DETERMINATION OF CONDITIONS FOR FRACTIONATION OF ETHYL CELLULOSE

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INTRODUCTION

Three independent and almost simultaneous applications for patents describing processes for manufacturing ethyl cellulose and cellulose ethers were made in 1912. Leuchs (40) applied in Germany and described a process using dry sodium cellulose and ethyl chloride. Lilienfeld (41), who applied in England, used dry sodium cellulose and ethyl sulfate. Dreyfus (12) also used dry sodium cellulose and ethyl sulfate in his French patent. In 1923 a United States patent issued to Backhaus (3) described a method for making plastic compositions of ethyl cellulose combined with various alkyl-acetoacetates in a suitable solvent. The same year a patent was issued to Olsen (57) which proposed the use of films of ethyl cellulose as wrapping tissue.

However, it was not until 1936 that ethyl cellulose was first used in this country in the form of sheets and powders. Since that time, the production of ethyl cellulose has increased yearly as new uses for this plastic have been exploited.

Ethyl cellulose is flexible even at low temperatures; and this property combined with excellent insulating qualities, toughness, and compatibility with many other substances makes it one of the most versatile of the cellulose derivatives. Fabric coatings, artificial leather, adhesives, films and foils,

lacquers, and electrical insulations are a few of its numerous applications in this day when a plastic must stand up under use and also must be produced cheaply.

STATEMENT OF PROBLEM.

As will be explained in a later section, many of the properties of ethyl cellulose that make it useful in different ways are a result of the varying lengths of the cellulose chains arranged within the chain bundles. This investigation was undertaken in order to find a method of separating these ethyl cellulose chains into more homogeneous groupings and to determine the distribution of chain lengths. The conditions and procedure are to be so determined that the results from one fractionation may be duplicated in succeeding ones.

LITERATURE REVIEW

Consideration should be given to the present day concept of the structure of cellulose and of ethyl cellulose, as well as the methods of fractionation of high polymeric substances, before a discussion of the investigation is undertaken.

STRUCTURE OF CELLULOSE.

All cellulose had its origin in some plant, the more common examples being flax, cotton, and wood pulp. So far, no one knows how to make cellulose in the laboratory, and neither is it known exactly how the plant produces cellulose. Some rather recent studies by Ruben (65,66) indicate that carbon dioxide reacts in the absence of light with whatever type of sugars are in the plant and that this carboxyl then reacts with

$$RH + CO_2 \longrightarrow RCOOH$$

another molecule of water in the presence of chlorophyll under the influence of light. The cycle is repeated until long carbo-

$$RCOOH + H_2O \xrightarrow{\text{Chlorophyll}} RCH_2OH + O_2$$

hydrate chains are formed.

Evidence for and against the various theories as to cellulosic structure is too voluminous to be considered here. A complete resume of the data may be found in one of the standard works on the subject (26,49,61). However, some of the basic

principles of the modern concept will be given without discussing the reasons or evidences for them.

As early as 1883 Flechsig (14) obtained glucose from cotton cellulose. Haworth (20) in 1925 represented glucose as a six membered ring. The glucose obtained from cellulose is called beta glucose to distinguish it from alpha glucose obtained from starches. The hydroxyl groups attached to the number 1 and 4 carbon atoms of beta glucose are on opposite sides of the plane of the ring. Sponsler and Dore (78) stated that cellulose consisted of long parallel chains of glucose residues linked by primary valences and held together by secondary valences. Haworth (21) modified this by showing that the primary valences are between the number 1 carbon of one glucose unit and the oxygen of the number 4 carbon atom of the adjoining glucose residue. This requires inversion of every other one of the glucose units. Thus the structural formula for a cellulose chain may be represented as in Figure 1. In this, the X could have values of from 25 to 3000 - 4000. This indicates that cellulose is a generic name for a homologous series of compounds which have the same chemical properties but whose physical properties depend upon the length of the chain. The preparation of a tri-acetate cellulose as the highest acetate obtainable (59)

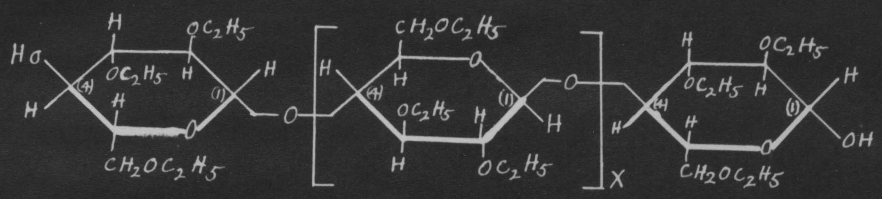


Figure I

STRUCTURE OF CELLULOSE (61a)
(The tri-ethyl ether)

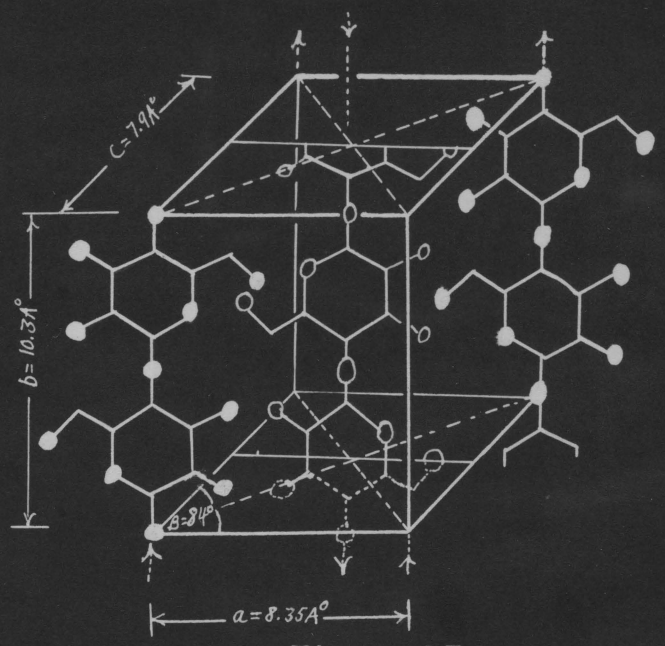


Figure II

CRYSTAL UNIT OF CELLULOSE
(Meyer and Misch, from Ott (61b))

For the sake of clarity the chains forming the second front edge and the fourth back edge of the crystal have been omitted.

established the presence of the three hydroxyl groups per glucose residue.

Inspection of Figure 1 shows that at each end of the cellulose chain, regardless of its length, there is an additional hydroxyl group. When the chains are very long, these two OH groups do not affect the average number of hydroxyl groups. Referring again to Figure 1, it is well to note that the OH group on the extreme right is a latent aldehyde group and as such is a reducing group. Advantage is taken of this in the end group methods for determining molecular weights (77). The number of chains (ends of chains) divided into the total weight gives the average molecular weight of the cellulose chains. The OH group on the extreme left is just another alcoholic OH group as far as its activity is concerned (77). It has been suggested that the end groups may loop around, so to speak, to form large cyclic molecules (22). This may account for some of the apparent chemical inactivity of cellulose.

The cellulose chains are held together by secondary valences which by modern interpretation means hydrogen bonding between the chains. These form the submicroscopic fibrils. However, the chains are not all perfectly aligned as there are alternating crystalline and amorphous regions within the fibrils (43,47).

These submicroscopic fibrils are held together by hydrogen bondings to form microscopic fibrils which in turn combine to form the macro fibers. As the size of the fibril increases, the number of hydroxyl groups close enough to each other to form bonds between the fibrils decreases. Therefore, the larger the fibrils the weaker are the forces holding them together.

The estimates of crystalline portions of the fibers indicate multiples of a crystal unit which Meyer and Misch (52) represented as in Figure 2. In this figure they give the size and shape of the crystal.

ETHYLATION OF CELLULOSE

The early patents for manufacture of ethyl cellulose required sodium cellulose to be treated with an ester of ethyl alcohol. Not only is the soda cellulose more reactive toward the ester than untreated cellulose, but the alkali treatment of cellulose loosens the hydrogen bonds between the chains of cellulose, thus permitting a more nearly complete addition to the hydroxyl groups. Because of its high surface tension, water is able to penetrate only the macrocapillary system. This accounts for approximately 30% of the hydroxyl groups present in the cellulose. Eighteen per cent sodium hydroxide solution will penetrate the microcapillaries and also the chain bundles. This

penetration causes some swelling which allows water to penetrate further into the fiber. However, it must not be construed that this forms the tri-sodium alcoholate of cellulose. Scherer and Hussey (70) made the tri-sodium alcoholate of cellulose in liquid ammonia as solvent. Exactly how much sodium hydroxide is combined with the cellulose has been the subject of many investigations. Of these, D'Ans and Jager (9) state that a compound with a composition corresponding to $(C_6H_{10}O_5)_2NaOH$ is formed when the initial concentration of NaOH is between 16 and 24%. The compound $C_6H_{10}O_5NaOH$ appears at a concentration of 36% NaOH. Hess, Trogus and Schwarzkopf (25) stated that $C_6H_{10}O_5NaOH$ may possess 4-8 molecules of chemically bound water which they called "NaCell I". The water-free compound they called "NaCell II". It is probable that greater amounts of sodium hydroxide are absorbed, thus obscuring the chemical reaction (67,71,72) which is confined to only a relatively few of the total number of hydroxyl groups.

The composition of the soda cellulose and its uniformity is carefully controlled in commercial production of ethyl cellulose. Water is necessary both as a solvent for the NaOH and as a solvating or swelling agent for the soda cellulose. An increase in the NaOH:H_2O ratio increases both the rate of ethylation and the degree of substitution. A low H_2O:cellulose ratio also

increases the degree of substitution. The two ratios affect the amount and kind of by-products. A high H_2O:cellulose ratio increases the side reactions, and a high NaOH:H_2O ratio gives predominately diethyl ether; when the latter is low, alcohol predominates (42).

Even in the solvated form the cellulosic hydroxyls are generally in the solid phase and surrounded by the sodium hydroxide. The etherifying agent must dissolve in the alkali solution to get to the hydroxyl groups (13). Although the ethyl bromide is more reactive, ethyl chloride is preferred because it is less expensive. The high cost and high rate of saponification of alkyl sulfates and phosphates have limited their use as etherifying agents.

Diethyl sulfate is extensively used in the laboratory production of ethyl cellulose. The soda cellulose is crumbed and aged properly before a large excess of the diethyl sulfate is slowly added at temperatures below 0° C. (10). This excess of diethyl sulfate in turn requires a high concentration of NaOH to prevent the solution from becoming too acid when etherification ceases. The initial degree of substitution is between 1.5 and 2 ethyl groups per glucose unit. Repetition of the process will increase the degree of substitution but not to the

completely substituted form. The principal reaction may be represented as

$$Cell\text{-}ONa + (C_2H_5)_2SO_4 \longrightarrow Cell\text{-}OC_2H_5 + \begin{matrix} NaO \\ C_2H_5O \end{matrix}\!\!\diagup SO_2$$

and the side reactions as

$$(C_2H_5)_2SO_4 + 2NaOH \longrightarrow 2C_2H_5OH + Na_2SO_4$$

$$\begin{matrix} NaO \\ C_2H_5O \end{matrix}\!\!\diagup SO_2 + C_2H_5OH \longrightarrow (C_2H_5)_2O + NaHSO_4$$

Ethyl chloride is the etherifying agent used commercially. The almost dry soda cellulose is heated under pressure at 130° for eight hours with three parts of ethyl chloride (based on the original cellulose) (40). The excess ethyl chloride is removed by distillation, and the by-product salts are leached out. As stated above, ethyl ether and ethyl alcohol are also formed as by-products. The principal reaction may be shows as

$$Cell\text{-}ONa + ClC_2H_5 \longrightarrow Cell\text{-}OC_2H_5 + NaCl$$

and the side reactions as

$$NaOH + ClC_2H_5 \longrightarrow NaCl + C_2H_5OH$$

$$C_2H_5OH + NaOH + ClC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaCl + H_2O$$

By this method the degree of substitution will go as high as 50%, although the average commercial ethyl cellulose has between 43.5 and 50% ethoxy content (23). Usually 46.8 to 48.5%

ethoxy content ethyl cellulose is the form used. Working with medical cotton in sealed glass tubes Berl and Schupp (4) were able to get an ethoxy content of 54.76% when 54.87% is theoretically the tri-ethyl ether of cellulose.

Except for the tri-ethyl ether of cellulose it must not be construed that substitution occurs in an uniform manner. The cellulose chain is a large one along which the ethyl groups will be distributed among the available positions in a purely random manner. Spurlin (79) did not consider the ratio of the reactivities of the number 2-, 3-, or 6-hydroxyl group affected by any prior substitution, either along the chain or in the same glucose unit, when he calculated the statistical distribution of substituent groups. Any uniformity along the chain is probably due to all hydroxyls being equally available (45). Experimental evidence shows that ether groups are not as uniformly distributed over the chains of cellulose as are ester groups such as acetate and nitrate. The lower the degree of substitution the more evident the non-uniformity becomes. It has been possible to separate the low degree of substitution cellulose ethers into fractions having different alkoxyly content (27). However, Okamura (56) working with commercial ethyl cellulose of 49.4% ethyoxyl content obtained fractions varying in the molecular weight but not in ethoxyl content.

The degree of substitution of ethyl cellulose is therefore the average of substitution on all the cellulose chains present.

THEORIES OF SOLUBILITY

It is well known that like dissolves like or that a polar solvent will be more likely to dissolve a polar compound than a non-polar solvent would, and vice versa. With some cellulose derivatives solvation occurs between the polar groups on the cellulose derivative and the polar constituents of the solvent and similarly between the two sets of non-polar groups. But in the case of cellulose ethers evidence does not support the theory of solvation of the alkoxyl group. It seems more important to have the same internal pressure in the solvent and cellulose derivative (29). By internal pressure is meant the difference in the free energy necessary to separate solute molecules from their neighbors and solvent molecules from their neighbors and the free energy gained when solute molecules come in contact with solvent molecules(53).

It has been found that ethyl cellulose with 0.6 ethoxyl groups per glucose residue uniformly distributed, as prepared in quaternary ammonia base, is soluble in water (5). This is explained by the assumption that an uniform distribution of the ethoxyl groups permits a better separation of the cellulose chains, thus giving water easy access to the hydroxyl groups. Both methyl-

and ethyl-cellulose of low degree of substitution are soluble in cold water but insoluble in hot water. As the temperature increases, the kinetic energy of the solvated water molecules increases until they are able to break away from the cellulose chain. The long cellulose chains are then able to coagulate to a gel. At the same time the viscosity of the solution decreases (28). Thus, heating a cold aqueous solution of ethyl cellulose will cause precipitation, and cooling the suspension will bring about redissolution. This precipitation and redissolution may be repeated indefinitely (10).

When the degree of substitution is less than 0.6, the ethyl cellulose is not soluble in water but is soluble in dilute alkali. In this case, the number of ethoxyl groups is insufficient to wedge the cellulose chains apart and to permit the entrance of agglomerated water molecules. Aqueous alkalies do not form the molecular aggregates, nor do they have the surface tension of water; therefore they can enter the submicroscopic capillaries. Above 0.6 degree of substitution ethyl cellulose again becomes insoluble in water due to the hydrophobic nature of the increasing number of ethoxyl groups (69).

Three theories as to the state of cellulose derivatives in solution were presented and discussed pro and con for some time

before the proponents of the first two theories finally agreed with the third theory. It was assumed by Hess (24) that the cellulose derivatives of high molecular weight were actually complexes of low molecular weight molecules held together by some force peculiar to lyophilic colloids. The second theory according to Meyer and Mark(51) assumed that the cellulose molecules were grouped in bundles or micelles. The theory which is now generally accepted is that of Staudinger (82) who maintained that each molecule is molecularly dispersed and that any occasional association of two or more molecules is soon broken up by thermal agitation. A discussion of these theories would be too lengthy to be undertaken here, although this investigation is dependent upon the truth of the last theory.

VISCOSITY-CONCENTRATION RELATIONSHIPS

By viscosity is meant the resistance offered by one portion of a liquid to another portion moving over it. More specifically it may be defined "as the force per unit area required to maintain a unit velocity gradient between two parallel plates kept a constant distance apart." (31). The unit of viscosity, the poise, is defined as "The viscosity of a hypothetical liquid such that a force of one dyne causes two parallel liquid surfaces one square centimeter in area and one centimeter apart to slide past one another with a velocity of one centimeter per second" (18). Two

other important definitions are specific viscosity

$$\eta_{sp} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}}$$

and intrinsic viscosity

$$[\eta] = (\eta_{sp/C})_{C \rightarrow 0}$$

where C is the concentration of solute. Intrinsic viscosity is often calculated from graphical extrapolation of the line $\eta_{sp/C}$ versus C.

From a study of the effect of the shape of the solute molecule upon the viscosity it was found that if the solute molecules are larger than those of the solvent and if the Brownian motion has a greater effect on the distribution of solute molecule orientation than does the velocity gradient, the ratio of specific viscosity to concentration is a constant for spherical solute molecules, is proportional to the square of the number of rod-like solute molecules, and is proportional to the number of randomly kinked solute molecules (32). The last relationship is the basis of Staudinger's equation which will be discussed in a later section.

Kauppi and Bass (37) made a study of the viscosity-concentration relationship of ethylcellulose. From Philippoff's (63) equation

$$\eta_{rel} = \left(1 + \frac{[\eta] C}{8}\right)^8$$

where C is the concentration they calculated the absolute viscosity as

$$\eta_{abs} = K\left(1 + \frac{[\eta]\, C}{8}\right)^{8}$$

or expressed in another form $\eta_{abs} = K' + KC$. This last form should give a straight line when the concentration is plotted against the eighth root of the absolute viscosity. When such curves were drawn for solutions ranging in concentration from 1 to 15% ethylcellulose, it was found that the line was straight above 5%. At 5% a break occurred, and below that concentration the slope of the line increased. They also made viscosity measurements on low viscosity ethyl cellulose and found that the resulting line was straight all the way up to 25% concentration. In much the same way they found that changing the solvent simply moved the line up and down without changing its general shape. The intrinsic viscosity was different with each solvent used. When similar curves were drawn for viscosities measured at different temperatures, they found that the curves were again displaced due to a change in the intrinsic viscosity. They also found that samples having different ethoxyl content gave curves which again varied only in position.

Karrer, Berl, and Umstatter (36) along with other investigators noted that an increase in temperature caused a decrease in the viscosity and vice versa.

According to Alfrey (1) the intrinsic viscosity of a high polymer in a solvent-nonsolvent mixture is lower than that of the polymer in pure solvent. As more nonsolvent is added, the intrinsic viscosity continues to decrease to a final value, the limit of solubility, which is also the point where precipitation occurs. This critical intrinsic viscosity should have the same value regardless of the solvent and nonsolvent used as long as the composition of the solute is the same in all solvents. The nature of the solvent determines the effect of temperature on the intrinsic viscosity. In a poor solvent an increase in temperature would give rise to more uncurling of the molecule and thus increase the intrinsic viscosity. On the other hand, in a good solvent the more extended configuration of the molecule is favored so that an increase in temperature would lower the intrinsic viscosity. These generalizations hold for dilute solutions of flexible polymers, but as the cellulose chain is relatively more rigid the change in intrinsic viscosity is less noticeable.

From the above discussion, it is evident that the solvent, concentration of solute, and temperature must be given when reporting the viscosity or any related property calculated from the viscosity before that report will have definite meaning to later investigators. The early reports do not give this

information and some of the more recent papers also neglect to list this important data.

FRACTIONATION METHODS

The methods for fractionation may be classified under two general headings, analytical and preparative (8). The analytical methods are those that enable the determination of molecular-weight distribution in the heterogeneous substance without the homogeneous fractions being separated. The preparative methods are those that enable the preparation and separation of fractions that approach homogeneity with respect to molecular weight. Another classification of fractionation methods may be based on the principle of separation involved (8). These are solubility methods which includes fractional precipitation, fractional solution, the ultracentrifuge method, chromatographic method, ultrafiltration method, and molecular distillation. Of these, the solubility methods are the ones more commonly used, and fractional precipitation is the most important one.

The lower molecular-weight or the shorter chains of heterogeneous polymers are more soluble in a given liquid than are those of higher molecular weight. The solvent power of a binary liquid mixture of solvent and non-solvent depends upon the ratio of the two components. Upon these two facts the solubility methods are based. Bronsted (6) suggested that with members of a single

homologous series of polymers the potential energy of the molecule is proportional to the molecular weight and that the less mobile large molecules collect in the phase with the lower potential energy which is the precipitated phase. In the same way the smaller and more mobile ones would collect in the phase of higher potential energy, the supernatant liquid.

In fractional precipitation by non-solvent the heterogeneous polymer is dissolved in a suitable liquid and then partially precipitated by the addition of a non-solvent liquid. After the precipitate has settled, the supernatant liquid is decanted and the process is repeated. It is also possible to cause fractional precipitation by lowering the temperature of the solution without the addition of a non-solvent. Very often a combination of the two methods is used. The choice of solvent and non-solvent will depend upon the conditions controlling the fractionation, and the investigator should consider the possibilities carefully. The addition of non-solvent will cause an increase in the turbidity of the solution. This increase has been considered as the end-point in the titration and may be observed directly (35) or instrumentally (68). However, neither way proved satisfactory in this investigation as will be explained when discussing experimental procedures.

Morey and Tamblyn (55) state that in the initial coalescence only a few cross links are necessary to form a nucleus or embryo aggregate. The probability of establishing these first links is related to the chain length. However, the number of links required for coalescence is practically independent of the chain length. The formation of initial aggregates may be noted experimentally by the first signs of optical haze. It is evident that low molecular-weight molecules may start coagulating and form a precipitate before the high molecular-weight ones, if the concentration of the former is much greater than the concentration of the latter. Therefore, the heterogeneity or homogeneity of the precipitate is determined in part by the distribution of the various molecular weight particles in the original sample. When the different weight particles are present in equal amounts, the low weight ones may precipitate first; this is known as the true-reverse-order. As these aggregates of "small" molecules increase in size, larger molecules are able to form aggregates, and these latter ones actually form the precipitate.

A very good discussion of the three theories explaining the selective precipitation of molecules having different molecular weight may be found in the report of Morey and Tamblyn (55). For the purposes of this investigation much of their paper is too theoretical and involved to warrant a full discussion. However,

a brief statement concerning each would indicate the theoretical approaches which have been made to the problem of fractional precipitation. Schulz (75) based his theory on the Bronsted-Boltzmann expression for the distribution of a substance in two immiscible liquids. Theoretically, these immiscible solvents may be replaced by the solution and precipitate if the latter may be considered a fluid. Schulz assumed that the activities in the two solvents could be replaced by the actual concentration and that the concentration in the precipitated phase is a constant. He then arrived at the equation

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

where K, A, and B are constants, k is the Boltzmann constant, P_ν is the per cent of precipitant, and C_ν is the saturation concentration of a polymer with a given molecular weight. Flory (15), Gee (17), and Huggins (33,34) have developed the thermodynamic approach from the entropies and heats of mixing for the solution and precipitate phases. Morey (54) considered the start of the growth of the precipitate as a reversible reaction in his treatment of the mechanics of aggregation.

The fractional solution procedure calls for bringing the polymer into intimate contact with a solvent-nonsolvent mixture

and allowing the system to reach equilibrium. The supernatant liquid is decanted and a fresh mixture of solvent and nonsolvent is added to the residue. This second mixture and each succeeding mixture is made richer in solvent than the preceding one. Thus the process can be repeated until all of the residue has been dissolved or until no more of it will dissolve. In this method the low molecular weight fractions are the first ones removed. It has been found (50) that the solubility of cellulose depends on the amount of undissolved solid in contact with the solution. Thus, the solution may be saturated with respect to the high-molecular-weight molecules but not with respect to the low-molecular-weight ones; and if more solid material is added, more of the low-molecular-weight material will dissolve.

Fractionation by means of distribution between two immiscible liquids has been used to fractionate polyethylene oxide by Schulz and Nordt (76) and to fractionate lignin by Lovell and Hibbert (43). They have found that distribution of the polymer in the two liquid layers depends upon the molecular weight of the particles.

The rate-of-solution method of fractionation depends upon the difference in rate of diffusion of the large and small molecules. The smaller molecules diffuse the more rapidly and are the first to be separated. This difference in rate of diffusion is to be distinguished from the difference in solubility of the large and small

molecules. In this method the solvent is removed from the residue after a definite time interval before equilibrium sets in.

As an analytical method ultracentrifugation is perhaps the best method of fractionation available. Carothers (7), Mark (48), and Staudinger (84) are among those who recommend it. An ultracentrifuge is a very complex and costly piece of equipment which few laboratories can obtain. It can be used to measure the rate of settling of a particle in a given centrifugal field or to measure the concentration gradient after equilibrium is reached between sedimentation and diffusion. In the centrifugal field the high and low molecular weight particles will settle at different rates according to their size. The heavier, or larger, particles being the first to settle. As the particles settle more and more, the boundaries between the high and low molecular weight ones will spread out. From this spread the distribution of high and low molecular weight molecules can be calculated.

In chromatographic adsorption the solution of the heterogeneous polymer is filtered through a column containing some adsorbent in which the smaller molecules are preferentially adsorbed and remain in the upper part of the column. When cellulose or cellulose derivatives are chromatogramed, there are no separate bands but a gradual transition from lower to higher fractions.

How the column is divided determines the constitution of the fraction obtained. Those poorly adsorbed may go on through the column and appear in the filtrate.

Ultrafiltration, or filtration through graded membranes of cellulose or nitro-cellulose, offers a means of fractionation. The membrane selected must not react with the solution. This method is satisfactory with spherical shaped particles, but the long cellulose chains find it rather difficult to pass through the pores. The coiling of the chains would retard their progress once they started through, and unless the solution above the membrane was agitated occasionally, many of the chains would settle flat against the membrane and not be in position to pass.

Molecular distillation is more useful for the purification of a high polymer than for the separation of fractions. It involves distillation at very low pressures. The distance from the distilling to the collecting plate is shorter than the mean free path of the evaporating molecules which eliminates collisions in the vapor phase. The lighter molecules distill first thus leaving a purer residue.

Of all of these methods, only fractional precipitation has been used for the fractionation of ethyl cellulose, and a search of the literature reveals only three reports of such fractionations. The first of these was made by Okamura (56) in 1933.

From a 1% solution of ethyl cellulose in glacial acetic acid he obtained three fractions by the addition of water. The first of these he refractionated, by the same method, into four fractions, and from the other two he obtained two fractions each for a total of eight fractions. He found that the viscosity of fractions obtained from acetic acid solution dropped very rapidly in succeeding fractions. This is what would be expected from the discussion above. He also maintained that a partial acetylation of any free hydroxyl groups in the ethyl cellulose did not take place as subsequent treatment with aqueous ammonia did not change the viscosity as would have been the case if the ammonia has caused a splitting off of any acetyl groups. In the same report a very brief description of a similar fractionation of ethyl cellulose from a benzene solution by the addition of hexane is given.

In 1938 Staudinger and Reinecke (85) obtained three fractions of ethyl cellulose by precipitation with water from a dioxane solution. These three fractions had identical chemical composition but varied in molecular weight. Ushakov and Geller (88) in 1939 used gasoline to fractionally precipitate ethyl cellulose from a 4% solution in alcohol. They reported that these fractions differed chemically as well as in molecular weight.

DETERMINATION OF MOLECULAR WEIGHT

The usual method for determining molecular weight of an organic substance in a suitable solvent is the measurement of the depression of the freezing point or of the elevation of the boiling point. In the case of cellulose derivatives the freezing point method will likely give erroneous results because of their tendency to cause delayed crystallization as well as the probable presence of small amounts of short chains (16). In order to get measurable results relatively high concentrations of the solute are required. However, concentrations of 0.1 to 2.0% are the highest desirable for an accurate extrapolation to infinite dilution necessary for molecular weight determinations. At this low concentration the lowering of the freezing point would be so little as to made it practically indeterminable even with the most careful experimental technique.

Extrapolation to zero concentration was also found necessary for satisfactory molecular-weight determination by the osmotic-pressure method (60). Dobry (11) showed conclusively that the molecular weight is independent of the solvent. Various types of osmometers have been designed and used, but the one designed by Schulz (74) has been used more than any of the others.

This osmometer consists of a metal vessel containing the solution and provided with a capillary. A membrane supported

by a perforated plate is clamped over the open face of the metal container. When the assembled unit is filled with solution, it is plunged into the solvent in such a manner that the membrane is maintained in a horizontal position. Collodion or cellophane membranes are sufficiently semipermeable for use with large molecules such as found in cellulose. Low molecular weight impurities diffuse through the membrane and do not affect the osmotic pressure as measured in the manometer.

Generally a linear relationship exists between the concentration (C) and the osmotic pressure (P) divided by C. In the low concentration range this is true, and extrapolation is relatively simple. However, curved lines are obtained and Dobry (11) and Schulz (74) claim that though the curvature is not always prominent it is real and is not due to experimental errors. It has been found that in pure hydrocarbon solvents three or four molecules of ethyl cellulose are strongly associated (86). At concentrations below 0.1% the P/C versus C lines tend to curve upward. The P/C versus C lines for solutions of nitro-cellulose bend downwards (11,74). No completely satisfactory explanation for curving up or down has been presented, but the problem is simplified in that the curvature becomes less as the concentration approaches zero (80). Thus, the extrapolation should be carried out from data obtained from very dilute solutions. It

is also recommended that the solvent used be one in which association is held at a minimum.

The determination of the sedimentation equilibrium of a very dilute solution in the ultracentrifuge is the most satisfactory method for determining molecular weight. The use of the ultracentrifuge has been discussed in the section of fractionation methods and need not be repeated here. According to Kraemer (38) the ultracentrifuge has the following advantages over the other methods for determining molecular weights:

"1. It has the same thermodynamic foundation as osmotic pressure or vapor pressure methods.
2. It is accordingly not influenced by particle shape.
3. In general, it is not affected by solvation.
4. Its sensitivity increases with increase in particle size.
5. It can be used with complex solvents like cuprammonium with which osmotic pressure measurements would be difficult.
6. It avoids difficulties associated with the use of semipermeable membranes.
7. It permits recognition of the uniformity or nonuniformity of particle size, and it can give a quantitative rating of the degree of nonuniformity.
8. For solvents containing relatively small molecular weight contaminates, it is much less adversely affected than osmotic pressure and other methods" (38).

According to Staudinger (83) the molecular weight is proportional to the specific viscosity (η_{sp}) of a very dilute solution. This may be expressed as

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta_{solution}}{\eta_{solvent}} - 1 = KmMC$$

in which Km is the constant of proportionality, M is the molecular weight, and C is the concentration of solute in grams per liter. The K_m was calculated by substituting in the above equation molecular weights determined by cryoscopic methods. At first there was some doubt as to accuracy of this equation when applied to high-molecular-weight polymers, for it is based upon several assumptions. One of his assumptions was that in solutions the molecules of cellulose and of cellulose derivatives are separated and are individual molecules. He also assumed that the solvent and the phenomena of solvation do not affect the viscosity measurements. Another assumption was that the cellulose chain molecules are rod-shaped units which retain their shape in solution. All of these assumptions have been challenged, but when the ultracentrifuge and osmotic pressure methods were applied to high molecular-weight-polymers, the validity of the equation was established for certain systems. Kraemer (38) states that the particle in solution should be considered as a single molecule until the existence of some skin substance or cementing material which is capable of holding an assembly of molecules together in the same manner through etherification, esterification, bleaching and hydrolyzing reactions either without being affected

or at least not causing a change in intrinsic viscosity can be proved. This was his conclusion after using the ultracentrifuge extensively for molecular weight determination.

Huggins (30) states that Staudinger's equation is not generally valid as plots of the intrinsic viscosity $[\eta]$ against average molecular weight $\bar{M}$ deviate from the straight line which would be expected from a theoretical viewpoint. These deviations depend on the tightness or looseness of the coiling of the kinked double-chain molecule as well as on other factors which are not itemized. He also states that for the measurements of the viscosity of solutions of polymers to be used to estimate the molecular weight the course of the $[\eta]$ versus $\bar{M}$ curve should be known.

It has been found that the K_m obtained from $[\eta] = K_o + K_m M^{\nu}$, where K_o is a constant but is negligible except for small values of M, and ν is a constant that varies little from unity, gives better agreement with the experimentally determined curves. Since the deviations are relatively slight and since the calculated molecular weights are only average weights and not absolute weights, the Staudinger equation is the one most often used.

Various types of viscometers have been used (62). The short-tube efflux type is used principally in the petroleum industry. The rotational type does not give accurate results when the viscosity is below 100 centipoises. The falling-ball method is used

for liquids of high viscosity. The capillary-tube method has been used more often for viscosity measurements of solutions of high-molecular-weight polymers. The best known of these is the Ostwald viscometer which consists of a capillary which discharges into a wide U-tube. By adding the same amount of material each time the effect of liquid level in the wide tube is made negligible.

If two liquids having viscosities η and η_1, densities D and D_1, and time of flow through the capillary T and T_1, then

$$\eta / \eta_1 = DT/D_1T_1$$

when equal volumes of liquid is placed in the viscometer. This equation requires knowledge of the time of flow and of the density. At the very dilute concentrations used for molecular weight determinations the density of the solution varies little from that of the solvent so the density terms may be neglected. The time of flow of each may be measured. Then if the viscosity of the solvent is known the viscosity of the solution can be calculated. Substitution of these values into the Staudinger equation along with the K_m for the polymer in that particular solvent makes possible the calculation of the molecular weight.

At this point, it would be well to note the difference in average molecular weight determined by number methods and the

average molecular weight calculated from weight methods. The number average of the molecular weights is the ordinary arithemetic average based on the number of molecules present. Cryoscopic and osmotic-pressure methods depend upon the number of particles present, and from them the number-average molecular weight is determined. In these the number of low molecular weight particles affects the calculated molecular weight. The viscosity and centrifuge methods depend upon the weight of the particles thus giving more importance to the high molecular weight particles. Thus, the two values are not numerically the same. It is important that the method of determining the molecular weight be given along with that weight.

DISTRIBUTION CURVES

As stated previously, the purpose of this investigation is to separate ethyl cellulose into fractions each of which will be composed of chains of approximately the same length. Such a process might be pictured as reaching into a solution of ethyl cellulose and picking out all the chains with a certain degree of polymerization. If it were possible to do this and to lay them with the longer chains on the bottom and those with gradual decreasing length on these, a smooth curved line could be drawn through the ends of the chains. Any point on this curve would give the number

of chains which have that degree of polymerization plus those which are longer. This would be the integral distribution curve for that sample.

Differentiation of this integral distribution curve may be done mathematically when the equation of the curve is known, or may be done mechanically by drawing the tangent to various points along the curve if the equation is unknown. Plotting the slopes of these tangent lines against the degree of polymerization gives the differential distribution curve. Any point on this curve gives the percentage of the sample having that degree of polymerization, i.e., within a very small range of that degree of polymerization.

The degree of polymerization of a cellulosic substance is commercially important because it determines:

"1. The percentage of the material lost on treatment with reagents having some solvent action, such as mercerizing baths or nitrating mixtures;
2. The flow and knitting characteristics of the material in solution or during a molding operation;
3. The type of interaction with other ingredients of a useful composition;
4. The nature of film-casting or filament spinning process, especially if partial coagulation is involved during the initial steps; and
5. The physical properties of the product" (81).

EXPERIMENTAL

MATERIALS USED

The ethyl cellulose used throughout this investigation was a commercial grade type N200 with 48.7% ethoxy content and with a viscosity of 169 centipoises in 5% solution obtained from Hercules Powder Company of Wilmington, Delaware. Before being used, the granular ethyl cellulose was dried for 24 hours in a forced draft oven set at 50°C. and was dried over calcium chloride in a desiccator for at least 24 hours.

The benzene used was 99-100% purified and was obtained from Baker and Adamson of Marcus Hook, Pennsylvania.

The normal heptane used was 99 mol % minimum obtained from Phillips Petroleum Company, Bartlesville, Oklahoma.

The acetone used was chemically pure and obtained from Commercial Solvents Corporation of Baltimore, Maryland.

The ethyl acetate, commercial grade, was also obtained from Commercial Solvents Corporation of Baltimore, Maryland.

Two grades of glacial acetic acid were used. First, 99.5% technical grade as manufactured and sold by Arthur S. LaPine and Company, Chicago, Illinois, was used. Then 99.5% chemically pure acetic acid which met American Chemical Society specifications was used. The latter was obtained from J. T. Baker Chemical Company of Phillipsburg, New Jersey.

The chemically pure potassium acid phthalate was also obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey.

The sodium hydroxide solution was prepared from reagent grade sodium hydroxide in pellet form as obtained from Baker and Adamson, New York.

The aniline, chemically pure, was obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Since this had a yellow color, it was distilled, and the distillate, recovered between 176° and 178° C., was used in the test for furfural.

Chemically pure butyl acetate was obtained from Eastman Kodak Company of Rochester, New York. Before being used this was distilled through a packed column and the distillate between 118° and 120° C. was recovered and used.

THE BENZENE-HEPTANE SYSTEM

Okamura (56) reported successful fractionation of ethyl cellulose from a 1% solution of ethyl cellulose in benzene with hexane as precipitating agent. He added sufficient hexane to produce a turbidity, but gave no indication of the exact procedure used nor of the amount of precipitate obtained. Therefore, it was decided to investigate this system further except that heptane, which was available, would be used in place of the hexane.

In order to conserve solvent and non-solvent an attempt was made to use a 5% solution of ethyl cellulose in benzene, but this proved to be too viscous for accurate measurements of aliquot portions. It was found that a 2½% solution was sufficiently fluid to pour easily, so this concentration was used throughout the rest of the study of this system.

The addition of heptane caused the solution to become turbid whereas the benzene solution originally had a clear yellow color. A series of tests was run to determine the degree of turbidity which would give the desired amount of precipitate, but with a Hellige Nephelometer this could not be done. It was found that the same amount of heptane would not give identical readings on different samples and that when the nephelometer readings were the same the amount of precipitate varied as shown in Table I.

TABLE I

NEPHELOMETER READINGS AND THE AMOUNT OF PRECIPITATE OBTAINED

(25 grams of ethyl cellulose were dissolved in 1100 ml. of benzene.)

Sample	ml. Heptane Added	Filter	Nephelometer Reading	Weight Precipitate
Original solution		Milk	19	-
1	625	Milk	26	8.19
2	600	Milk	26	5.20

Marschner and Cropper (46) found that benzene and heptane form an azeotropic mixture with the following composition: 99.1% benzene by volume, 99.3% benzene by weight, or 99.5 mol % benzene. Since the benzene and heptane were being recovered by distillation, it was decided to add enough heptane to the commercial benzene to give the azeotrope; the results could then be duplicated later when the recovered benzene and heptane would be used. The addition of such a small amount of heptane did not impede the dissolution of the ethyl cellulose, nor did it noticeably affect the color of the solution.

The precipitates obtained from the azeotropic mixture and heptane were soft gels which would flow down the side of the

flask during the decanting of the super-natant liquid. Sometimes a sharp separation of liquid and precipitate was possible, but at other times it was not. This meant that duplicate results could not be obtained when the solutions stood overnight at 15° C.

At this time it became apparent that a standardized procedure was necessary so the following plan was followed throughout this study unless otherwise stated. The ethyl cellulose was slowly poured into the flask containing the azeotropic mixture which was constantly agitated. The dissolution was visually complete after about 30 minutes of constant shaking. The solution was allowed to stand 18 hours at 25° C. to insure a complete and homogeneous solution. The weighed amount of heptane was added rapidly, and the solution was again shaken until it appeared to be homogeneous.

The samples were then maintained at 15° C. for a period of 20 hours, and the supernatant liquid decanted. The flask containing the precipitate was then placed on a water bath and the benzene and heptane were removed by a stream of air under a partial vacuum. When only the dry film remained, water was added to the flask, and in a few minutes the ethyl cellulose film could be easily removed. It was then thoroughly dried at 105° C. and weighed.

Even with the 10 degree temperature drop reproducible results were not obtained. Upon using larger batches of solution

it was noted that the addition of heptane caused a drop in the temperature. To overcome this drop, the solution was rewarmed to 25° C. and maintained at this temperature for two hours before cooling to 15° C. The results from these tests could not be duplicated so the solutions were heated to 50° C. for the same period of time and then cooled to 15° C. Again reproducible results were not obtained.

The 10 degree drop in temperature was tried again but this time the solution was maintained at 15° C. for 42 hours. The resulting precipitate was slightly harder than previously but still too soft for satisfactory decanting. It had been found that using ethyl acetate as solvent and heptane as precipitating agent gave a hard precipitate when cellulose nitrate is fractionated (64). Therefore, it was decided to try adding some ethyl acetate to the solvent and observing the type of precipitate obtained. After a series of experiments it was found that 30 ml. of ethyl acetate added to the solvent somewhat hardened the precipitate without appreciably increasing the amount of heptane required. When more than 30 ml. of ethyl acetate was added, the amount of heptane required for a precipitate increased rapidly. It was also found that when the solution was maintained at 15° C. for 47 hours the precipitate was firmer and that the same amount of precipitate could be obtained from similar samples.

However, the other fractions varied as shown in Table II. Since a rigid time schedule along with the temperature drop gave good results with the first fraction, a rigid time schedule was set up for the other fractions. The supernatant liquid was decanted and heated to 25° C. and maintained at that temperature for two hours before the heptane was added. After the addition of heptane the solution was again maintained at 25° C. for two hours before being cooled and maintained at 15° C. for twenty hours.

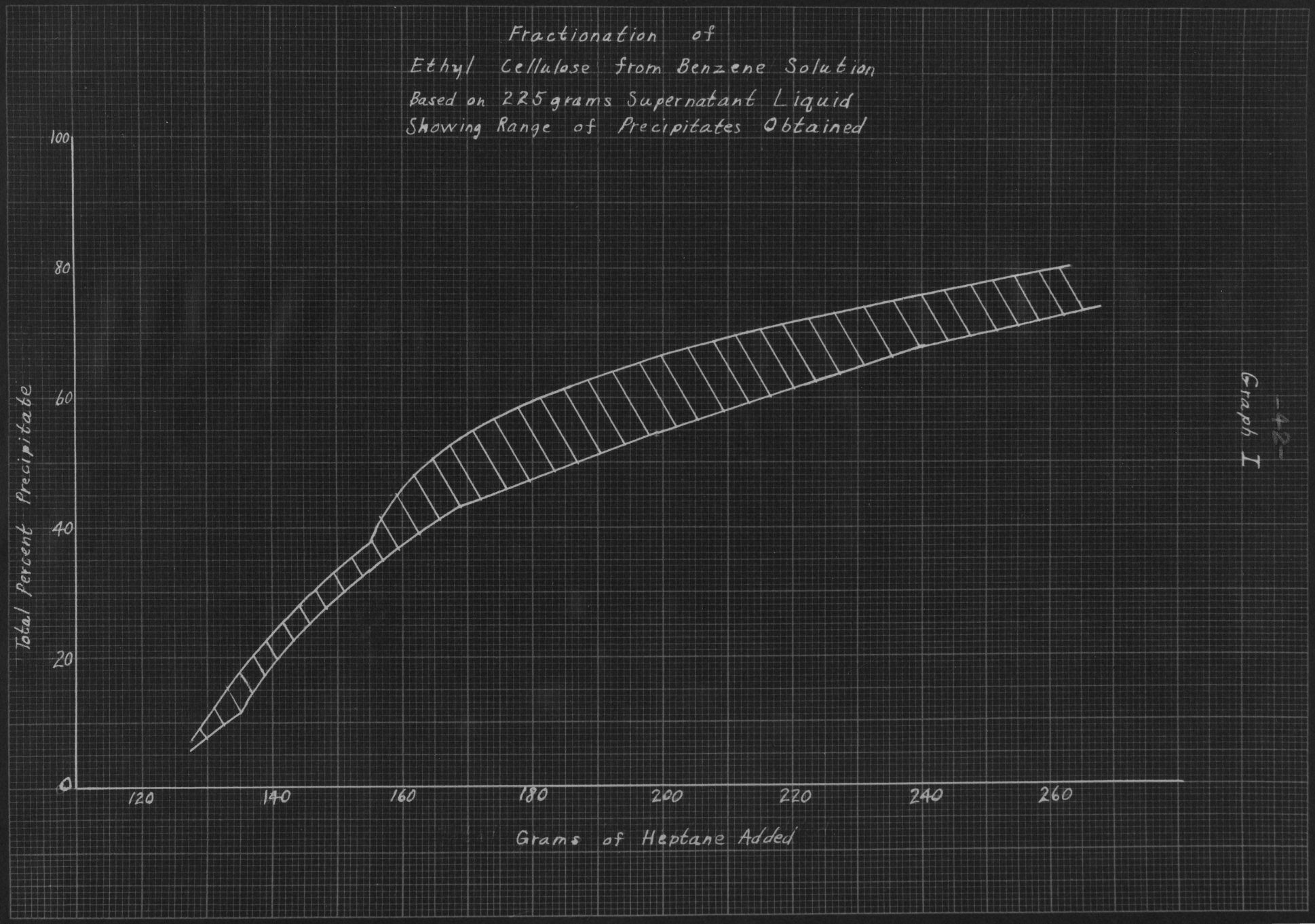
Yet, this did not enable the duplication of results to a satisfactory degree. Then it was noted that the weight of precipitate plus the absorbed benzene and heptane varied greatly even between two otherwise similar samples. As the amount of precipitate was almost the same in the two samples the amount of absorbed solvent and non-solvent could not be controlled. Therefore, the ratio of solvent to non-solvent for the same fraction in successive runs would not be the same. Table II shows these discrepancies in weight. Therefore, it was apparent that a system of solvent and non-solvent which would give hard precipitates, i.e., precipitates with very little absorbed liquids, would be the one which should also give reproducible results.

Table II shows the results obtained from two simultaneous runs. Both batches contained 22.5 grams of ethyl cellulose

TABLE II

RESULTS OF FRACTIONATION OF ETHYL CELLULOSE FROM A BENZENE SOLUTION

Fraction	Wt. Soln.	Wt. of ppt. and absorbed solution	Wt. of heptane per 225 grams of solution	Wt. of ppt.	Condition of ppt.	% ppt.
I	900	-	127.5	1.569	soft	7.0
	900	-	127.5	2.313	very soft	10.3
II	1349.4	60.6	10.0	2.969	soft	13.2
	1341.9	68.1	10.0	1.957	soft	8.7
III	1331.5	77.8	7.5	2.246	soft	10.0
	1344.9	56.3	7.5	2.208	soft	9.8
IV	1317.4	58.5	13.5	3.343	soft	14.8
	1322.0	67.7	13.5	3.411	soft	15.2
V	1327.7	68.7	10.5	1.978	firmer	8.8
	1341.7	59.6	10.5	0.616	firmer	2.7
VI	1351.4	36.3	17.0	0.687	firm	3.1
	1388.7	15.6	17.0	1.808	firm	8.1
VII	1439.1	14.4	27.0	2.125	firm	9.5
	1462.3	31.2	27.0	2.157	firm	9.6
VIII	1580.6	36.0	62.0	2.144	firm	9.5
	1602.0	35.8	62.0	2.168	firm	9.6
IX	Benzene and heptane boiled off			4.976	-	22.1
				4.513	-	20.0


Fractionation of
Ethyl Cellulose from Benzene Solution
Based on 225 grams Supernatant Liquid
Showing Range of Precipitates Obtained
100
80
60
40
20
0
Total Percent Precipitate
120
140
160
180
200
220
240
260
Grams of Heptane Added

Graph I

dissolved in 7 grams of heptane, 24 grams of ethyl acetate, and 846.5 grams of benzene. The time schedule and temperature changes were rigidly adhered to throughout the tests. Graph 1 shows the spread in percentage of total weight obtained from eight successive runs handled as explained above.

THE ACETONE-WATER SYSTEM

Two and one-half percent solutions of ethyl cellulose in acetone and water (5% by weight) were prepared. The same procedure for temperature control was followed as has been described. Five percent by weight of water was added to acetone so the solvent would have the same composition in all samples. It has been found that acetone absorbed varying small amounts of water vapor from the air, depending upon time of standing in a seemingly closed container and upon atmospheric conditions (87). Pure water was added as precipitating agent and precipitates from which decantation was easy were obtained. About 20% by weight of the ethyl cellulose in solution was precipitated. All attempts to reduce this to 10% in the first fraction resulted in loose flocculent precipitates being formed from which complete decantation was impossible.

This loose-flocculent precipitate could not be filtered rapidly through a fluted filter. Slow filtering would permit the evaporation of considerable amounts of acetone, and as this

evaporation could not be controlled from day to day due to the changes in atmospheric conditions the composition of the supernatant liquid could not be controlled. As was shown in the case of the benzene-heptane system, the same composition of solution is essential for duplicating weights of precipitate. When the precipitates were filtered through a Buchner funnel under reduced pressure, the flocks proved to be sufficiently colloidal for the majority of them to go through the filter paper.

A mixture of 50% acetone and 50% water by weight was used as precipitating agent and still loose flocculent precipitates were obtained when the percentage of precipitation fell below 40%. The same results were obtained when the original solution contained 5, 4, 3, or 1% ethyl cellulose.

THE ETHYL ACETATE-HEPTANE SYSTEM

Six per cent solutions of ethyl cellulose were prepared in ethyl acetate and heptane was added as precipitating agent. The addition of a weight of heptane nearly equal to that of the original solution was necessary to obtain a precipitate. Thus, the concentration of ethyl cellulose was actually about 3%. Precipitates ranging from 50 to 100% of the total weight of ethyl cellulose were obtained.

In order to reduce the volume of solutions handled, 3% solutions of ethyl cellulose were prepared in mixtures of ethyl

acetate and heptane. It was found that a 300 gram solution of a 50-50 mixture (by weight) required 250 grams of heptane to give a 29% precipitate. A similar 300 gram sample of 60% heptane and 40% ethyl acetate solution required 170 grams of heptane to give a 33% precipitate (by weight). Using a 67% heptane and 33% ethyl acetate mixture as solvent, an attempt was made to reduce the amount of precipitate obtained in the first fraction. In both a 3 and 1% ethyl cellulose solution, a soft gel or a loose flocculent precipitate was obtained when 58 and 50 grams, respectively, of heptane was added. Complete decantation from these precipitates was impossible so this system was abandoned.

MISCELLANEOUS SYSTEMS

The type of ethyl cellulose used in this investigation is soluble in alcohols, esters of acetic, formic and lactic acids, ethers, symmetrical and asymmetrical ketones, aromatic hydrocarbons, chlorinated hydrocarbons and certain mixed solvents (23). It is insoluble in aliphatic hydrocarbons and water. Thus, while there is a wide choice of solvents, only those which are miscible with the non-solvents can be used.

Staudinger and Reinecke (85) divided ethyl cellulose with 2.6 ethoxy content into three fractions by dissolving the commercial grade of ethyl cellulose in dioxane and slowly adding

water as non-solvent. They did not describe their method in detail, but they did show that they obtained fractions of decreasing molecular weight without any noticeable change in the ethoxy content. A 5% solution of ethyl cellulose was prepared in dioxane and water was added. A soft gel was formed from which complete decantation was impossible.

A solution of ethyl cellulose in acetone was prepared as described in the section on acetone-water system. Heptane was added as precipitating agent, but before enough was added to cause precipitation two immiscible layers were formed. This was due to the slight miscibility of heptane and the water present in the acetone.

A 2½% solution of ethyl cellulose was prepared in methyl alcohol. The same procedure for temperature control was followed as has been previously described. To one such sample, water was added and a soft precipitate was obtained. As this was no improvement over the benzene-heptane system no further study was made of it. To another sample heptane was added, but before a precipitate was formed, the methanol and heptane became immiscible and separated into two layers. Therefore, methanol was elimated as a possible solvent, and alcohols as a class of solvents were eliminated.

A 2½% solution of ethyl cellulose was prepared in a mixture of 80% by weight of benzene and 20% by weight of acetone. Again the same method of temperature control was followed. To this, heptane was added and a precipitate too soft for accurate decantation was obtained. No further study of this system was undertaken.

THE ACETIC ACID-WATER SYSTEM

As stated previously, Okamura (56) did not describe his method of fractional precipitation of ethyl cellulose from a glacial acetic acid solution; therefore, this system was selected for study. War surplus technical grade glacial acetic acid was first used for this investigation as a large supply of it was available. The solutions of ethyl cellulose in this acid were hazy and had a yellow color. Pure water when added slowly immediately gave a hard precipitate so that it was necessary to shake the flask several minutes in order to redissolve the precipitate. This agitation whipped in minute bubbles of air, so it was necessary to wait about five minutes for the solution to clear up before taking turbidity readings on the Klett-Summerson Photoelectric Colorimeter. For all tests which required its use the colorimeter was set at zero with distilled water in the cell and with the blue filter in place.

By using a 50-50 mixture by volume of water and acetic acid as precipitating agent, the amount of immediate precipitate was materially reduced. It was also found that the turbidity of the solution decreased upon addition of the precipitating agent until so much had been added that the ethyl cellulose could not be redissolved. At this point the turbidity increased rapidly. The amount of precipitate obtained was much larger than the desired 10%, so it was still considered possible to determine the precipitation end-point by nephelometric measurements.

Since a turbid solution indicates that not all of the particles have been dissolved, a series of tests was run to determine the concentration of acetic acid which would be the best solvent, i.e., the concentration which would give the lowest nephelometer reading. The ethyl cellulose content was the same in all tests, 2½% by weight. It was found that 95% acetic acid as solvent gave the clearest solution and could be considered the best solvent.

The following procedure was used to determine the strength of all the acetic acid solutions used throughout this investigation: 45 grams of sodium hydroxide pellets were dissolved in one liter of boiled distilled water. Then a little barium chloride was added to remove any carbon dioxide that might be present,

and the entire mixture was filtered while hot. The clear solution was stored in a glass bottle with a cork stopper. This solution was titrated against a fourth normal potassium acid phthalate solution prepared by dissolving 204.22/4 = 51.055 grams of dry potassium acid phthalate in boiled distilled water and making up to one liter of solution. Phenolphthalein was used as indicator in all the titrations during this investigation. Having determined the normality of the sodium hydroxide solution, the strength of the acetic acid solution could be found. From the volume of acetic acid and sodium hydroxide used the grams per liter of acetic acid could be calculated. Then from the specific gravity table given in a handbook (19) the percentage composition of the acid could be calculated as shown below.

2.11 ml. NaOH were required to neutralize 10 ml. N/4 $KHC_8H_4O_4$.

$$2.13 \times N = 10 \times 0.25$$

$$N = 1.185 \text{ normal NaOH}$$

14.87 ml. NaOH were required to neutralize 2.00 ml. acetic acid.

$$\frac{14.87}{2} \times 1.185 \times \frac{60}{1000} \times 1000 = 528.6 \text{ grams/liter}$$

According to the handbook a 50% solution of acetic acid contains 528.8 grams per liter, and a 49% solution contains 517.8 grams/liter. By interpolation, the above acid was calculated to be 49.98% acetic acid.

A series of tests was also run to determine the most satisfactory water-acetic acid combination to use as non-solvent. A 2½% ethyl cellulose solution in 95% acetic acid was used for these tests. It was found that 50% acetic acid gave the least amount of immediate precipitate and also that it gave a large range of nephelometer readings.

Another series of tests showed that the time the solutions were stirred after the non-solvent was added affected the amount of precipitate formed. In order to standardize the procedure, each sample was stirred mechanically for ten minutes. This improved the technique, but still there was no correlation between colorimeter readings and the amount of precipitating agent added or with the amount of precipitate obtained. Table III, page 51, shows the results of these tests.

One possible reason for the lack of correlation between the nephelometer readings and the amount of non-solvent added or with the percentage of precipitate obtained may be found in the size of the particles of the solute. The addition of the non-solvent caused an immediate increase in the turbidity of the solution which gradually disappeared when the solution was agitated. By the time the solution was free of air bubbles, the colloidal particles had started to form the larger aggregates prior to settling. These larger particles being fewer in number than

TABLE III

NEPHELOMETER READINGS AND THE PERCENT OF TOTAL PRECIPITATED

Sample	ml. Non-solvent Added	Nephelometer Reading	Percent Precipitate
1	193	66.5	-
2	195	76.5	-
3	205	56.0	19.9
4	215	58.0	24.9

TABLE IV

PRECIPITATION OF ETHYL CELLULOSE FROM 95% ACETIC ACID 50% ACETIC ACID USED AS PRECIPITANT

ml. Non-Solvent Added	Percent of Total Precipitated					
	Test 1	2	3	4	5	6
203	0.26	-	-	2.5	-	10.8
205	-	6.33	-	5.46	0.38	8.8
207	3.75	24.5	12.6	-	-	-
208	-	-	-	4.85	0.62	9.57
209	6.05	-	-	-	-	-
210	-	19.4	-	10.1	2.42	9.76
212	9.75	23.0	19.4	16.9	3.24	12.2
214	-	19.0	-	-	-	-
215	-	-	21.1	7.85	9.83	9.0

those in the original solution did not absorb or reflect as much light as did the numerous small particles. The rate of aggregation could not be controlled; therefore, the turbidity readings could not be controlled.

The procedure at this point was to prepare 95% acetic acid and to 975 ml. of it add 25 grams of ethyl cellulose. This gave a 2½% ethyl cellulose solution by weight. Aliquot portions of this solution were taken when dissolution appeared to be complete, and the non-solvent was added immediately. The solution was then stirred 10 minutes before being cooled and maintained at 15° C. for 20 hours. The precipitates obtained by this method were hard, and it was believed that complete separation of solution and precipitate was obtained by decanting. A small portion of 95% acetic acid was used to redissolve the precipitate. Then an excess of water was added, and the ethyl cellulose formed a white fibrous precipitate which could be easily filtered, dried at 105° C, and weighed.

A series of six tests was run as described above except that varying amounts of non-solvent were added to the samples. The results did not duplicate each other as shown in Table IV, page 51.

A possible reason for these discrepancies might be found in the technical grade of acetic acid used. It was noted that

a bottle of this acid after being opened and exposed to the air would change from water clear to a yellow. This indicated the presence of an oxidizable substance. Scott (73) listed possible impurities in acetic acid as formic acid, furfural, acetone, sulfuric acid, sulfurous acid, hydrochloric acid, and metals. Of these, furfural was the most likely to be oxidized. Scott also described the following test for furfural in acetic acid: 5 ml. of aniline is dissolved in 2 ml. of C.P. glacial acetic acid and this solution is added to 100 ml. of the sample. The development of a red color indicates the presence of furfural.

The stock solutions, 95 and 50% acetic acid, as well as several bottles which had not been opened gave a positive test for furfural. A blank test on C.P. acetic acid did not give a positive test for furfural. At this time, 50% acetic acid was being recovered by distillation from the used acid, and this too gave a positive test for furfural. An attempt was made to purify the acetic acid by refluxing for an hour and distilling from over 2% of its weight of potassium permanganate (44,58). The distillate also gave a positive test for furfural.

The following test was used for acetone (2): 3 to 5 drops of 10% sodium hydroxide are added to 2 ml. of acetic acid and half normal iodine solution is then added dropwise until a faint yellow color develops. If the purplish red color of

iodoform develops, the presence of acetone is indicated. All of the samples listed above gave a negative test for acetone.

Since the acetic acid could not be conveniently purified, a change was made to chemically pure acetic acid. From this source the 95 and 50% concentrations were prepared as described. Somewhat the same time schedule and temperature control as that set up for benzene was followed. It was also found that 42 hours at 15° C. were required to give a reasonably hard precipitate for the first fraction.

From one test it was found that 84% of the original ethyl cellulose could be recovered by adding a total of 762 grams of 50% acid to a 300 gram sample of 3% ethyl cellulose in 95% acetic acid. Ten fractions were thus removed. By adding an excess of water to the above, the total solute recovered amounted to 95% of the original. Simultaneously, distilled water was added to a similarly prepared sample and approximately the same amount of ethyl cellulose was recovered when only 161 grams of water were added. However, the difficulty of immediate localized precipitation upon the addition of pure water was still present. Also, the amount of water added to bring about the precipitation of an additional 10% was so small that any slight error in weighing the samples would result in a large variation in the amount of precipitate obtained.

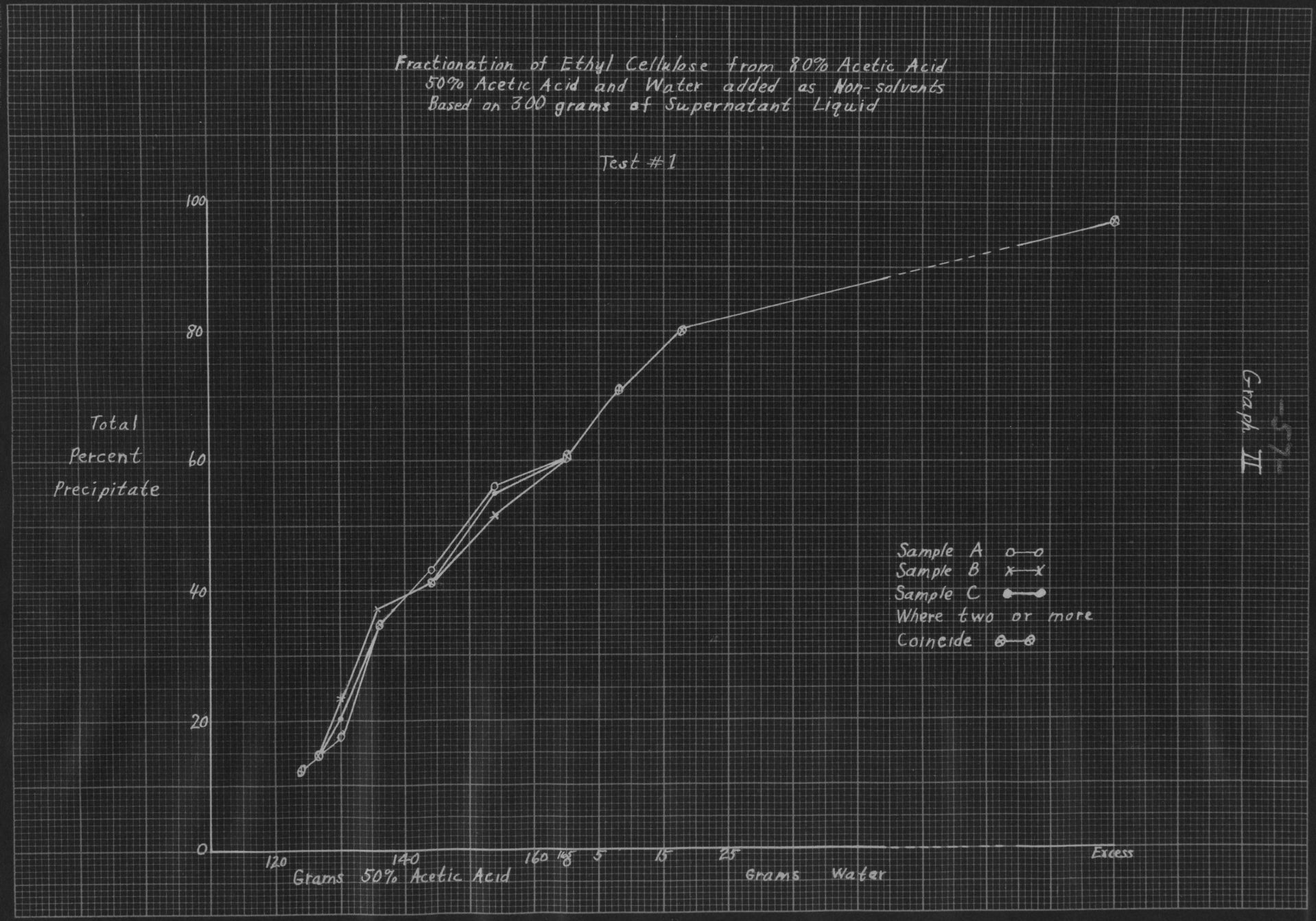
It was decided to reduce the strength of the solvent acid to see if better control of the precipitates could be obtained. It was found that although 75% acetic acid seemingly dissolved the ethyl cellulose, upon standing 18 hours at 25° C. some settling out had occurred. Therefore, 80% acetic acid was chosen as solvent. To a 300 gram sample containing 3% ethyl cellulose pure water was added as non-solvent. It was found that when a total of 50 grams of water had been added, 72% of the original ethyl cellulose was recovered. This meant that it would still be difficult to control the amount of precipitate obtained. A similar sample gave a recovery of 81% when 260 grams of 50% acetic acid were added. This meant the volume of solution would nearly double during the period of fractionation.

Since the addition of 50% acetic acid did not cause any immediate localized precipitation, it was decided to use 50% acid as non-solvent for the first few fractions and then change to distilled water for the last part of the fractionation. It had been noticed throughout that the first few precipitates were somewhat soft and that complete decantation was almost impossible. Without complete decantation, control of the amount of precipitate obtained is impossible. Therefore, it was decided to try pouring off the same amount of supernatant liquid from each sample in

order to control the amount of precipitate. The amount to be poured off was determined by decanting as completely as possible one sample and then pouring off the same weight from the others. Experience showed that sometimes this meant part of the thick, heavy precipitate would be decanted from one sample while in the next sample some of the thin supernatant liquid would be left with the precipitate.

This combination of precipitating agents and the method of decanting a known weight of supernatant liquid was tried on one set of three samples. The results are shown in Graph II, page 57. It can be seen that the change in precipitating agent from 50% acetic acid to distilled water took place when 60% of the original had been recovered. This is approximately the point at which it was necessary to add relatively large quantities of 50% acid to obtain further precipitation. Thus, by adding water at this point, the upward swing of the curve was continued until 80% had been precipitated.

The first fraction was decanted to a known weight, but the next two were not. By then the difference in the weight of supernatant liquid had become so great that it took a couple of adjustments to bring the three samples back to constant weight. The precipitates from these samples were the ones used in determination of degree of polymerization and distribution which


Fractionation of Ethyl Cellulose from 80% Acetic Acid
50% Acetic Acid and Water added as Non-solvents
Based on 300 grams of Supernatant Liquid
Test #1
Graph II
Total Percent Precipitate
100
80
60
40
20
0
120
140
160
145
5
15
25
Excess
Grams 50% Acetic Acid
Grams Water
Sample A
Sample B
Sample C
Where two or more Coincide

will be discussed later. A comparison of Graph I with Graph II shows that a great improvement in the control of precipitation has been acquired.

Another set of three samples was fractionated under the following schedule and conditions: 24 grams of dried ethyl cellulose were dissolved in 776 grams of 80% acetic acid. The solution was maintained at 25° C. for 18 hours before the first addition of 50% acetic acid was made. After slight agitation to give a visually homogeneous mixture, the solutions were maintained at 25° C. for one more hour. Then they were cooled and maintained at 15° C. for 42 hours. A definite weight of supernatant liquid was poured off and warmed to 25° C. for three hours. The non-solvent was added, and the solution held at 25° C. for another hour before cooling to 15° C. After 20 hours at 15° C. a definite amount of supernatant liquid was again poured off. This schedule was followed throughout the rest of the fractionation.

A small amount of glacial acetic acid was added to the precipitate in order to soften and dissolve it. An excess of acetic acid was avoided as then a colloidal suspension would be formed when an excess of distilled water was added. Besides being hard to filter, the colloidal particles are not in a form that can be easily handled in later tests. When water was added to the

softened precipitate, a fibrous precipitate was formed from which small samples could easily be taken for other tests. The fibrous ethyl cellulose was separated by filtration, dried at 105° C., desiccated, and weighed.

The only deviation from the above procedure occurred in the last fraction when some of the precipitate was found floating in the supernatant liquid. An excess of water had been added, and as no attempt would be made to obtain another fraction, the precipitate was separated by filtration without being redissolved. While this formed a heavy cake on the filter paper when wet, upon drying, the ethyl cellulose had a tendency to crumble. This indicated that only a low degree of polymerization products were in this last fraction.

The results from this second set of samples are shown in Table V, page 60, and Graph III, page 61. In these results, it can be seen that complete control of the amount of precipitate has been acquired.

DEGREE OF POLYMERIZATION

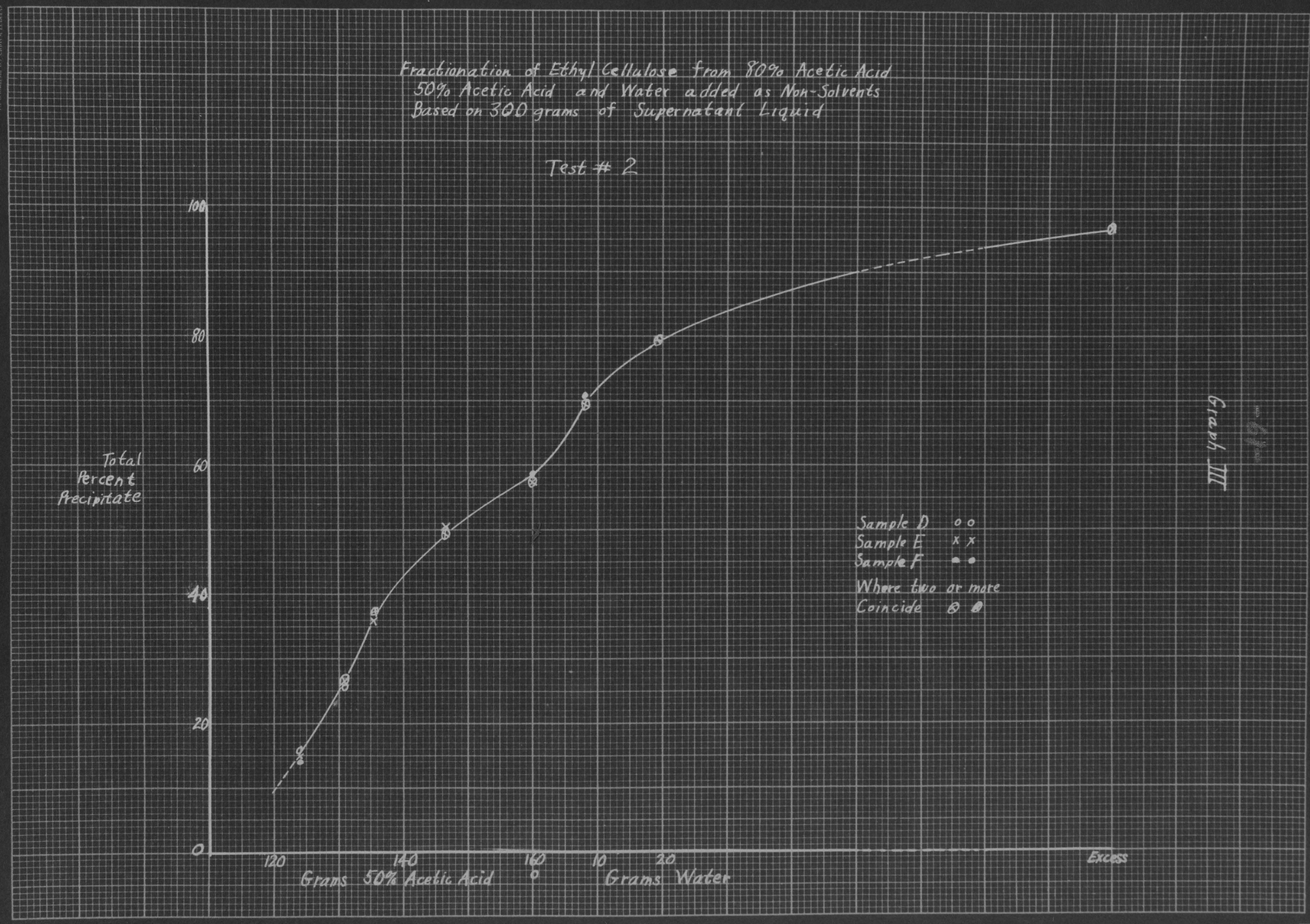
In order to show that the ethyl cellulose had actually been separated into more homogeneous groupings according to chain length, viscosity measurements were made. The data so obtained was substituted into Staudinger's equation, and the degree of polymerization was calculated.

TABLE V

FRACTIONATION OF ETHYL CELLULOSE FROM A 80% ACETIC ACID SOLUTION.*

Fraction	Weight Solution	Wt. of non-solvent added per 300 gm. solution	Wt. non-solvent added	Precipitate Wt.	Precipitate %
1 D	800	124	330	3.756	15.6
E	800	124	330	3.555	14.8
F	800	124	330	3.369	14.0
2 D	1070	7	25	2.442	10.2
E	1071	7	25	2.808	11.7
F	1071	7	25	3.110	13.0
3 D	1055	4.5	15.8	2.744	11.4
E	1053	4.5	15.8	2.255	9.4
F	1055	4.5	15.8	2.510	10.5
4 D	1037	11	38	2.841	11.8
E	1036	11	38	3.546	14.8
F	1035	11	38	2.807	11.7
5 D	1047	13.5	47.1	1.970	8.2
E	1040	13.5	46.8	1.572	6.6
F	1040	13.5	46.8	2.214	9.2
6 D	1075	8	28.6	2.981	12.4
E	1074	8	28.5	2.942	12.2
F	1068	8	28.5	2.915	12.1
7 D	1083	11	39.8	2.430	10.1
E	1084	11	39.8	2.470	10.3
F	1078	11	39.7	2.206	9.2
8 D	1110	Excess of Water		4.144	17.3
E	1108	Excess of Water		4.079	17.0
F	1114	Excess of Water		4.101	17.1

*Note: 50% Acetic acid used as non-solvent for fractions 1 through 5, distilled water used as non-solvent for last three fractions.


Fractionation of Ethyl Cellulose from 80% Acetic Acid
50% Acetic Acid and Water added as Non-Solvents
Based on 300 grams of Supernatant Liquid
Test # 2
Total Percent Precipitate
100
80
60
40
20
0
120
140
160
10
20
Excess
Grams 50% Acetic Acid
Grams Water
Sample D o o
Sample E x x
Sample F • •
Where two or more Coincide ⊗ ⊕
Graph III

Staudinger and Reinecke (85) had used butyl acetate as the solvent and had also reported the η sp/c and degree of polymerization obtained from the study of ethyl cellulose at 20, 40, and 60° C. Therefore, it was decided to use butyl acetate as the solvent and to operate the constant temperature water bath at 40±0.1° C.

The viscosity determinations were made in Ostwald viscometers, size 80-100 seconds, by measuring the time for 2 ml. of solution to flow through the capillary. The time of efflux of the solvent and of the solution varied from viscometer to viscometer so the time of efflux from each one used had to be determined. This became the η solvent, viscosity of solvent, in the equations below.

The following procedure was used for the viscosity determinations: The samples of ethyl cellulose were dried at 105° C. for at least 1 hour, desiccated, and then about 0.05 gram was accurately weighed in a large test tube. Fifty ml. of n-butyl acetate was added from a pipet, and the mixture was shaken until solution was complete. It was found that a few glass beads in the test tube would prevent the ethyl cellulose from sticking to the sides of the tube as it was shaken. When completely dissolved, the solution was maintained at 40° C. for at least 1 hour to insure homogeneity. The solution was then filtered

through a sintered glass filter into another test tube. This removed any dust particles or pieces of cork which might interfere with the accuracy of the viscosity measurements. The corks used had previously been extracted for three hours at 50° C. with butyl acetate so as to remove any waxes or other soluble material which might affect the viscosity of the solution. Five ml. of the solution was transferred to the Ostwald viscometer which was placed in the 40° C. bath and about 15 minutes were allowed for the solution to reach temperature equilibrium after which the solution was raised through the capillary and allowed to efflux. This left a thin film of the solution on the sides of the capillary so that in succeeding runs the flow of the solution would be against this film and not against the sides of the viscometer. The solution was raised through the capillary and allowed to flow out again as often as it was considered necessary to get an accurate measurement of the time of efflux. All the test tubes, viscometers, and other apparatus with which the solution was handled were scrupulously cleaned with acetone and dried before being used again.

From the measured time of efflux, the degree of polymerization was calculated as shown in the following sample calculation. Staudinger and Reinecke (85) stated that at 40° C. a solution of ethyl cellulose in butyl acetate had a η sp/C of

0.192 and a degree of polymerization of 180, and that another sample had a η sp/C of 0.283 and a degree of polymerization of 270. These values were substituted in Staudinger's equation

$$K_p = \frac{\eta \text{ sp}}{C \times P}$$

where K_p is the constant of proportionality, C is the concentration in grams per liter, P is the degree of polymerization, and η sp/C is the specific viscosity as defined below. The K_p was determined as

$$K_p = \frac{0.192}{180} = 10.66 \times 10^{-4}$$

$$K_p = \frac{0.283}{270} = 10.48 \times 10^{-4}$$

The average of these two values, 10.57×10^{-4}, was used in all the calculations of D.P. or degree of polymerization. The specific viscosity, $\eta \text{ sp} = \frac{\eta \text{ solution} - \eta \text{ solvent}}{\eta \text{ solvent}}$

or $\frac{\eta \text{ solution}}{\eta \text{ solvent}} - 1.$

The time of efflux of the solvent was 62.9 seconds, and the time of efflux of the solution was 72.7 seconds when 0.0404 grams of ethyl cellulose were dissolved in 50 ml. of butyl acetate. Then

$$\eta \text{ sp} = \frac{72.7}{62.9} - 1 = 0.236$$

The known values were then substituted into Staudinger's equation

$$P = \frac{0.236}{10.57 \times 10^{-4} \times .0404 \times 20} = 181$$

The 20 appears in the denominator in order to give the concentration in grams per liter when the weight of ethyl cellulose was actually dissolved in 50 ml. of butyl acetate. The value calculated above was that of the average degree of polymerization for the original ethyl cellulose as obtained from the manufacturer.

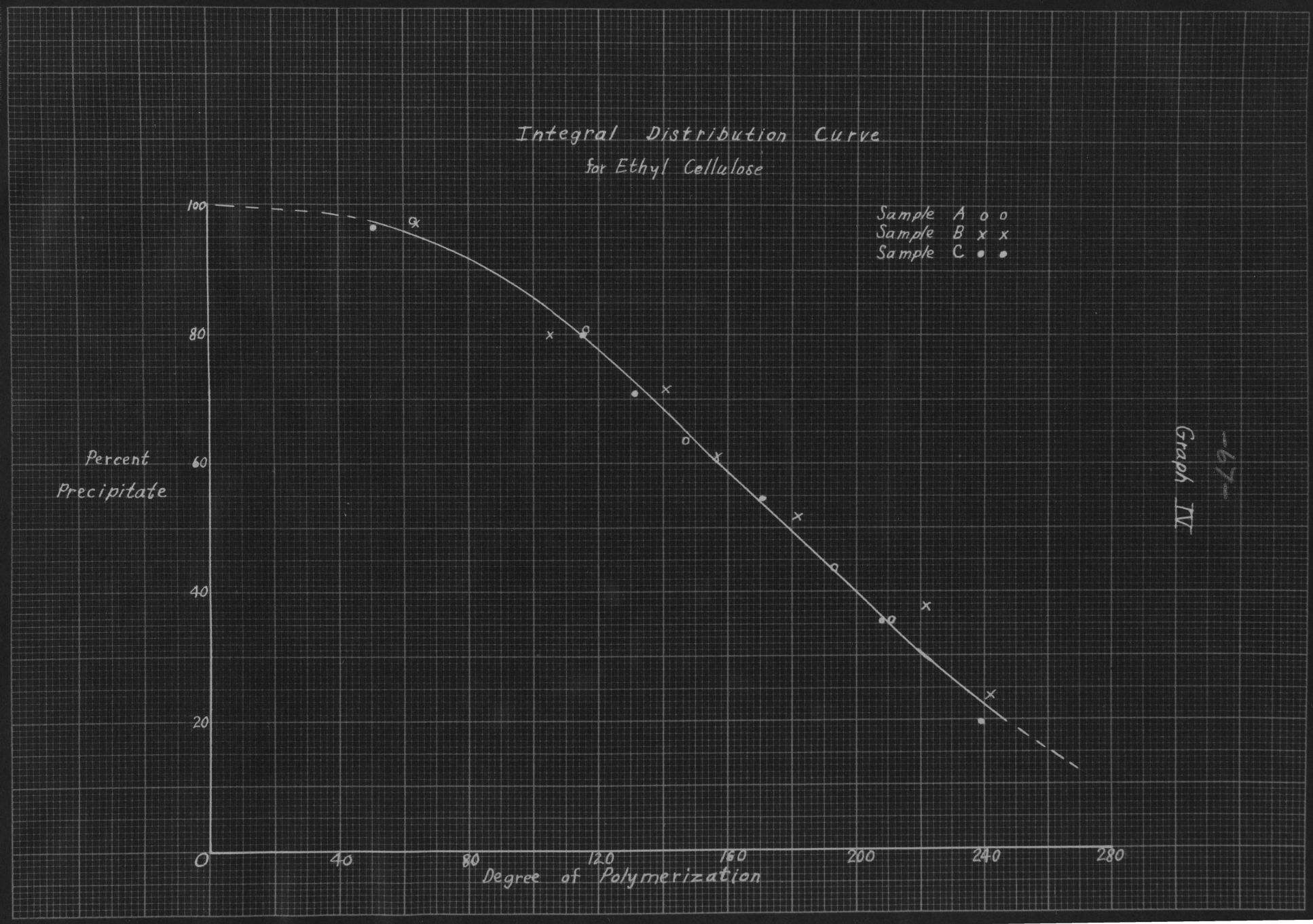
DISTRIBUTION CURVES

The results of the degree of polymerization of the three samples, A, B, and C of test 1, are shown in Table VI, page 66, and Graph IV, gives the integral distribution curve, page 67. The degree of polymerization of the first fraction was found to be less than that of the third fraction. The second fractions in this test were so small, as shown in Graph II, page 57, that it was not considered necessary to measure their viscosity. This contention was supported in the third fraction of sample C when 19.9% precipitate showed a degree of polymerization of 239 as compared to the 242 corresponding to 23.8% of sample B. The low values are not shown in Graph IV since they were probably due to large amounts of low molecular weight material being enmeshed by the heavier and longer chains as they settled to the bottom of the flask in the precipitate. All of the supernatant liquid and some of the soft precipitate were decanted when these first fractions were separated. Thus,

TABLE VI

DEGREE OF POLYMERIZATION DETERMINED FOR THE FRACTIONS OF SAMPLES A, B, AND C.

Sample A		Sample B		Sample C	
Total % Precipitate	D.P.	Total % Precipitate	D.P.	Total % Precipitate	D.P.
12.7	204	12.0	204	19.9	239
35.5	211	23.8	242	35.3	208
43.7	193	37.8	232	54.8	171
63.5	147	51.9	182	71.8	131
80.7	116	61.0	157	79.8	115
97.8	63	71.6	141	96.9	51
		79.9	105		
		97.5	64		

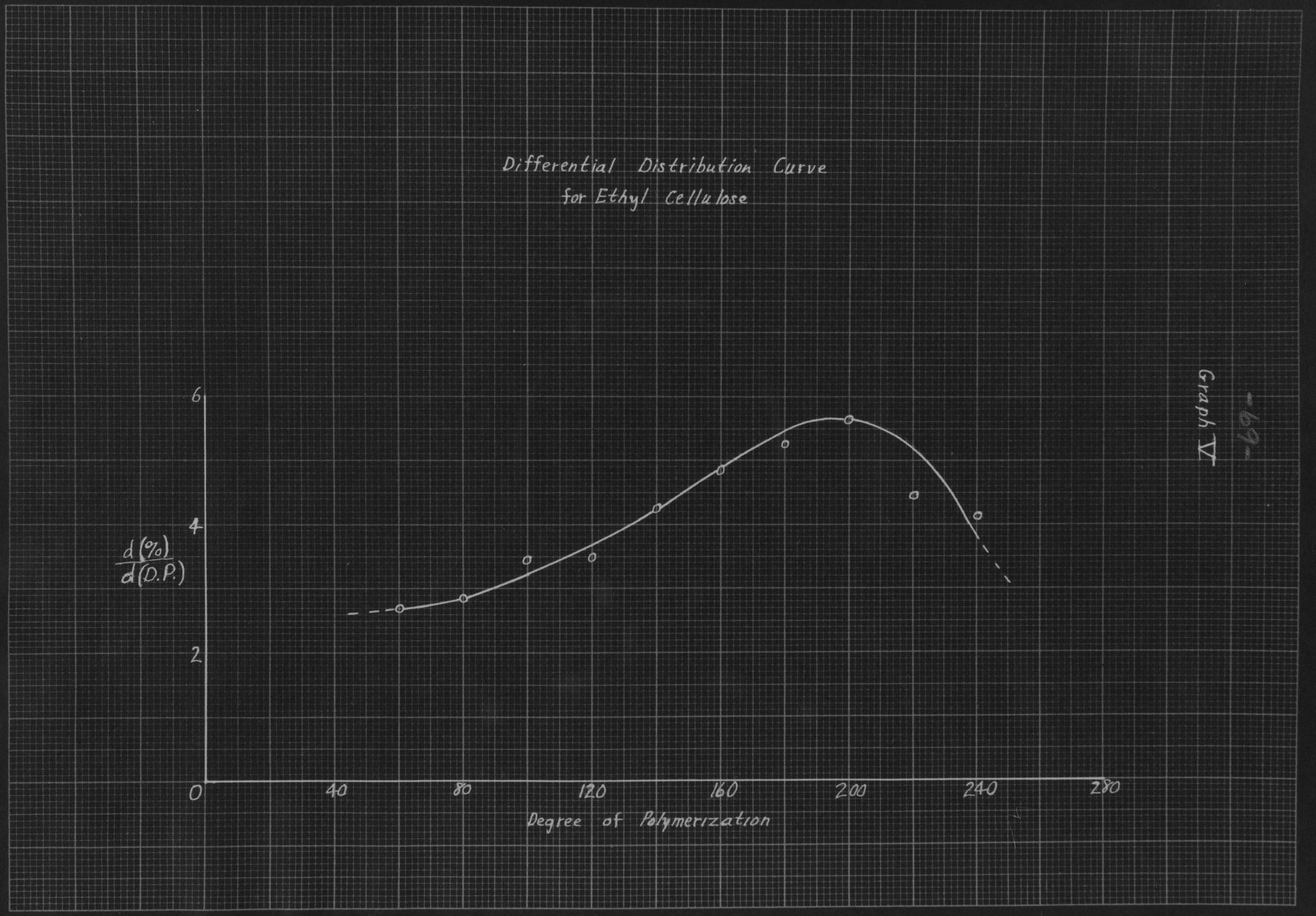

Integral Distribution Curve
for Ethyl Cellulose
Sample A o o
Sample B x x
Sample C • •
100
80
60
40
20
0
Percent Precipitate
40
80
120
160
200
240
280
Degree of Polymerization
Graph IV
-47-

the small chain particles could not have been in any supernatant liquid left with the precipitate.

Graph V, Differential Distribution Curve, page 69, was obtained by plotting the slope of the tangents to the curve of Graph IV against the degree of polymerization. To do this, tangents to the curve were drawn and the slope calculated from the mathematical relationship

$$\text{slope} = \frac{y - y_1}{x - x_1}.$$

According to Graph V, the majority of the ethyl cellulose chains have a degree of polymerization of about 200. Above this value the number of chains falls off rapidly while below this value the decline in number of chains is gradual.


Differential Distribution Curve
for Ethyl Cellulose
$\frac{d(\%)}{d(D.P.)}$
6
4
2
0
40
80
120
160
200
240
280
Degree of Polymerization

Graph V

CONCLUSIONS

1. A commercial grade of ethyl cellulose can be fractionated according to length of the chain, degree of polymerization, by the method worked out in this investigation. At the present time it is not known what effect dissolving the ethyl cellulose in 80% acetic acid and the subsequent treatments have had on the ethoxy content. It is possible for the degree of substitution to decrease from the first through the last fraction, but this is not considered likely in view of the distribution curve obtained.
2. It was possible from the relationships shown in Graph II to predict, within a reasonable degree of accuracy, the amount of precipitate which was shown in Graph III. Thus, it would be possible from Graphs II, III, and IV to determine the conditions for precipitation of ethyl cellulose of the desired degree of polymerization.

SUGGESTIONS FOR FUTURE STUDY

1. There are many other solvent-nonsolvent systems which might be investigated as possibilities for controlled fractionation of ethyl cellulose.
2. The benzene-heptane system could be studied again since a method for controlling the amount of liquid decanted has been used successfully.
3. A method for removing a very small first fraction, and with it the low molecular weight particles which lower the average degree of polymerization of the first fraction, would perhaps change the shape of the distribution curves.
4. A temperature differential greater than 10° C. would likely give harder precipitates, thus simplifying the fractionation procedure. When means of maintaining a temperature lower than 15° C. is available, this possibility should be investigated.
5. Any change in the ethoxy content in the series of fractions should also be determined.
6. Possibility of acetylation of free OH groups when acetic acid is used. should be investigated.

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