	66.7	64.2	62.7	35.6	34.5	42.82	.7373	23.88	1.3267

TABLE IX

SUMMARY OF DATA -- RUN NUMBER VII

RATIO OF CELLULOSE NITRATE/SOLVENT-NON SOLVENT = 0.2/2.5

Soln. No.	Cellulose Nitrate		Solvent-Non Solvent	Acetone				Acetone		Water	
	Grams	Moles	Grams	Initial Wt. %	Final Wt. %	Initial Mole %	Final Mole %	Initial Grams	Initial Moles	Initial Grams	Initial Moles
1	3.1184	0.01183	39.0	9.9	8.5	3.3	2.9	3.86	0.0665	35.41	1.9522
2	3.0334	.01150	37.9	20.4	19.2	7.4	6.8	7.73	.1331	30.17	1.6761
3	3.0948	.01174	38.7	29.9	27.8	11.7	10.6	11.57	.1992	27.13	1.5072
4	3.3788	.01281	42.2	34.9	32.6	14.3	13.2	14.73	.2536	27.47	1.5261
5	3.0189	.01145	37.7	39.6	37.2	17.0	15.5	14.93	.2571	22.77	1.2650
6	3.0154	.01143	37.7	44.7	42.1	20.0	18.4	16.85	.2901	20.85	1.1583
7	2.8918	.01097	36.2	49.8	47.0	23.5	21.5	18.03	.3104	18.17	1.0094
8	3.2985	.01251	41.2	54.6	52.0	27.0	25.1	22.50	.3874	18.70	1.0389
9	3.2346	.01227	40.4	59.4	56.7	31.3	28.8	24.00	.4132	16.40	0.9111
10	3.0994	.01175	38.8	63.7	61.7	35.5	33.4	24.69	.4251	14.01	.7783

TABLE X

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

RUN NUMBER II -- RATIO = 0.2/5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.033	0.032	0.967	0.968	11.2403	330.0818
2	.074	.070	.926	.930	22.4735	282.9335
3	.117	.111	.883	.879	33.9584	286.8732
4	.143	.137	.857	.863	39.6224	238.4612
5	.170	.163	.830	.837	44.8246	220.6228
6	.200	.190	.800	.810	50.7383	202.5233
7	.234	.224	.766	.776	56.0631	185.3052
8	.270	.257	.730	.743	61.9788	166.3035
9	.313	.300	.687	.700	67.4213	148.6887
10	.353	.341	.647	.659	72.4200	132.5800

TABLE XI

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

RUN NUMBER III -- RATIO = 0.2/2.5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.033	0.030	0.967	0.970	5.6185	164.9800
2	.074	.067	.926	.933	11.5829	145.8213
3	.117	.107	.883	.893	16.9758	128.3866
4	.144	.131	.856	.869	19.8712	119.0499
5	.169	.154	.831	.846	22.4990	110.7029
6	.200	.183	.800	.817	25.3295	101.5333
7	.234	.214	.766	.786	28.0553	92.7158
8	.268	.248	.732	.752	30.8901	83.5398
9	.313	.288	.687	.712	33.6760	74.5716
10	.350	.336	.650	.664	36.0468	66.8617

TABLE XII

SUMMARY OF DATA CALCULATED ON
BASIS OF ONE MOLE OF CELLULOSE NITRATE
RUN NUMBER IV -- RATIO = 0.2/5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.033	0.032	0.967	0.970	11.2394	330.0485
2	.075	.070	.925	.930	23.2789	291.2536
3	.117	.111	.883	.879	33.9398	256.7368
4	.144	.138	.856	.862	39.8427	237.7442
5	.170	.163	.830	.837	45.0569	220.8448
6	.200	.193	.800	.807	50.7665	202.6336
7	.238	.225	.762	.775	56.9206	183.6648
8	.272	.260	.728	.740	62.1933	165.5293
9	.313	.305	.687	.695	67.3013	149.0278
10	.356	.348	.644	.652	72.8484	131.0664

TABLE XIII

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

RUN NUMBER V -- RATIO = 0.2/2.5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.033	0.029	0.967	0.971	5.6071	164.7965
2	.074	.065	.926	.935	11.5985	145.9943
3	.117	.106	.883	.894	16.9224	128.5662
4	.143	.132	.857	.868	19.8305	119.3845
5	.170	.155	.830	.845	22.7374	111.4884
6	.200	.184	.800	.816	24.8584	101.4703
7	.237	.215	.763	.785	28.4083	91.6727
8	.270	.251	.730	.746	30.9691	83.0446
9	.313	.290	.687	.710	33.6899	74.6269
10	.356	.341	.644	.659	36.4700	65.6405

TABLE XIV

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

RUN NUMBER VI -- RATIO = 0.2/5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.033	0.031	0.967	0.969	11.2314	330.0786
2	.074	.070	.926	.930	23.1579	291.4840
3	.116	.111	.884	.889	33.8542	257.2830
4	.143	.137	.857	.863	39.6300	238.5661
5	.170	.162	.830	.838	44.9652	221.2543
6	.200	.193	.800	.807	50.7692	202.6260
7	.234	.225	.766	.775	56.2751	184.5463
8	.270	.259	.730	.741	62.0405	166.4453
9	.313	.303	.687	.697	67.2798	158.9637
10	.356	.345	.644	.655	72.8557	131.0968

TABLE XV

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

RUN NUMBER VII -- RATIO = 0.2/2.5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.033	0.029	0.967	0.971	5.6179	165.0211
2	.074	.068	.926	.932	11.5739	145.7478
3	.117	.106	.883	.894	16.9676	128.3816
4	.143	.132	.857	.868	19.7970	119.1335
5	.170	.155	.830	.845	22.4541	110.4803
6	.200	.184	.800	.816	25.3806	101.3386
7	.235	.215	.765	.785	28.2954	92.0146
8	.270	.251	.730	.749	30.9672	83.0456
9	.313	.288	.687	.712	33.6756	74.2543
10	.355	.334	.645	.666	36.1787	66.2383

TABLE XVI

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

AVERAGE VALUES: RUNS NUMBER II, IV, VI -- RATIO 0.2/5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.0330	0.0317	0.9670	0.9683	11.2370	330.0696
2	.0743	.0700	.9257	.9300	22.9701	288.5570
3	.1167	.1110	.8833	.8890	33.9175	256.9643
4	.1433	.1373	.8567	.8627	39.6984	238.2572
5	.1700	.1627	.8300	.8373	44.9489	220.9073
6	.2000	.1920	.8000	.8080	50.7580	202.5943
7	.2353	.2247	.7647	.7753	56.4496	184.5054
8	.2707	.2587	.7293	.7413	62.0709	166.0927
9	.3130	.3027	.6870	.6973	67.3341	148.8934
10	.3550	.3447	.6450	.6553	72.7080	131.5811

TABLE XVII

SUMMARY OF DATA CALCULATED ON

BASIS OF ONE MOLE OF CELLULOSE NITRATE

AVERAGE VALUES: RUNS NUMBER III, V, VII -- RATIO 0.2/2.5

Soln. No.	Acetone		Water		Acetone	Water
	Initial Mole Fraction	Final Mole Fraction	Initial Mole Fraction	Final Mole Fraction	Initial Moles	Initial Moles
1	0.0330	0.0293	0.9670	0.9707	5.6145	164.9322
2	.0740	.0667	.9260	.9332	11.5851	145.8545
3	.1170	.1063	.8830	.8937	16.9553	128.4448
4	.1433	.1317	.8567	.8683	19.8329	119.1893
5	.1697	.1547	.8303	.8453	22.5635	110.9805
6	.2000	.1837	.8000	.8163	25.1895	101.4474
7	.2353	.2147	.7647	.7853	28.2530	92.1344
8	.2693	.2500	.7307	.7500	30.9421	83.2100
9	.3130	.2887	.6870	.7113	33.6805	74.4843
10	.3537	.3370	.6463	.6630	36.2318	66.2468

IX. METHOD OF CALCULATION

The initial type of calculation attempted was based on the assumption that the sorption of solvent-non solvent solution was directly proportional to the quantity of cellulost nitrate present. Therefore, two series of samples were run, one series having a ratio of cellulose nitrate to solvent-non solvent of 0.2 to 5; the other series having a ratio of 0.2 to 2.5. From the two sets of data, a series of simultaneous equations were derived based on a relationship between the initial and final mole fraction of solvent present in the system. Solution of the system of equations, however, yielded completely anomalous results; some values were unreasonably large, while others were unreasonably small or even negative.

Several other methods of calculation were attempted without success. These included efforts to apply the Langmuir and Freundlich adsorption equations, the Donnan Membrane Equilibrium equation and numerous attempts to derive a method of calculation based on mole fraction relationships of solvent and non solvent before and after solvation occurred.

A method of calculation capable of obtaining approximate results was not achieved until it was reasoned that possibly the solvation process was similar to the

sorption of caustic by cellulose where a logarithmic curve results from a plot of caustic uptake against initial caustic concentration. The assumption was made, therefore, that the acetone was chemically fixed by the nitrate groups in the fiber and that simultaneously a mixture of acetone and water was physically sorbed by the fiber. The total amount of acetone thus fixed in the fiber was regarded as being proportional to the composition of the surrounding solvent, and it was assumed that the proportionality was logarithmic. On this basis the following equations were obtained:

$$(1)\quad x = a \log(N'_a+1)$$

$$(2)\quad y = b \log(N'_w+1)$$

where x = the moles of acetone sorbed per mole of cellulose nitrate

y = the moles of water sorbed per mole of cellulose nitrate

N'_a = the initial mole fraction of acetone in the solvent-non solvent

N'_w = the initial mole fraction of water in the solvent-non solvent

a and b = proportionality constants.

The proportionality constants a and b were evaluated as follows:

(1) Let $N_a^f = \frac{A-x}{T-(x+y)}$

where N_a^f = the final mole fraction of acetone in the solvent-non solvent

A = the initial number of moles of acetone present

T = the total number of moles of acetone and water present

x = the number of moles of acetone sorbed per mole of cellulose nitrate

y = the number of moles of water sorbed per mole of cellulose nitrate.

(2) Assume $x = a \log(N_a'+1)$

$$y = b \log(N_w'+1)$$

(3) Substitute

$$N_a^f = \frac{A - a \log(N_a'+1)}{T - a \log(N_a'+1) - b \log(N_w'+1)}$$

(4) Expand

$$N_a^f T - aN_a^f \log(N_a'+1) - bN_a^f \log(N_w'+1) = A - a \log(N_a'+1)$$

$$a \log(N_a'+1) - aN_a^f \log(N_a'+1) - bN_a^f \log(N_w'+1) = A - N_a^f T$$

$$a[\log(N_a'+1)](1-N_a^f) - bN_a^f \log(N_w'+1) = A - N_a^f T$$

The constants were evaluated by choosing combinations of experimental data within a given run and solving the above equations simultaneously as follows, (Average values

were used for this purpose.):

Run Nos. II, IV, VI	Run Nos. II, IV, VI
Combination 10-6	
Solution No. 10	Solution No. 6
$N'_a = 0.355$	$N'_a = 0.2000$
$N'_w = 0.645$	$N'_w = 0.8000$
$A = 72.7080$	$A = 50.7580$
$W = \underline{131.5811}$	$W = \underline{202.5943}$
$T = 204.2891$	$T = 253.3523$
$N^f_a = 0.3447$	$N^f_a = 0.1920$
$(1-N^f_a) = 0.6553$	$(1-N^f_a) = 0.8080$
$\log(N'_a+1) = \log 1.355 =$	$\log(N'_a+1) = \log 1.200 =$
0.13194	0.07918
$\log(N'_w+1) = \log 1.645 =$	$\log(N'_w+1) = \log 1.800 =$
0.21617	0.25527
$a[\log(N'_a+1)](1-N^f_a) -$	$a[\log(N'_a+1)](1-N^f_a) -$
$bN^f_a\log(N'_w+1) = A - N^f_aT$	$bN^f_a\log(N'_w+1) = A - N^f_aT$
$(0.13194)(0.6553)a -$	$(0.07918)(0.8080)a -$
$(0.3447)(0.21617)b =$	$(0.1920)(0.25537)b =$
$72.7080 -$	$50.7580 -$
$(0.3447)(204.2891)$	$(0.1920)(253.3523)$

$0.08646a - 0.07451b = 72.7080 - 70.4185$

$0.08646a - 0.07451b = 2.2895$

$1.1604a - b = 30.7274$

$0.06398a - 0.04901b = 50.7580 - 48.6436$

$0.06398a - 0.04901b = 2.114$

$1.3054a - b = 43.1422$

$$1.3054a - b = 43.1422$$
$$\underline{1.1604a - b = 30.7274}$$
$$0.1450a = 14.4148$$

$$a = 85.6193$$
$$b = 68.6252$$

Nine combinations out of a possible 45 combinations of data were chosen for runs III, V, and VII and similarly for runs II, IV, and VI, and a set of constants was calculated. Since the two constants were calculated from a system of nine simultaneous equations a mean of the constants was calculated in accordance with accepted practice when the calculated values arise from the solution of a greater number of equations. A weighted mean was not calculated since there was no reason to believe that any one set of equations was more valid than another. A summary of the constants is contained in Tables XVIII and XIX. Once the constants for the sorption equations were determined, the number of moles of solvent and non solvent sorbed per

mole of cellulose nitrate was calculated by arranging the data in tabular form as shown in Tables XX and XXI. Plots of the results are shown in Graphs I and II.

TABLE XVIII

SUMMARY OF EVALUATION OF PROPORTIONALITY CONSTANTS

BASIS: ONE MOLE CELLULOSE NITRATE

AVERAGE VALUES RUNS NUMBER II, IV, VI

Combination of Soln. Nos.	Proportionality Constants a	b
10-1	46.1302	22.8021
10-2	83.0732	66.1470
10-3	96.0732	80.7559
10-4	54.3710	32.3647
10-5	50.6058	27.9956
10-6	86.6193	68.6252
10-7	87.4615	70.7629
10-8	201.3376	202.9047
10-9	1016.3536	1148.6493
Total	1721.4358	1721.0074
Average	191.2706	191.2230

TABLE XIX

SUMMARY OF EVALUATION OF PROPORTIONALITY CONSTANTS

BASIS: ONE MOLE CELLULOSE NITRATE

AVERAGE VALUES RUNS NUMBER III, V, VII

Combination of Soln. Nos.	Proportionality Constants a	b
10-1	121.8635	122.3263
10-2	103.5458	100.4458
10-3	102.3160	98.9768
10-4	85.3197	78.6747
10-5	110.3018	108.5158
10-6	97.9258	93.8898
10-7	135.1335	138.1773
10-8	156.5705	163.7838
10-9	161.8080	170.0400
Total	1074.7846	1074.8303
Average	119.4205	119.4255

TABLE XX

SUMMARY OF CALCULATIONS

BASIS: ONE MOLE CELLULOSE NITRATE

AVERAGE VALUES RUNS NUMBER II, IV, VI

Calculation:

$x = a \log(N'_a+1)$

$y = b \log(N'_w+1)$

where:

x = the number of moles of acetone sorbed per mole of cellulose nitrate

y = the number of moles of water sorbed per mole of cellulose nitrate

N'_a = the initial mole fraction of acetone in the solvent-non solvent

N'_w = the initial mole fraction of water in the solvent-non solvent

a = proportionality constant = 191.2706

b = proportionality constant = 191.2230

Soln. No.	N'_a	N'_a+1	$\log(N'_a+1)$	x	N'_w	N'_w+1	$\log(N'_w+1)$	y
1	0.0330	1.0330	0.01410	2.70	0.9670	1.9670	0.29358	56.14
2	.0743	1.0743	.03112	5.95	.9257	1.9257	.28459	54.42
3	.1167	1.1167	.04793	9.17	.8833	1.8833	.27492	52.57
4	.1433	1.1433	.05816	11.12	.8567	1.8567	.26874	51.39
5	.1700	1.1700	.06819	13.04	.8300	1.8300	.26245	50.19
6	.2000	1.2000	.07918	15.14	.8000	1.8000	.25527	48.81
7	.2353	1.2353	.09178	17.55	.7647	1.7647	.24734	47.30
8	.2707	1.2707	.10405	19.90	.7293	1.7293	.23787	45.49
9	.3130	1.3130	.11826	22.62	.6870	1.6870	.22712	43.43
10	.3550	1.3550	.13194	25.24	.6450	1.6450	.21617	41.34

TABLE XXI

SUMMARY OF CALCULATIONS

BASIS: ONE MOLE CELLULOSE NITRATE

AVERAGE VALUES RUNS NUMBER III, V, VII

Calculation:

$x = a \log(N'_a+1)$

$y = b \log(N'_w+1)$

where:

x = the number of moles of acetone sorbed per mole of cellulose nitrate

y = the number of moles of water sorbed per mole of cellulose nitrate

N'_a = the initial mole fraction of acetone in the solvent-non solvent

N'_w = the initial mole fraction of water in the the solvent-non solvent

a = proportionality constant = 119.4205

b = proportionality constant = 119.4255

Soln. No.	N'_a	N'_a+1	$\log(N'_a+1)$	x	N'_w	N'_w+1	$\log(N'_w+1)$	y
1	0.0330	1.0330	0.01410	1.68	0.9670	1.9670	0.29358	35.06
2	.0740	1.0740	.03100	3.70	.9260	1.9260	.28466	34.00
3	.1170	1.1170	.04805	5.74	.8830	1.8830	.27485	32.82
4	.1433	1.1433	.05816	6.95	.8567	1.8567	.26874	32.09
5	.1697	1.1697	.06808	8.13	.8303	1.8303	.26245	31.34
6	.2000	1.2000	.07918	9.46	.8000	1.8000	.25527	30.49
7	.2353	1.2353	.09178	10.96	.7647	1.7647	.24734	29.59
8	.2693	1.2693	.10356	12.37	.7307	1.7307	.23823	28.45
9	.3130	1.3130	.11826	14.12	.6870	1.6870	.22712	27.12
10	.3537	1.3537	.13152	15.71	.6463	1.6463	.21651	25.86

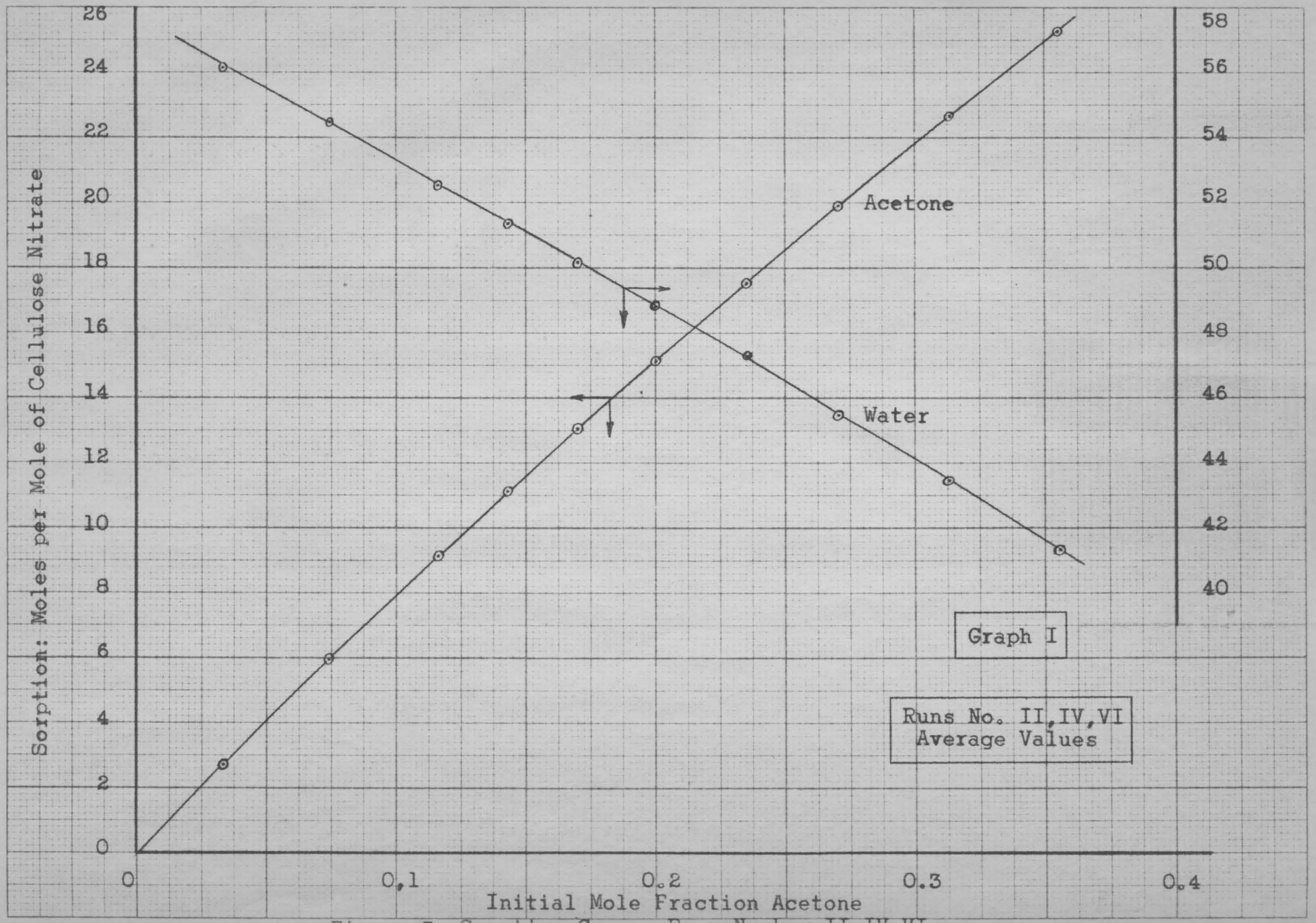

Figure 7. Sorption Curve. Runs Number II, IV, VI.

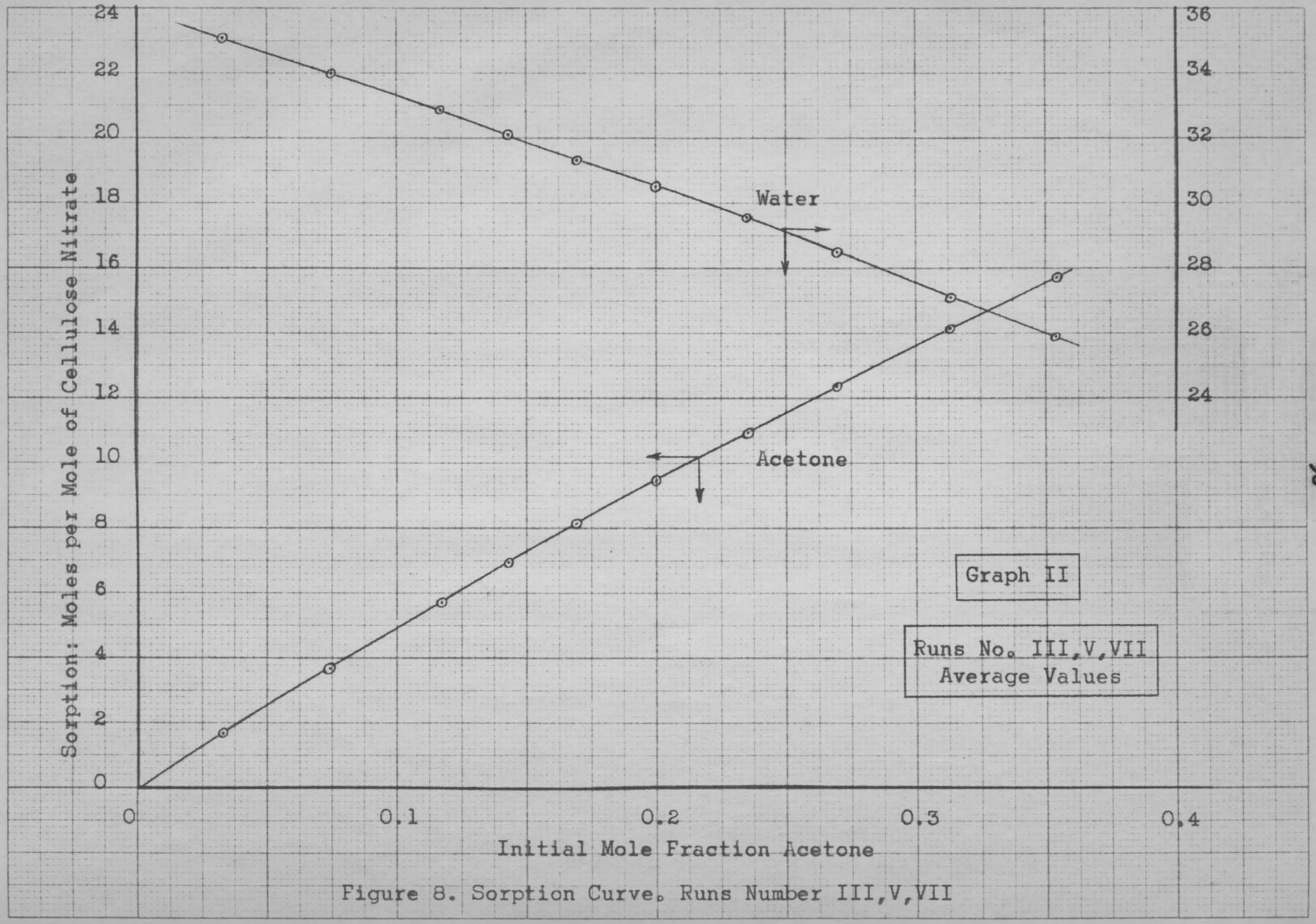

Figure 8. Sorption Curve. Runs Number III, V, VII

X. DISCUSSION OF RESULTS

The solvation of cellulose nitrate in a solvent-non solvent system composed of acetone and water has been studied by reacting a given ratio, by weight, of cellulose nitrate to solvent-non solvent solution and determining, by refractive index measurements, the change in composition of the liquid phase of the system caused by solvation. The results of calculations based on the change in concentration of solvent mixture on contact with cellulose nitrate indicate that the solvation is not capable of being measured simply by that change in concentration. It is apparently dependent upon a number of factors such as: the initial mole fraction of solvent present in the solvent-non solvent system; the ratio of cellulose nitrate to solution present in the system, and the change in solvent concentration occurring during solvation. It is also possible that solvation is a function of additional unrecognized variables and that interaction among the variables themselves may likewise occur. Inasmuch as the detection of these variables was dependent upon the development of an analytical method whereby quantitative data could be gathered, it was impossible to foresee, and thus to evaluate, the extent of their effect on the solvation process prior to the completion of the experiment. Therefore,

the calculations presented represent an attempt to demonstrate a probable trend occurring during solvation rather than an attempt to present an absolute quantitative picture of the process.

Based on the assumption of a logarithmic type sorption which is dependent upon the initial mole fraction of solvent present in the solvent-non solvent system, a correlation of data has been obtained which is in agreement with the findings of both Doolittle and Moore in their studies of solvent-non solvent interaction of polymeric systems. Doolittle [15], in studying the solution of resinous substances by a technique similar to that described in this investigation, concluded that, "... at constant temperature the rate of solvation is a function primarily of the solvent concentration." Moore [66], in his studies of solvent-non solvent interaction with cellulose nitrate, also concluded that the swelling of fibers was proportional to the concentration of solvent present initially.

It is also apparent that the failure of the Freundlich and Langmuir adsorption isotherms to apply to the treatment of data actually supports the assumption of a logarithmic type sorption upon which the experimental curves were calculated. Although the Freundlich and Langmuir equations are logarithmic in nature, the probable reason

they could not be applied to the data from this investigation is that in the cases of these equations a given increase in vapor pressure produces an increase in the amount of sorbed gas which is less than proportional to the vapor pressure rise. Therefore, according to the equations, the amount of sorbed gas approaches a limit asymptotically as the pressure is increased [76].

Inspection of the experimental curves, however, indicates that the analogous sorption of solvent by the cellulose nitrate, while also logarithmic in nature, does not approach an asymptotic limit but proceeds to a very large value. Thus, the failure to fit the data to the Freundlich and Langmuir equations represented an attempt to force these equations to a situation beyond the limits permitted by their parameters rather than being indicative of erroneous basic assumptions.

The logarithmic nature of the equation may be explained by assuming that there are two shells of solvent-non solvent surrounding the cellulose fiber. The innermost shell may be considered as consisting primarily of solvent which is chemically bound or fixed to the nitrate groups. This assumption is given affirmation by Spurlin who states that there is, "... evidence that the solvent, particularly acetone, is bound only to the nitrate groups." [96]. There-

fore, since experimental evidence has been advance [3] to show that nitration is a homogeneous reaction so that there is little difference in the degree of nitration of the various glucose units, the inner shell should have a fairly constant composition. The outer shell, however, may be conceived of as being a physically bound layer whose composition is determined primarily by the composition of the surrounding solvent-non solvent solution. Thus, while the inner shell has an inherently fixed composition, the composition of the outer shell is considerably more variable and probably makes the major contribution to the logarithmic nature of the calculation.

The trend exhibited by the sorption curves would indicate that as more solvent becomes available--through increased solvent concentration--there is an ever-increasing tendency for penetration deeper into the fiber. As the penetration continues the distance between the cellulose nitrate chains increases with a corresponding decrease in attraction between the chains. At the same time more "active centers" of solvation--nitrate groups-- become available since measurements show that approximately 70 per cent of the groups are present on the microfibrils which are accessible via the microcapillary system of the fiber. This process is accompanied by a continual swelling of the fiber-

gel formation--as solvent pushes deeper into the structure until, "... with unlimited swelling, the swelling gradually changes into solution." [93]. Therefore, it would appear that at some point of infinite solvent concentration, complete dispersion would occur. The concept explains the trend of the experimental curves toward an infinite sorption value.

XI. CONCLUSIONS

It was originally hoped that a study of the changes in concentrations of mixtures of solvents and non solvents in contact with cellulose nitrate would permit the determination of the extent of solvation. If the solvation layer depended solely on the polar-non polar nature of the ester two series of experiments would have supplied sufficient data for solution of the problem. A technique was developed for measuring the small changes in composition resulting from preferential absorption of one constituent from a solution by cellulose nitrate.

However, attempts to calculate the solvation from the data obtained soon indicated that the solvation depended on a series of variables. In addition to the polar-non polar nature of the ester the following were also found to have a marked influence.

1. Original composition of the liquid phase.
2. Ratio of weight of solid phase to weight of liquid phase.
3. Change in composition of the liquid phase due to preferential absorption.
4. The coabsorption of the non solvent.
5. Possible interreaction between the above five variables.

Owing to the lack of time it was not possible to carry out further experiments which might possibly lead to a knowledge as to the effect of each of the above variables and so to a knowledge of the composition of the solvated film.

Possibly the most valuable results of this study are two.

1. The development of a method capable of accurately measuring very small changes in composition of the liquid phase as is shown in Tables X through XVII.

2. Indication that solvation is not a simple process and the uncovering of the hidden variables upon which solvation depends. This should open the way for experiments designed to solve the problem.

XII. SUGGESTIONS FOR FUTURE WORK

A statistically designed experiment should be set up to determine the nature and effect of the variables affecting the process of solvation.

Study the effect of varying D. S. on solvation.

Determine an additional physical property of the system, such as viscosity or density, and use of the dipping refractometer to study the entire range of solvent concentration.

Disperse the cellulose nitrate in solvent; precipitate it out of solution with non solvent and study its solvation.

Study the solvation of a cellulose nitrate sample in different solvent-non solvent systems.

XIII. BIBLIOGRAPHY

[1] Ambronn, H.: Kolloid-Z., 18, 273 (1916), cited by W. A. Sisson in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York, (1945).

[2] Barsha, J.: in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York, (1945) p. 622-662.

[3] Barsha, J.: Ibid., p. 651.

[4] Beck, A., Clement, L., and Riviere, C.: Mon. produite chim. 16, No. 184, 13-14; No. 185, 3-7 (1934).

[5] Berl, E. and Hefter, O.: Cellulosechem. 14, 65-77 (1933).

[6] Blom, A. V.: Z. Angew. Chem., 53, 40 (1940).

[7] Braconnot, H.: Annales des Chimie et de Physique 52, 290, (1833); cited by C. E. Worden in "Nitrocellulose Industries", D. Van Nostrand Co., New York, (1911) p. 21.

[8] Calvet, E. and co-workers: Compt. rend. hebd., 212, (1941) 542; 213, (1941) 126; 215, (1942) 138 in "Physics and Chemistry of Cellulose Fibers", edited by P. H. Hermans, Elsevier Publishing Co., Inc., Netherlands, (1949).

[9] Centola, G.: Atti del X Congr. Intern. di Chimica, Roma IV, (1939) 117 in "Physics and Chemistry of Cellulose Fibers", edited by P. H. Hermans, Elsevier Publishing Company, Inc., Netherlands, (1949).

[10] _____.: Atti del X Congr. Intern. di Chimica, Roma IV, (1939) 129. in "Physics and Chemistry of Cellulose Fibers", edited by P. H. Hermans, Elsevier Publishing Company, Inc., Netherlands, (1949).

[11] _____.: Ann. Chim. Applicata, 26, (1936) 788. in "Physics and Chemistry of Cellulose Fibers", edited by P. H. Hermans, Elsevier Publishing Company, Inc., Netherlands, (1949).

[12] Davidson, J. and Reid, E.: Ind. Eng. Chem. 19, 977 (1927).

[13] Desmaroux, J. and Mathieu, M.: Compt. rend. hebd., 194, (1932) 2053.

[14] Doolittle, A. K.: Ind. Eng. Chem. 36, 239-44 (1944).

[15] _____.: Ibid., p. 240.

[16] Doree, C.: "The Methods of Cellulose Chemistry", D. Van Nostrand Co., New York, (1947) p. 170.

[17] _____.: Ibid., p. 233-250.

[18] Ekenstamm, A.: Ber., 69, (1936) 549, 553.

[19] Faust, O.: Kolloid-Z., 46, (1928) 329.

[20] Gilsen, E.: "La Cellule", 9, 337, (1893), cited by W. A. Sisson in "Cellulose and Cellulose Derivatives", edited by E. Ott, Vol. V, High Polymers, Interscience Publishers, New York, (1943).

[21] _____.: Ibid., p. 21

[22] Gibb, T. R. P., Jr.: "Optical Methods of Chemical Analysis", McGraw-Hill Book Co., Inc., New York, (1942) p. 321.

[23] _____.: Ibid., p. 323.

[24] _____.: Ibid., p. 325.

[25] Haworth, W. N.: "Nature", 116, 430 (1925).

[26] Hercules Powder Co.: "Hercules Nitrocellulose, Properties and Uses", (1947).

[27] Hermans, P. H.: "Physics and Chemistry of Cellulose Fibers", Elsevier Publishing Co., Inc., Netherlands, (1949). Part I, Chap. I, p. 4-41; Part II, Chap. I, p. 163-179.

[28] _____.: Ibid., Chap. II, p. 42.

[29] _____.: Ibid., p. 45.

[30] _____.: Ibid., p. 48.

[31] _____.: Ibid., p. 51.

[32] _____.: Ibid., Footnotes 51, 52, 53, 54, 55, 56, 57; p. 55.

[33] _____.: Ibid., p. 56.

[34] Herzog, R. O. and Lange, B.: Ber., 62, (1929) 491.

[35] Hess, K.: Z. Angew. Chem., 47 (1934)30.

[36] Hess, K. and Ulmann, M.: Ber. 74, (1941) 119, 136.

[37] Heuser, E.: "The Chemistry of Cellulose", John Wiley and Sons, Inc., New York, (1944) p. 1.

[38] _____.: Ibid., p. 7-41.

[39] Heuser, E. and Charbonnier, H. Y.: Cellulosechem. 18, (1940) 118.

[40] Hull, A. W.: Phys. Rev., 10, 661 (1917).

[41] Jones, G. G. and Miles, F. D.: J. Soc. Chem. Ind., 52, T251 (1933).

[42] Katz, J. R.: Cellulosechem., 6, 37 (1925).

[43] Katz, J. R. and Derksen, C.: Rec. trav. chim., 50, (1931) 149. in "Physics and Chemistry of Cellulose Fibers", Elsevier Publishing Co., Inc., Netherlands, (1949).

[44] Kratky, O. and Mark H.: Z. physik. chem., 336, 129, (1937).

[45] Lange, N. A. and Forker, G. M.: Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio, (1946) p. 912.

[46] Leiser, Th.: Kolloid-Z., 81 (1937) 234.

[47] Leiser, Th. and co-workers.: Z. physik. chem., B74 (1941).

[48] Mark, H.: Chem. Revs., 26, 169 (1940).

[49] Mathieu, M.: Trans. Faraday Soc., 29, 122 (1933).

[50] _____.: Ibid., p. 125.

[51] _____.: Ibid., p. 131.

[52] _____.: Compt. rend. hebd., 199, 55-57 (1934).

[53] _____.: Ibid., 200, 143 (1935).

[54] _____.: "Theories Chimique", XIII, "La Gelatinisation des Nitrocelluloses. Actualities Scientifiques et Industrielles", No. 317, Herman and Cie, Paris (1936).

[55] _____.: Cited by P. H. Hermans in "Physics and Chemistry of Cellulose Fibers", Elsevier Publishing Co., Inc., Netherlands, (1949).

[56] McBain, J. W. and Scott, D. A.: Ind. Eng. Chem., 28, 470 (1936).

[57] Meyer, K. H.: Z. Angew. Chem., 41, 935 (1928).

[58] _____.: Z. Angew. Chem., 40, 850 (1927).

[59] Meyer, K. H. and Mark, H.: Ber., 61B, 593 (1928).

[60] Meyer, K. H. and Van der Wijk, A. J. A.: Kolloid-Z, 101, (1942) 52.

[61] _____.: Ibid., Elektrochem, 47, 353 (1941).

[62] _____.: Ibid., Helv. chim. acta., 20, 1321, 1331 (1937).

[63] Miles, F. D.: Trans. Faraday Soc., 29, 110 (1933).

[64] Miller, B.: "Dielectric Investigations of the Effect of Precipitant Addition to Cellulose Nitrate Solutions." M. S. Thesis. V. P. I. Library, June, 1949.

[65] Moore, W. R.: J. Poly. Sci., Vol. V., No. 1, 1950. p. 91-109.

[66] _____.: Ibid., p. 95.

[67] Murray, G. E. and Purves, C. B.: J. Am. Chem. Soc., 62, 3194-3197 (1940).

[68] Nageli, C.: "Die Starkekorner", F. Schulthub, Zurich, 1858, cited by W. A. Sisson in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York, 206 (1943).

[69] Nageli, C. and Schwendener.: "Das Mikroscop", 2. Aufl., W. Englemann, Leipsig, 1877, cited by W. A. Sisson in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York, p. 206 (1943).

[70] _____.: Ibid., p. 209.

[71] Nishikawa, S. and Ono, S.: Proc. Math-Phys. Soc., Tokyo, 7, 131 (1931), cited by W. A. Sisson in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York, p. 206 (1943).

[72] Ott, E.: "Cellulose and Cellulose Derivatives", Vol. V, High Polymers, Interscience Publishers, New York, (1943).

[73] Ott, E.: "The Chemistry of Large Molecules". Vol. I, Frontiers in Chemistry. R. E. Burk and Ol. Grummitt, Eds. Interscience Publishers, p. 250 (1943).

[74] _____.: Ibid., p. 258-9.

[75] _____.: Ibid., Chap. III, p. 203-351.

[76] _____.: Ibid., p. 380.

[77] Petitpas, T.: J. Chim. phys., 37, 6 (1940).

[78] Polanyi, M.: "Naturwissenschaften", 9, 288 (1921).

[79] Polanyi, M.: Ibid.

[80] Powers, P. O.: "Synthetic Resins and Rubbers", J. Wiley and Sons, Inc., New York. p. 236-237 (1943).

[81] Sakurada, J. and Morita, T.: Chem. Ind. Japan, 41, 381B (1938).

[82] Sauter, E.: Z. physik. chem., B35, 83 (1937).

[83] Scherrer, P.: Nachr. Ges. Wiss. Gottingen, 98, (1918).

[84] _____.: Ibid., 99, (1918).

[85] Schramek, W.: "Papierfabrikant", 36, 226 (1938) in "Physics and Chemistry of Cellulose Fibers", by P. H. Hermans, Elsevier Publishing Co., Inc., Netherlands, (1949).

[86] Schultze, G. V.: Z. physik. chem., A. 184, 1, (1939).

[87] Seifriz, W.: Am. Naturlist, 63, 423 (1929).

[88] Sharpe, L. H.: "Further Studies of the Effect of Precipitant Addition to Cellulose Nitrate Solutions". B. S. Thesis. V. P. I. Library, June, 1950.

[89] Sisson, W. A.: Textile Research, 3, 242, 295 (1933); 4, 429 (1934).

[90] _____.: in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York. p. 212-215, (1943).

[91] _____.: Textile Research, 6, 143 (1936).

[92] _____.: Ind. Eng. Chem., 30, 530 (1938).

[93] _____.: in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York. p. 258, (1943).

[94] Sisson, W. A. and Sansen, W. R.: J. Phys. Chem., 43, 687, (1939).

[95] Sponsler, O. L.: J. Gen. Physiol., 9, 677 (1926).

[96] Spurlin, H. M.: in "Cellulose and Cellulose Derivatives", edited by E. Ott. Vol. V, High Polymers. Interscience Publishers, New York. p. 867, (1943).

[97] _____.: Ibid., p. 868.

[98] Staudinger, H.: "Die Hockmolecularen organischem Verbindergen, Kantschuk and Cellulose", Berlin, (1942).

[99] _____.: "Organische Kolloidchemie", Braunschweig (1940).

[100] Testerman, M. K.: "A Study of Dielectric Dispersion in Cellulose Nitrate Solutions", Ph. D. Thesis. V. P. I. Library, p. 45 (1950).

[101] _____.: Ibid., p. 53.

[102] Trogus, C., Tomonari, T., and Hess, K.: Z. physik. chem., B16, 351-373 (1932).

[103] Zsigmondy, R.: "Lehrbuch der Kolloidchemie", 3. Aufl., O. Spamer, Leipzig, (1920).

[104] Zwicky, F.: Proc. Natl. Acad. Sci., U. S., 15, 253, 816 (1929).

[105] Zwicky, F.: Phys. Rev. 38, 1772 (1931); 40, 63 (1932); 43, 765 (1933).

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