DIELECTRIC INVESTIGATIONS OF THE EFFECT OF PRECIPITANT ADDITION TO CELLULOSE NITRATE SOLUTIONS

by

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INTRODUCTION

In 1946[37][46] an extensive investigation of fractionation procedures for cellulose nitrate, cellulose acetate, and ethyl cellulose was initiated at Virginia Polytechnic Institute. The motivation was the need for a process which would yield sharp fractions of different degrees of polymerization, which were then to be used in ascertaining the effect of degree of polymolecularity distribution on the mechanical properties of films made from the cellulose derivatives.

It was found that, using the conventional method of fractional precipitation, a precise fractionation which would yield reproducible results could not be obtained. One of the difficulties which was most evident was that it was not possible to just reach the precipitation threshold. The first fraction which came down always contained too large a fraction of the total solute.

The investigators thought that this might be due to their inability to catch the exact endpoint, and that some type of mechanical endpoint indicator might solve the problem. An attempt to use dielectric constant measurements for this purpose was made. No success was evident on the first few trials and, due to the priority of other phases of the investigation, this work was discontinued.

However, it still seemed to be a plausible idea which had definitely not been investigated thoroughly. Since the state of knowledge concerning precipitation mechanisms of high polymer solutions is tenuous, the value of any successful results might be extensive.

The basic problem of this investigation can be stated as:

Can dielectric constant measurements be used in studying the effect of adding a precipitant to cellulose nitrate solutions?

HISTORICAL AND LITERATURE REVIEW

Cellulose Nitrate

Cellulose nitrate, which is synonymous with the erroneous term "nitrocellulose", is the oldest known derivative of cellulose. Though a number of cellulose-containing materials were nitrated previously, Schonbein[58] is generally credited with first nitrating cellulose in 1845. Its value in the production of military explosives was soon recognized, but it was not until the twentieth century that it was extensively applied to the manufacture of synthetic fibers, celluloid plastics, and lacquers. The first of these processes is practically extinct in the United States today, while the other two are important components of the chemical industry.

Cellulose can be nitrated to different degrees since there are three hydroxyl groups available per glucose unit. Therefore the mono-,di-, and tri-nitrates can theoretically be prepared. However the nitration proceeds with statistical haphazardness, and the ester groups will be distributed over all the chains. Only the average number of nitrate groups per glucose unit can be determined, and this may be any value up to the tri-nitrate, depending on the conditions of nitration.

However, nitration is an extremely rapid reaction[2], penetrating almost immediately to the internal portion of the

cellulose fiber. Therefore the nitration along the chains should be relatively homogeneous. This has been verified by experiment[27]. Cellulose nitrate can be generally described as being homogeneous with respect to nitrogen content and heterogeneous with respect to chain length. The latter property is inherent in cellulose and all its derivatives.

Solubility

The action of solvents on cellulose and its derivatives is probably the most important unit operation connected with the cellulose industries. Since cellulose itself has only a limited solubility, the more easily dispersed derivatives are usually employed whenever solution is necessary. Naturally, the theretical aspects of the solubility of these polymers have been of interestininvestigations for many years.

The solubility of cellulose nitrate depends upon a number of factors[50]: the nitrogen content, the degree of polymerization, the nature of the solvent, and transient conditions such as time and temperature. For example, the nitrogen content has a marked effect on the solubility. Esters[12] having nitrogen contents between 10.0% and 12.8% are soluble in ether-alcohol mixtures, while on either side of this range they are insoluble. The acetone solubility of the nitrates decreases with the nitrogen content until, at about the mono-nitrate, acetone is no longer a solvent[51].

Attempts to correlate the above variables with the solubility have been undertaken in the following general directions:

(1). Attempts to explain the markedly improved dissolving power of mixtures whose components are virtually non-solvents.

(2). Attempts to explain the viscosity changes of solutions on addition of non-solvents.

(3). Attempts to describe the state of the polymer in solution, and the mechanism of solution.

Baker[1], in attempting to explain the first of these phenomena for ether-alcohol mixtures, proposed that the actual solvent was a molecular complex of ether and alcohol. He based this on the fact that neither one of these liquids is a solvent alone, yet a mixture results in high solubility.

Esselen[17] studied the similar peculiarities of cellulose acetate solvent mixtures, such as alcohol-chloroform. Since the former is a non-solvent, yet improves the solvent power of the chloroform, he suggested that the alcohol was absorbed by the acetate. The part of the alcohol molecule attracted to the polymer would be the hydroxyl group, leaving the hydrocarbon radical projecting out into the solution. The chloroform is assumed to have a greater attraction for this form than for the original acetate.

Extensive experimentation with, and classification of, mixed liquids as solvents for cellulose derivatives were made[32], and it was shown that definite optimum solvent mixtures are the

rule rather than the exception.

Whiteby[56] introduced the concept that the chemical nature of the high polymer is also a factor. He found that the solubility characteristics of hydrocarbon polymers are almost exactly the reverse of those of cellulose esters. He made the very important observation that the reason for this is found in the different molecular polarity of the two types. The hydroxyl and ester groups impart a relatively high polarity to the molecules, as compared to the non-polar hydrocarbon chain. Whiteby's more detailed work on dielectric constants will be cited later.

Highfield[28] formulated the general theory of specific interaction of solvent molecules with certain portions of the polymer molecule having the same type of polarity. In the case of cellulose nitrate, a solvent having polar groups would be necessary to solvate the hydroxyl and nitrate groups, while the non-polar hydrocarbon part will require a non-polar solvent. The solvent power of ether-alcohol mixtures can be said to be due to the achievement of the proper polar-nonpolar ratio in the mixtures.

Viscosity changes with solvent composition changes, of ether-alcohol solutions of cellulose nitrate[24], were investigated, and it was found that a small change in solvent composition has, in certain cases, a marked effect on the viscosity. A study[35] of the change in viscosity with time, employing acetone solutions of cellulose nitrate, showed that there is a

rapid initial increase in viscosity, followed by a gradual decrease. From this it was proposed that the solvent was first absorbed by the solid, and the resulting gel gradually dispersed by the remaining liquid.

Upon addition of water to the acetone solution, the viscosity is sharply decreased. For a 5% solution of a sample containing 12.3% nitrogen, the minimum was reached when 11% water had been added. On further addition of water, the viscosity tended to increase again, until precipitation occured[6]. (See Figure I).

McBain[36], in attempting to explain the viscosity relationships and their changes with time and other conditions, deduced a solvation mechanism for the interaction of solvent and colloid. He stated that the colloid exists in solution as a neutral micelle, which becomes solvated to the point at which a sufficient degree of similarity to the solvent is reached. Changes in viscosity were considered to be due to aggregation of the micelles.

Hatschek[26] forcefully criticized this concept of aggregation, claiming that no experimental results warranted it. He maintained that high viscosity and even gelation could occur without aggregation, and even without the approach of particles to each other. This viewpoint became more popular later.

The minimum viscosity corresponding to a certain solvent mixture was considered to be indicative of the best possible

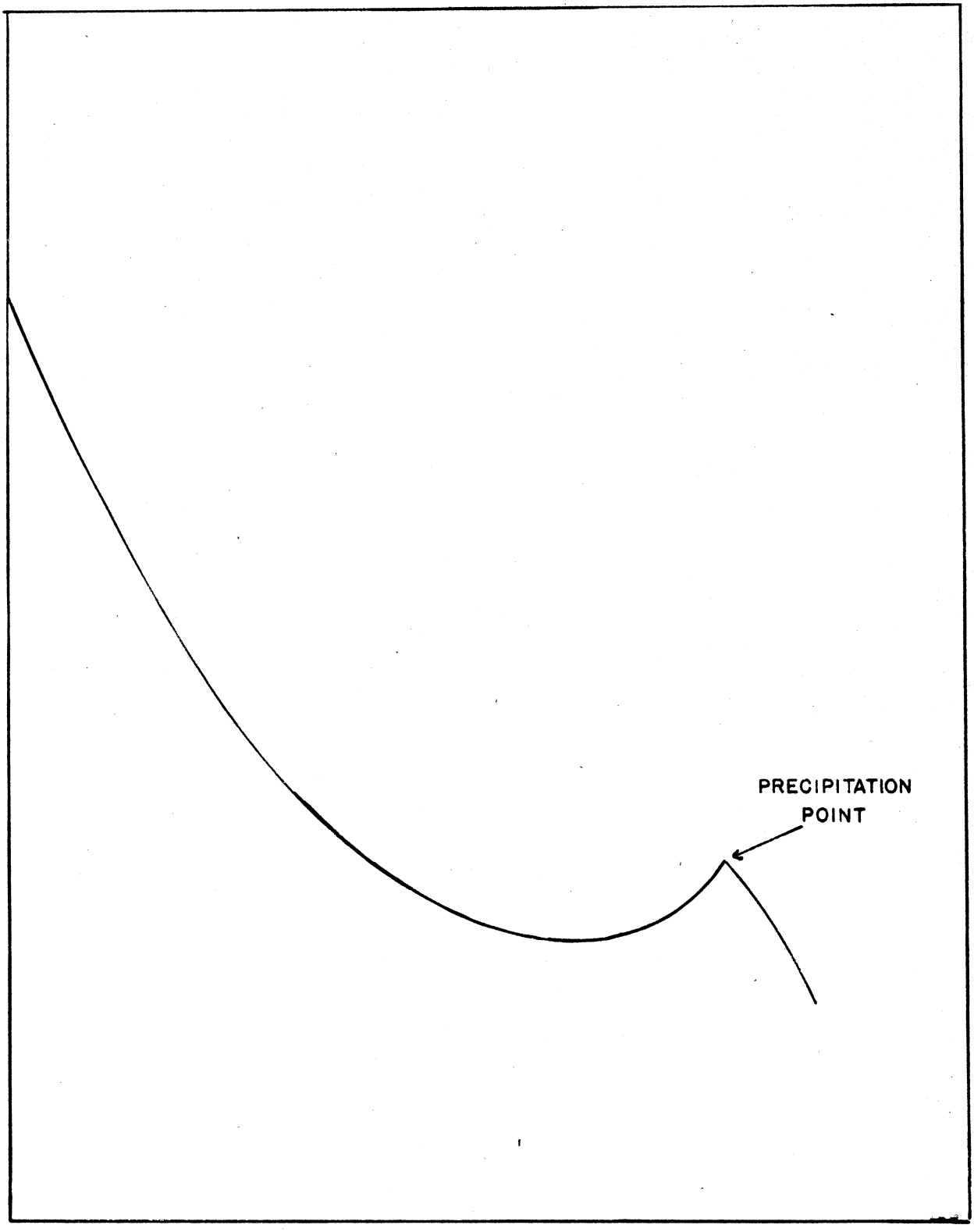


FIGURE I

A VISCOMETRIC PRECIPITATION TITRATION CURVE
(Cragg and Hammerschlag: Chem. Rev. 39 93 1946)

solution, for the particular system[33]. It was observed that the effect of a colloid upon a binary mixture of liquids is, in general, such that the shape of the viscosity-composition curve becomes exaggerated; any special feature of it becomes obvious[32].

Attempts to describe the state of solution have centered around the question: Is the polymer actually dispersed into molecules? Basing their theories upon the past experiences with soaps and other colloids[36], most investigators from 1920 to 1932 maintained that the polymers are only dispersed to a micelle, which was inherent in the original cellulose material.

Staudinger[52] was the main proponent of the molecular dispersion theory, and most modern experimental evidance seems to favor it. In the absence of complicating factors, complete dispersion is considered to be highly probable.

The process of interaction of polymers with solvents has been followed through[3], and can be separated into two steps:

(1). Swelling of the solute as it imbibes some of the solvent, with the formation of a gel.

(2). Dispersion of the resulting gel due to its similarity to the solvent phase.

The solution of a polymer therefore depends upon whether or not the forces holding the chains together can be overcome. The insolubility of cellulose can be explained on this basis, since the chains are held together by strong hydrogen bonds[34].

Cellulose derivatives are more easily dissolved since a

large percentage of the hydroxyl groups have been replaced, and the interchain attraction has been reduced.

Since viscosity changes could not successfully explain the phenomenon of increased or decreased solubility[56], investigators began to explain the changes as an effect of some other mechanism. The Highfield theory was evoked, plus the very descriptive experiment of Urech[54]:

A polymer of the highly polar molecule, acrylic acid, $(CH_2=CH\ COOH)_x$, was found to be soluble in water and formamide, both highly polar. If the polymer was converted into the less polar ester, $(CH_2 = CH\ COO\ C_2H_5)_x$, the product was now soluble in benzene and acetone, and was precipitated by water, ether and alcohol. The ester was converted to the tertiary alcohol, $\left[CH_2 = CHC(OH)(CH_3)_2\right]_x$ which, owing to the presence of the hydroxyl group, is more polar than the ester; the product was found to be moluble in alcohol but not in benzene. If the alcohol is now reduced to the hydrocarbon, $\left[CH_2 = CHCH(CH_3)_2\right]_x$, the product is soluble in benzene, and is precipitated by alcohol. This experiment is tabulated in Table I.

Whiteby[57] very definitely related solubility to the dielectric constant in an experiment with the stereoisomeric symmetrical dichlorethylenes. The cis- and trans-isomers differ markedly in dielectric constant, the latter having a value about twice that of the cis compound.

The two forms were first tested for their ability to

TABLE I

SOLVENTS AND PRECIPITANTS FOR RELATED

POLYMERS WITH DIFFERENT POLARITIES*

Polymer	Solvent	ε	Precipitants	ε
$(CH_2 = CHCOOH)_x$	H_2O Formamide	81	acetone ethanol	20.5 25.8
$[CH_2 = CHC(OH)(CH_3)_2]_x$	ethanol	25.8	benzene	2.28
$[CH_2 = CHCOOC_2H_5]_x$	acetone benzene	20.5 2.28	H_2O ethanol	81 25.8
$[CH_2 = CHCH(CH_3)_2]_x$	benzene	2.28	ethanol	25.8

* Urech; Zurich Thesis, (1927)
Cited by Whiteby in "Colloid Symp. Mono." Vol IV, (1926) p. 212

dissolve rubber. The cis compound proved to be a much better solvent. They were then used as precipitants for acetone solutions of a cellulose acetate. The cis isomer proved to be the better precipitant: 10 cc. of a 2.5% solution of cellulose acetate in acetone required about 14 cc. of the cis, and about 24 cc. of the trans isomer, to produce turbidity.

This and the preceding experiment indicate very strongly that the polar natures of the components making up a high polymer solution are decisive factors in the extent of solubility.

Dobry[11] studied the effect of various polar diluents upon cellulose derivative solutions, and from the results deduced that the particle in solution was definitely a colloidal molecule, and not a micelle. However, this investigator reported that an extensive solvation effect was not indicated.

Glikman[25] dissolved the less polar benzyl cellulose in benzene and precipitated it with ethyl alcohol, noting the characteristic viscosity changes before precipitation. For the precipitation mechanism he offered the explanation that the decrease in the concentration of non-polar constituents of the solvent results in the forces between the particles becoming greater than those between particle and solvent, and precipitation occurs. An increase in temperature reverses this effect.

An intensive study of the process of solution of cellulose derivative polymers was reported by Watano and Inoue[55]. Cellulose nitrate samples of varying degrees of substitution were

dissolved in mixtures of acetone and other liquids. The solubility of the nitrate, and the amount of acetone sorbed by the nitrate, were determined. It was claimed that the results show that acetone and the nitrate radical are principally concerned in the mechanism of solution. The sorption mole ratios of acetone to nitrate were given for benzine- and benzene-acetone mixtures, but, unfortunately, not for water-acetone. Mathematical expressions for the dissolving power of solvent mixtures were offered, but the lack of clearly defined variables prohibits the use of these formulas.

Solvent Classification

Initially, solvents were classified directly on a basis of their resistance toward the effect of a precipitant. This is known, industrially, as the dilution ratio[5]. A solution is titrated with a precipitant until visible turbidity appears, and the amount of precipitant needed is a measure of the particular solvent's dilution ratio, as compared to other solvents. This method is theoretically unsound, according to Highfield's theory, but has been widely used because of its simplicity[7].

If a solvent's effect depends upon its polar non-polar nature, it should be possible to correlate dissolving power with some specific property of a molecule's polarity, such as the dipole moment, or dielectric constant. Investigation showed

that solvents for cellulose nitrate all have fairly large dipole moments[47], and that the values stay within a certain region. On the other hand, chloroform, which is beneath this range, does not dissolve the cellulose nitrate, but is a solvent for the less polar cellulose acetate[48].

The use of the function $\frac{\mu^2}{\epsilon}$, where μ was the dipole moment and ϵ the dielectric constant, was proposed as an indicator of a liquid's dissolving or precipitating power[42]. For a homologous series of alcohols, the precipitation effect increased with the $\frac{\mu^2}{\epsilon}$ value. A plot of the reciprocal of the amount of alcohol needed to precipitate against the reciprocal of the dielectric constant, showed a direct linear increase[14].

However, this function could not be successfully used for any variety of liquids, and it was obvious that other factors must be considered. Papkov[43] suggested that, since it was necessary for the liquid to penetrate the solid, before solution could occur, the surface tension of the liquid might have to be considered. Moll[38][39] experimentally determined ϵ, μ, and the surface tension σ, for a large assortment of liquids and plotted $\frac{\mu^2}{\epsilon}$ against σ. He found, with the liberal use of imagination, that "good solvents" could be found in a certain section of the graph. Around this group was an area containing "poor solvents", and non-solvents appeared throughout the rest of the plot. The major discrepancy which appeared in this analysis was that aromatic and aliphatic liquids had to be graphed separately, thus

indicating that there are other factors which must be taken into account[40].

Another method[53] using these three properties was to combine them in a function: $\frac{\mu^2}{\epsilon\sigma}$. It was found that in many cases the values for cellulose nitrate solvents fall within a certain definite range. The effect of the degree of substitution on this factor was also studied, and it was found that the critical solution range is displaced to higher values of the function, with increasing nitrate content.

Dielectric Investigations

Measurement of the dielectric constants of acetone and acetone-hexane solutions of cellulose nitrate were made by Lee and Sakurada[30]. It was found that in acetone the dielectric constant is not appreciably changed when the concentration of solute is altered. However, in the binary solvent, a change in concentration does effect the dielectric constant. For a highly nitrated solute, the specific polarization decreases with increasing concentration, while the effect is reversed for a low-nitrate solute. The investigators concluded from this that a very high degree of solvation is present in polar solvents[31].

The above investigation is questionable as far as its conclusions are concerned, since the important phonomenon of dielectric relaxation is overlooked. This idea was introduced

by Debye[9] to explain the anomalous dispersion of polar molecules at high frequencies. Under the influence of an alternating field, polar molecules tend to align themselves with the field. However, if the frequency is too high, the molecules do not have sufficient time to orient themselves. This would result in an electrically discontinuous region of randomly arranged molecules. This is known as relaxation.

From the description of this relaxation phenomenon, it is evident that the size of the unit particle should be of prime importance. The larger the particle, the lower the frequency needed to cause it to relax. Thus, substances in the colloidal state should be revealing guinea pigs for this type of study.

Errera[16] determined the dielectric constants of many colloidal solutions and found that in most cases the value remains essentially the same as that for the solvent alone. But for sols of V_2O_5 a markedly different set of results was obtained. The dielectric constant was not only exceptionally high, but was not constant. A definite decrease with increasing frequency was found. Errera interpreted this on the basis of the relaxation theory. V_2O_5 was known to have a rod-like micelle structure, which would be definitely susceptible to relaxation, and additional variables which influence the dielectric constant (Concentration, temperature, and age of solution) could all be conceived to affect the size of the particles.

Mathematical relationships based upon classical mechanisms have been developed for the relaxation time, and satisfactory agreement with experimental data has been found, for many large molecules[44]. However, when polymers were experimented upon, they were always either in the solid form or mixed with plasticizers, never in solution[20][29]. Research on relaxation of cellulose nitrate in acetone solution is currently being done at Virginia Polytechnic Institute, and incomplete results seem to follow the general theoretical possibilities.

Turbidity Investigations

Gehman and Field[21] first applied light-scattering measurements to an investigation of the state of colloidal rubber in solution. They made the significant observation that the experimental results were similar to what would be expected from units of pure liquid in solution, instead of colloidal particles. In a later work[22], they studied the changes caused by the addition of precipitants to rubber solutions. A large increase in the turbidity of the solution appeared long before precipitation. To explain this and the corresponding viscosity decrease, a rather improbable mechanism of increased aggregation, followed by de-aggregation and finally re-aggregation, was proposed.

Debye[10] offered the possibility that the measurement light-scattering in solutions may be used to determine the

molecular weights of high polymers. Experimental data has shown partial agreement with theory, but many discrepancies are still unexplained.

The mechanism of coagulation of rubber by precipitants was investigated for turbidity effect, by means similar to those of Gehman and Field[22]. Confirmatory results of increasing turbidity long before precipitation were acheived, but the later investigators assumed a more logical explanation. The change was considered to be caused by two factors[18]:

(1). Shrinkage of the swollen polymer molecules in solution.

(2). Selective absorption of mixed solvent by the polymer.

EXPERIMENTAL PROCEDURE

Object and Plan of the Investigation

All previous dielectric investigation[30] of polymer solutions have been run on static mixtures. Readings were taken only for certain set concentrations of solute and solvent, and no attempt was made to trace the effect of adding a precipitant. However, this was not the case with the viscosity and turbidity investigations. Here the experimental data wererecorded while the solvent composition was being changed, and the effect produced on the property being measured was used to infer the mechanisms of solution and precipitation.

Since it is highly probable that the dielectric constant of a solution is a characteristic function of the particles in solution, it was planned to apply the viscosity and turbidity techniques to the precipitation mechanism of cellulose nitrate solutions. Dielectric constant determinations were to be made under dynamic conditions, where the solvent composition was being gradually altered up to the past the incipient precipitation point. Essentially, the procedure studied was the same as the dilution ratio titration[7].

A cellulose nitrate solution was titrated with a precipitant. Small quantities were added at a time, and the mixture was agitated after each addition, to restore equilibrium.

The dielectric constant of the mixture was taken after each composition change.

The overall object was to study the precipitation effect, but since no previous work of this kind had ever been reported the prerequisite short-range aim was to determine whether or not any reproducible, useful results could be obtained. The conditions under which the best results would appear, and the variables which had to be controlled, were fundamental questions to be answered. It was necessary to start with the most general experiment, and handle each procedural defect as it appeared. As it turned out, the preliminary results channeled the investigation toward a specific problem, but many other possible research lines seem to be indicated.

Materials

High D. P. cellulose nitrate-Lot 1379, RS type 600-1000 seconds. Obtained from Hercules Powder Company, Parlin, New Jersey, Nitrogen content 12.10%

Low D. P. cellulose nitrate-Lot 6226, RS type 1/2-second. Obtained from Hercules Powder Company, Parlin, New Jersey. Nitrogen content 12.00%

Acetone (C.P.)-Obtained from Comercial Solvents Corporation, Peoria, Illinois.

n-Heptane (commercial grade)-Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma.

(Materials used in preparation of the apparatus calibration curve are described under Calibration.)

Apparatus

A method of measuring dielectric constants of liquids, both rapid and simple, and applicable over a wide range, was needed. An instrument meeting these requirements had been described by Fischer[19], and the apparatus used in this work was essentially a duplicate of his. Most of the changes from the original design were concessions to the availability of the parts.

Since the dielectric constant is by definition a ratio of capacitances, it follows that measurements depend upon a determination of electrical capacitances. The instrument makes use of a modified resonance method, for this purpose. Use was made of a novel high-frequency resonance detector, which has been used in commercial radio receivers for a number of years[4]. Known as an electron ray, or more popularly, "magic eye" tube, it visually indicates the resonance condition for an oscillating circuit. A target electrode which is visible to the operator is coated with a fluorescent material. A stream of electrons is directed at the target; it causes a bright green fluorescence on striking. In the path of the electrons there is a control electrode. If the latter has a potential which will repel the electrons, they will be deflected around it. The result will be a shadow of the control electrode appearing on the screen. As the control potential is changed, the shadow will be altered, and the tube is designed to indicate resonance when the shadow angle is at a minimum. However, as soon as resonance is reached, any slight additional

change causes the shadow eye to spring open immediately, and this is usually the reference point used.

A circuit diagram is given in Figure II. A quartz crystal controls the frequency of the circuit, and the electron ray tube is placed where the operator can see the fluorescent screen. The tuning part of the circuit is the variable condenser in parallel with the inductance coil inside which the liquid is placed.

The circuit oscillates whenever the following condition is satisfied:

$$f = \frac{1}{2\pi\sqrt{LC}}$$

where:

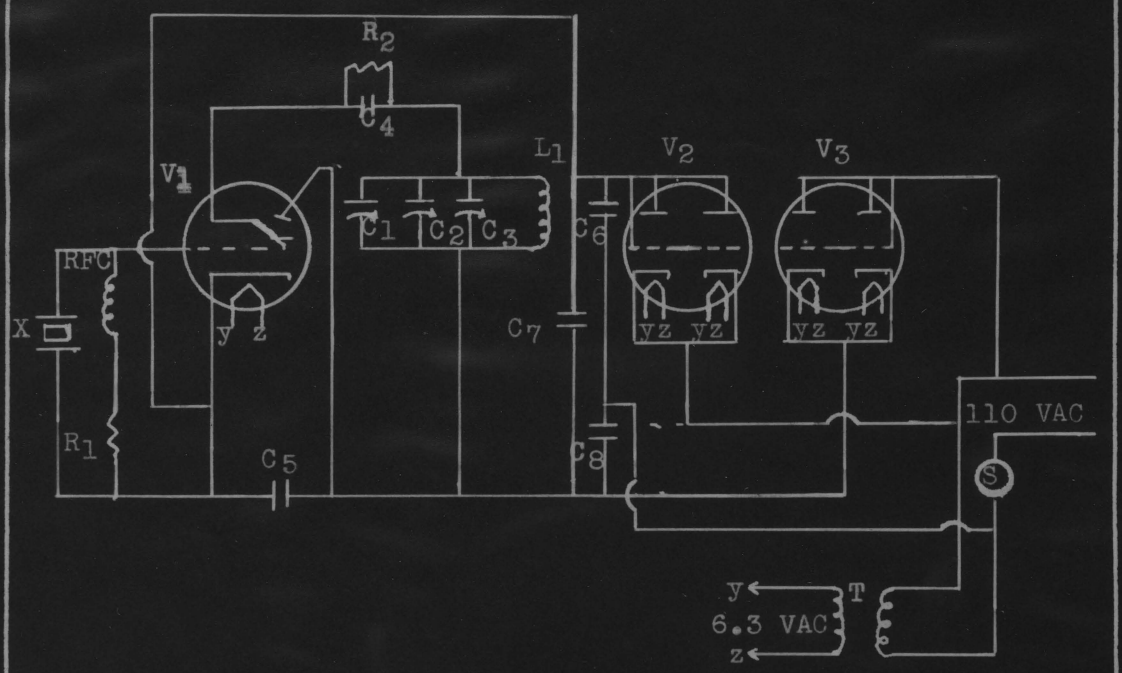
f = crystal frequency

L = inductance

C = capacitance

Since the frequency is fixed in all cases by the crystal, a change in either L or C will necessitate a proportional change in the other variable to re-establish resonance. In these measurements, the inductance of the coil with the liquid within it is actually measured by observing how much the capacitance must be changed. This measurement is then related empirically to the dielectric constant by means of a calibration curve prepared from a series of compounds with known dielectric constants.

Since fairly large volumes were to be used, the test-tube



R_1. 40,000-ohm resistor
R_2. 150,000-ohm resistor
T. Transformer.
S. Single-pole, single-throw switch
X. Quartz oscillating crystal, 3503.1 kilocycles
RFC. Radio frequency choke
V_1. 6E5 electron-ray tube
V_2, V_3. 6N7 adapted rectifier tubes
C_1. Single plate variable condenser
C_2, C_3. Small trimmer variable condensers
C_4. 0.001-mfd. fixed condenser
C_5. 0.01-mfd. fixed condenser
C_6, C_7, C_8. 16-mfd. electrolytic condensers, 450 volt
L_1. 44 turns of wire wound on lower portion of 7/8" test tube

FIGURE II

CIRCUIT DIAGRAM OF DIELECTRIC CONSTANT

MEASUREMENT INSTRUMENT

on which the coil was wound was supplemented by sealing a bulb-shaped reservior to the top of the tube. Volumes up to 375 cc. could then be handled.

To insure accurate results, it was necessary that the measuring coil be always in the exact same place in the circuit. Yet the tube had to be removed for cleaning after each run. To avoid disturbing any wires, the tube was connected to the rest of the set through two banana plug sockets in the side of the chassis. The tube was set in a small wooden block with a piece of polystyrene attached to the side. The male parts of the banana plugs were set in the polystyrene, and the leads to the coil form passed through the wood. The tube and coil were fixed rigidly with polystyrene glue.

This arrangement allowed the removal of the tube simply by unplugging the block from the side of the chassis, and it could be returned without disturbing any flexible wiring.

A burette for introducing liquid, and a stirrer, were set above the tube and could be employed without disturbing the electrical components.

Measurements could be made simply by turning the condenser vernier dial until the electron-ray tube indicated resonance. The dial reading was then converted to the dielectric constant through a calibration curve. The calibration of the apparatus will be described in the next section.

Calibration of Apparatus

Since a calibration curve over the entire range of 0 to 80 was desired, the following standardizing liquids were used:

(1). Distilled water, which was treated with a small amount of $KMnO_4$ and re-distilled.

(2). n-amyl alcohol (C.P.), which was distilled and kept in a desiccator.

(3). Benzene (C.P.), which was distilled and kept in a desiccator.

(4). Absolute ethanol, which was prepared by refluxing 99% ethanol for 24 hours with CaO, distilling and re-distilling the condensate[41]. The alcohol was used for measurement no later than one hour after preparation.

(5). 50% ethanol - 50% water (by weight), which was made up and used within 30 minutes.

By means of a trimmer/tuning condenser, the apparatus was set at 0 reading for air, before each run.

A preliminary run was first made to discover the minimum quantity of liquid which could be used. It was found that the readings changed with volume up to 75 cc. of liquid, and then remained constant. In all runs, the volume was kept about this figure. Furthermore, a criterion of five minutes of constant reading was established to indicate when equilibrium had been reached. The calibration data are given in Table II, and

plotted in Figure III.

TABLE II

CALIBRATION DATA FOR DIELECTRIC

CONSTANT APPARATUS, (Temperature = 25°C)

Standards	Dial Reading	ϵ *
Air	(set^0 before running)	1
Benzene	6.9	2.28
n-amyl alcohol	32.3	13.80
Absolute Ethanol	46.5	23.80
50% ethanol 50% H_2O	63.5	48.00
Water	77.9	78

* Int. Crit. Tables, Vol. VI

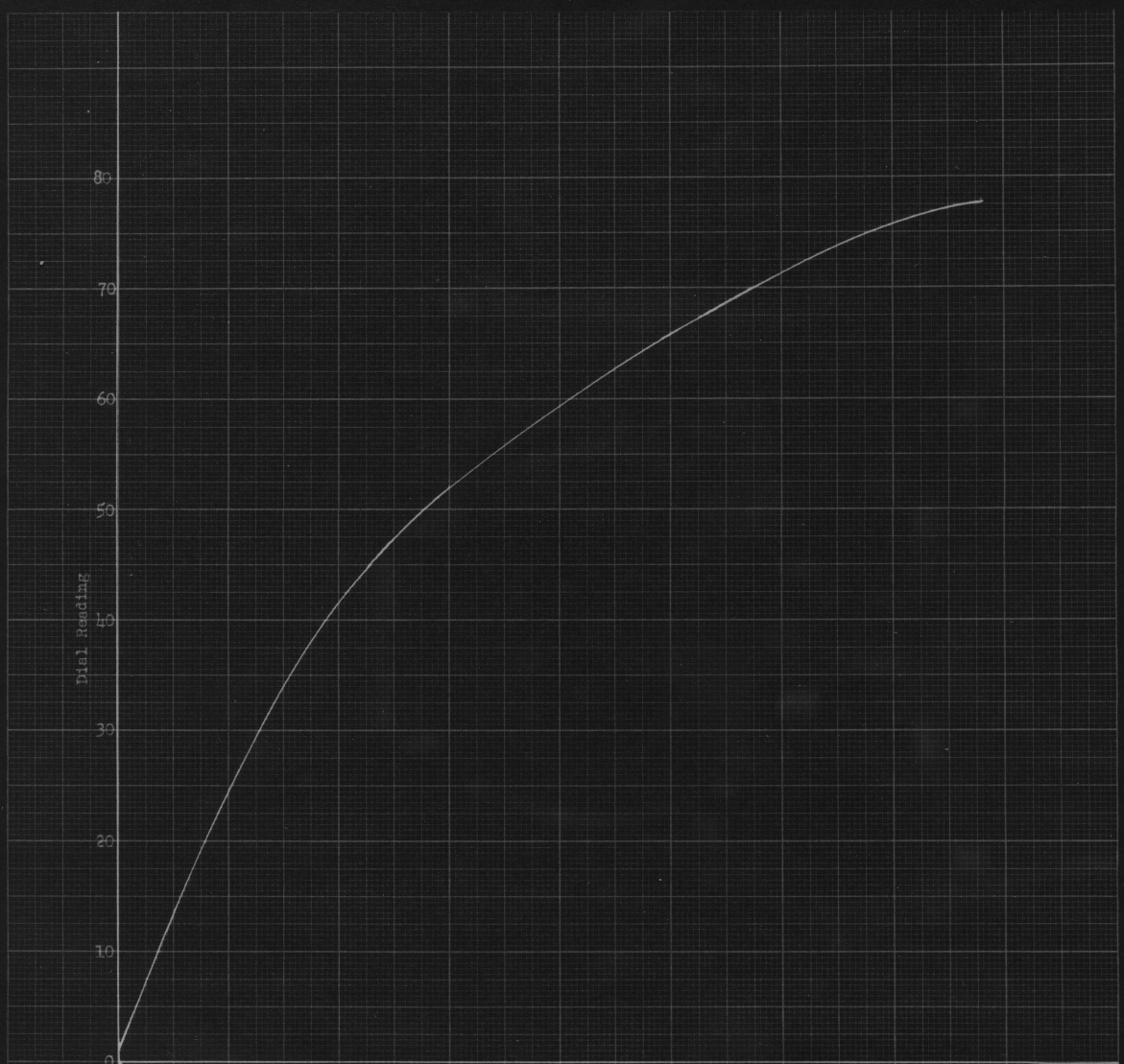


FIGURE III

CALIBRATION CURVE FOR DIELECTRIC CONSTANT INSTRUMENT (TEMP. 25°C.)

Dielectric Measurements

Water as a Preciptant

Series (1)

The first series of runs was made to determine the blank curve: the dielectric constant values for acetone-water binary mixtures. 70 grams of acetone were placed in the tube and a reading was taken. Water was added from the burette in 1 cc. portions, the solution stirred, and a reading taken after each addition. The stirrer had to be removed before the reading could be taken. The average values for four such determinations are shown in Table III.

To check the purity of the acetone, some of it was dried over CaCl for 24 hours, and then distilled[45]. The distillate was used for a check run; no appreciable difference from the runs made with stock acetone was found.

Series (2)

One gram of cellulose nitrate from the commercial stock, having an average DP of 420, was dried for 24 hours, dissolved in 99 grams of acetone, and the solution was titrated with 1 cc portions of water. Readings were taken for each titration after stirring. No reproducible smooth curves could be drawn for the data. The only coincident result noticeable was a sharp rise just at the precipitation point.

TABLE III

VALUES FOR ACETONE-WATER MIXTURES
(70 g. of Acetone)

cc. HOH added	% Acetone	Reading	ϵ
0	100	41.4	19.8
2	97.3	43.2	21.1
4	94.7	44.8	22.5
6	92.2	46.3	23.8
8	89.8	47.5	25.0
10	87.6	48.7	26.2
12	85.4	49.6	27.2
14	83.	50.6	28.6
16	81.4	51.9	30.1
18	79.6	52.6	31.0
20	77.8	53.5	32.2
22	76.1	54.1	32.9
24	74.5	54.8	33.8
26	72.9	55.4	34.8
28	71.5	56.1	35.7
30	70.1	56.6	36.5
35	66.7	57.9	38.4
40	63.7	58.8	40.4

Series (3)

The concentration of cellulose nitrate in solution was changed, and the above procedure was duplicated. Concentrations ranging from 0.3% to 5% were tried, but no consistent results could ever be found. It was noticed that an increase in concentration increased the dielectric readings somewhat.

Series (4)

The effect of concentration on the dielectric constant of cellulose nitrate in acetone solutions was investigated. Solutions of different concentrations were made and tested. The results are shown in Table III.

From the previous runs it was evident the solutions would have to be prepared more carefully, in order to eliminate a number of variables which were affecting the results.

Since the stock cellulose nitrate is kept wet with alcohol, and usually has other impurities in it, a method of purification was established: The cellulose nitrate was dissolved in acetone and a small amount of water was added to lower the viscosity. The solution was then poured into a large excess of water to precipitate out the nitrate. The latter was separated by filtration, and washed a number of times with water. It was then put in an aluminum can and dried at 55°C for 24 hours. After this, it was placed in a desiccator and kept at a temperature of 15°C. Before being used, it was placed in a weighing bottle and dried for one hour at 110°C.

TABLE III

DIELECTRIC CONSTANTS FOR CELLULOSE NITRATE SOLUTIONS OF DIFFERENT CONCENTRATIONS

Concentration of Cellulose Nitrate	ϵ
2%	20.3
3%	20.3
5%	20.4
6%	20.7
8%	20.7
9%	20.8
10%	20.1

Series (5)

Using the above purification procedure, a set of 1% and 2% solutions was run. While the results showed fair duplication, the readings stayed just above the base binary curve all the way, and there was no significant effect noticed in any case.

Series (6)

Some of the purified cellulose nitrate was dried at 110°C for 3 hours, in an attempt to insure the removal of all water. 1% solutions of this material were made up and run, but no improvement was found.

Series (7)

A control run was made on the effect of the length of time that the acetone solution was allowed to stand before using. A set of 1.5% solutions was run, no more than one hour after the nitrate went into solution. Another set of 1.5% solutions was let stand 24 hours before using.

The first set gave erratic, non-reproducible curves with a definite effect in the vicinity of the precipitation point. This is shown in Figure IV.

The next effect studied was that of varying degree of polymerization.

Series (8)

A stock cellulose nitrate having an average D.P. of 63 was thoroughly dried and used in making up 1.5% solutions in acetone.

All solutions were let stand for 24 hours, and were then titrated. The dielectric constant changes were noted. No significant effect was noticed, though the reproducibility was good.

A cellulose nitrate fraction prepared by B. P. Rouse[46], having an average D.P. of 75, was tested in a similar manner. Again there was no significant effect.

Series (9)

The 75 D.P. material was run again, but this time in 5% solutions, (3.68 g. cellulose nitrate to 70 g. acetone). The results were markedly different from all previous runs.

Another fraction was obtained, which had an average D.P. of 32, and 5% solutions were run. The results were again distinctive.

The stock cellulose nitrate (D.P. 63) was dried but not purified, and used to make up 5% solutions. But when this set was run, the readings once again followed the base line, with the only discontinuity at the precipitation point.

Another fraction, with an average D.P. of 140, was run in a similar fashion, and once again the results were distinctive. However, the curve lost its linearity.

A new fraction of 172 D.P. was made by dissolving and fractionally precipitating the 140 fraction. This was dried thoroughly, and run. The results showed a change in trend, but were still conclusive.

The composite results of this series are plotted in Figure V.

Heptane as a Precipitant

Series (1)

An acetone-heptane base curve was determined as in the section on acetone-water.

Data for this series are presented in Table IV. The relationship was not quite linear, showing a slight curve. (See Figure VI).

Series (2)

1.5% solutions of purified cellulose nitrate, D.P. (420), in acetone were titrated with heptane, with the dielectric constant being measured after each addition of heptane. The results are pictured in Figure VI. No discontinutity was ever found at the precipitation point, even when very small quantities of water were used in titrating.

Two runs similar to the above ones were made for the express purpose of determining how much effect the loss of volatile constituents during the experiment had on the results. The stirrer was sealed into the cell by the use of a mercury sealing unit, and the burette tip was fitted tightly into the sealing cork. It had been previously noted that the difference in readings produced by leaving the stirrer in was, at low values, never more than 0.1 of a dial division. The runs were made neglecting the effect of the stirrer. The results were within the average of the previous runs; this indicated that the effect of

volatility was negligible.

TABLE IV

DIELECTRIC CONSTANT VALUES FOR ACETONE-HEPTANE MIXTURES
(70 g. Acetone)

cc Heptane added	% Acetone	ϵ
0	100	19.9
10	91.1	17.9
20	83.7	16.2
30	77.4	14.8
40	72.0	13.6
50	67.3	12.8
60	63.2	12.0
70	59.5	11.2
80	56.3	10.7
90	53.3	10.0
100	50.7	9.6
110	48.3	9.1
120	46.2	8.8
130	44.2	8.4
140	42.4	8.1
150	40.7	7.8

RESULTS

The prime result has been the development of an experimental procedure for producing a definite dielectric effect when water is added to an acetone solution of cellulose nitrate. This effect depends not only on the purity, dryness and concentration of the cellulose nitrate, but also on the average degree of polymerization. This last dependancy is shown in Figure V, and its theoretical aspects will be discussed in the next section.

The discontinuity at the precipitation region is a general effect, not depending on such extreme conditions.

The data for the acetone-water binary blank (Table III), were used to make up an empirical equation describing the dielectric constant as a function of the water added. Using the method of averages[8], a straight line relationship was developed:

$$\epsilon = .57x + 19.4$$

This equation will be used in the mathematical interpretation offered in the next section.

The results using heptane as a precipitant were generally inconclusive. However the definite absence of a discontinuity in the precipitation region may be of some negative value.

An interesting result of the combined investigation is found on examining the dielectric constant readings at the precipitation point for both precipitants, when other variables were held

constant. Using the same concentration and D.P. (420), the reading for water at precipitation was about 30, while for heptane it was 12. The mean of these two values is 21, which is approximately the initial reading of the original solution. A gradient of 9 dielectric units seems to be the necessary condition for precipitation.

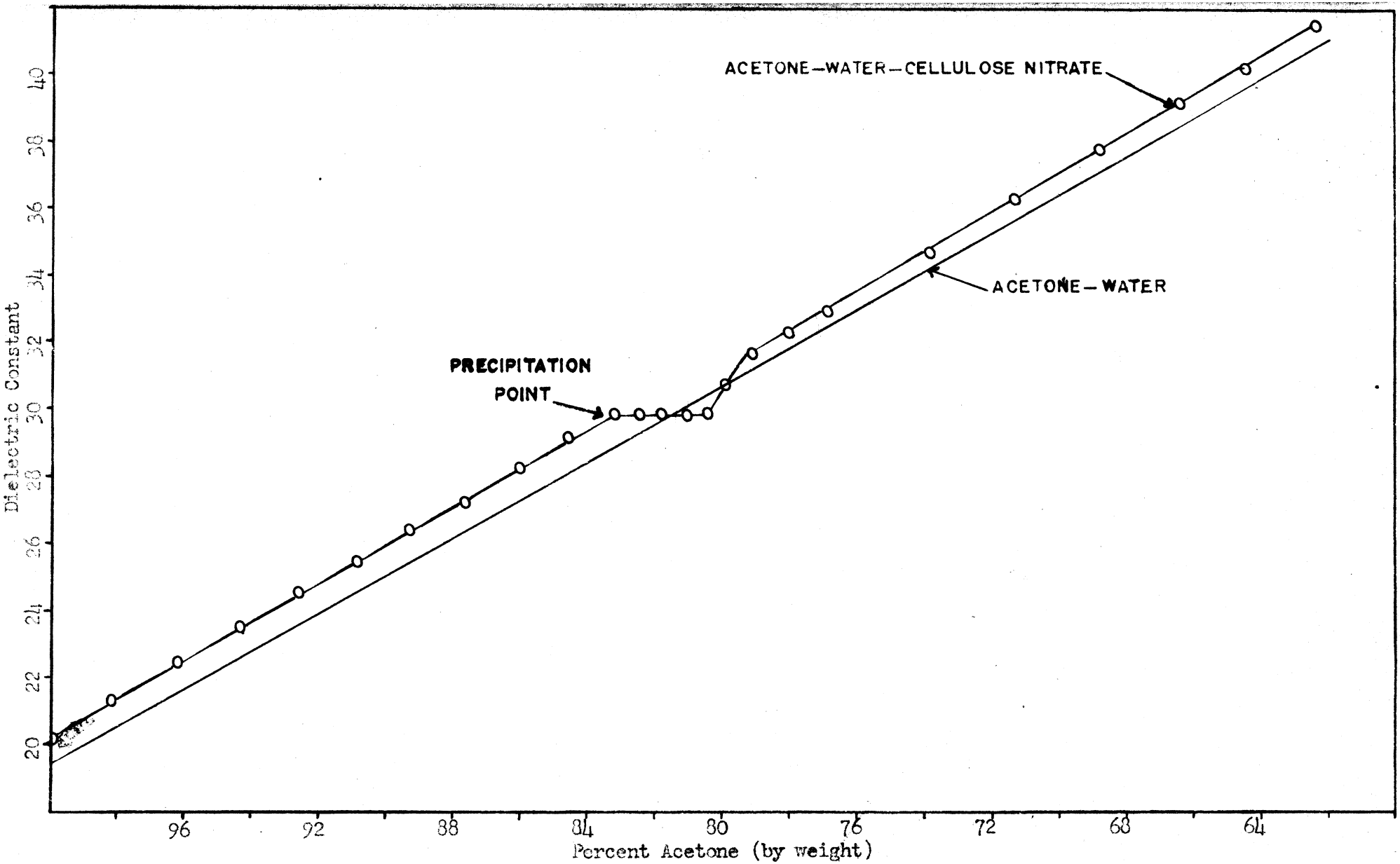


FIGURE IV

DIELECTRIC CONSTANT CHANGES ON ADDING WATER TO A 1.5% CELLULOSE NITRATE (D.P.420) SOLUTION IN ACETONE

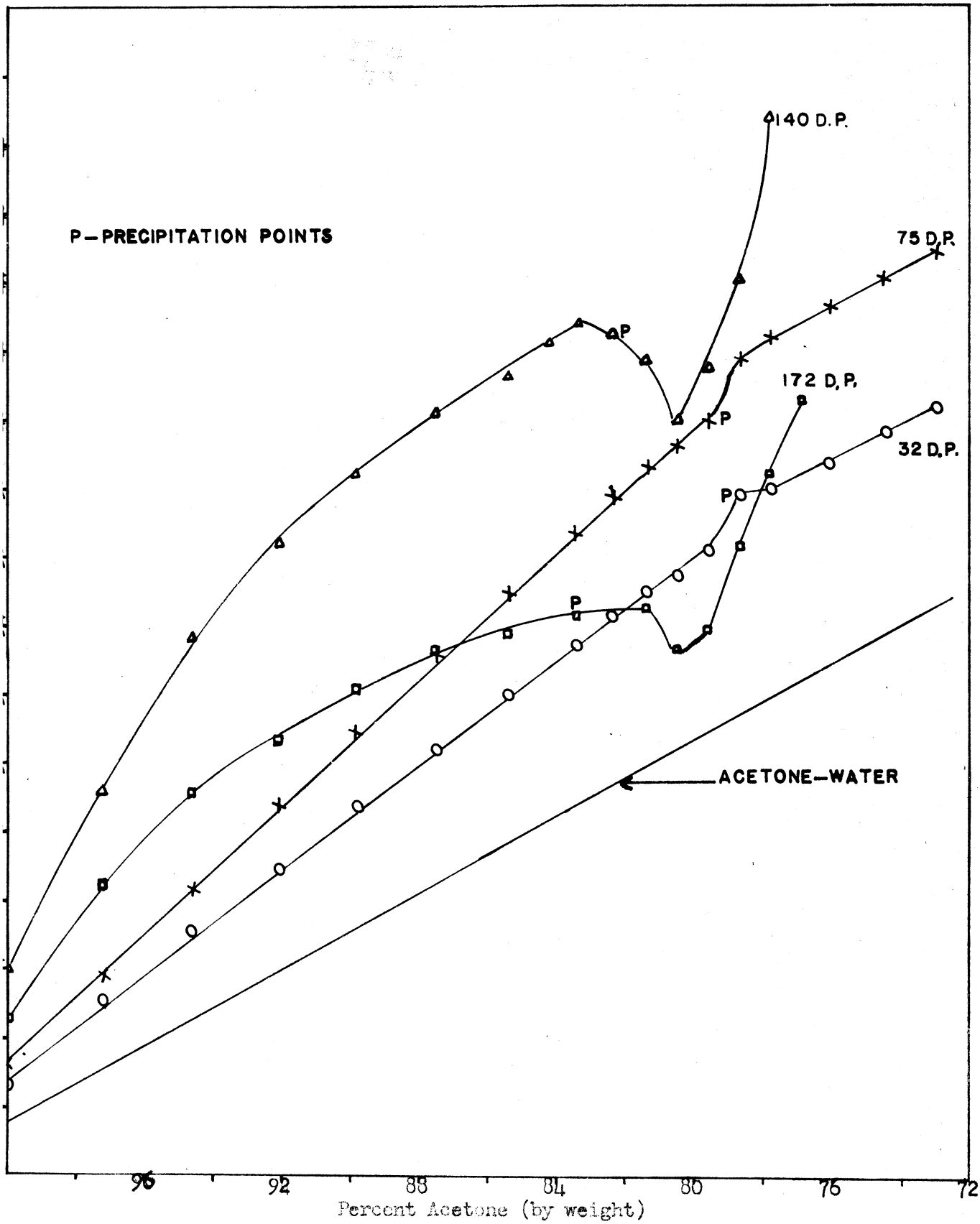


FIGURE V

THE EFFECT OF AVERAGE D.P. ON THE DIELECTRIC CONSTANT CHANGES OF ACETONE-WATER-CELLULOSE NITRATE SYSTEMS
(5% Cellulose nitrate)

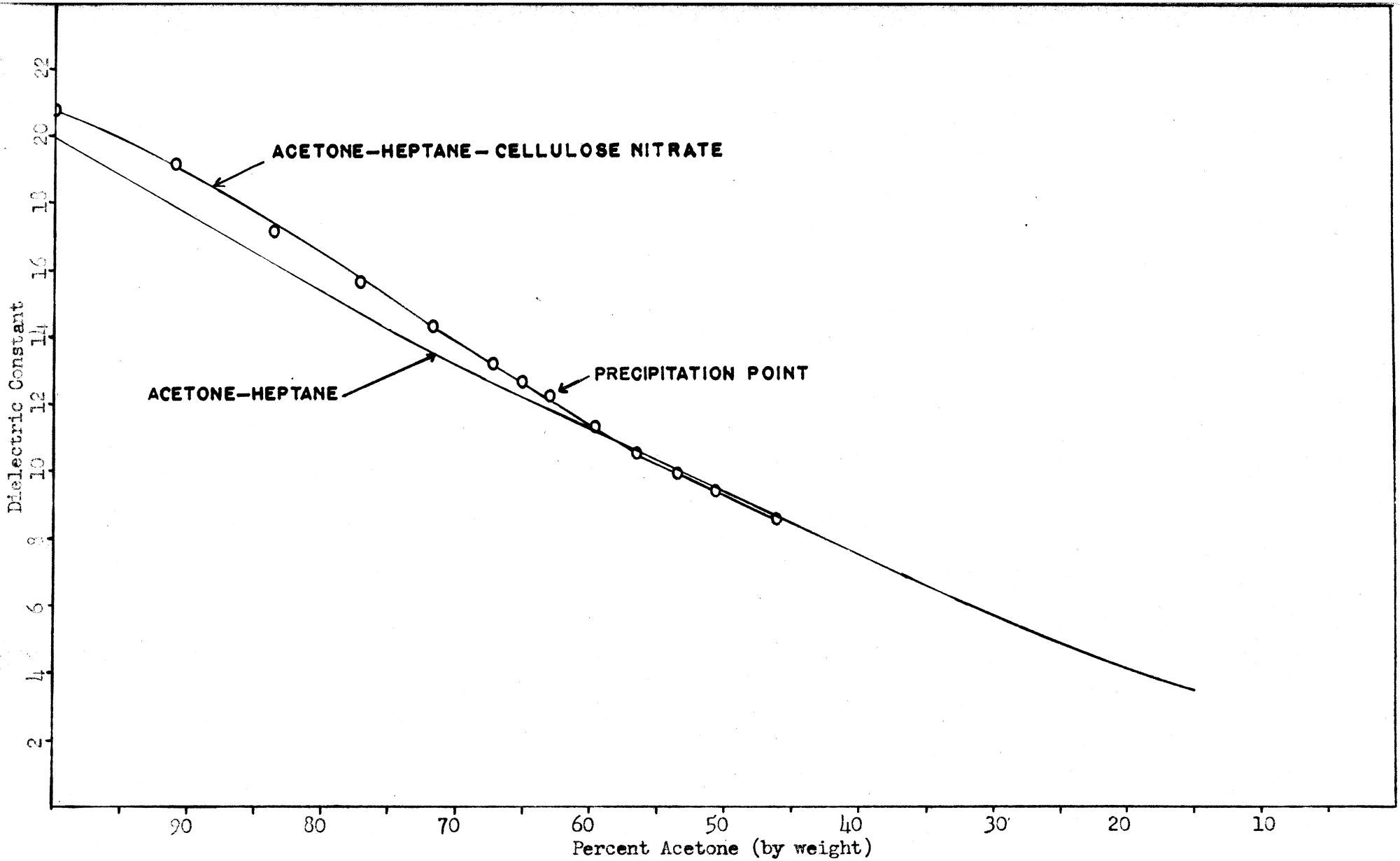


FIGURE VI

DIELECTRIC CONSTANT CHANGES ON ADDING HEPTANE TO A 1.5% CELLULOSE NITRATE (D.P.420) SOLUTION IN ACETONE

DISCUSSION OF RESULTS

The effect observed appears to be completely operative only under certain specific conditions. Since the frequency used for measuring is fixed the relaxation effect must be considered as a possible complication in all cases.

The results obtained here check with those of Lee and Sakurada[30] for the case of chainging concentration of high D. P. material. The fact that the dielectric constants of the solutions remain practically the same as that of pure acetone seems to be evidence favoring the possibility that relaxation is taking place. The high frequency used increases this possibility. Unpublished data by Testerman, working with the same material, indicates tentatively that the relaxation frequency is much lower than the 3503 Kc used.

This explanation seems even more plausible when the results using low D. P. material are studied. The increase in the dielectric constant throughout the run would seem to be explained only by some additional polar component responding to the field. Since the only alteration was in the D. P., the relaxation conclusion seems logical.

Since the material used was, in all cases, a heterogeneous mixture of chain lengths, the distribution of these lengths would also be important. Even if the average D. P. of the material was low, the presence of a large number of long chains

would greatly weaken the dielectric effect. This may explain the inconsistency found when the low D. P. stock was run. A distribution determination of this material showed a very wide range of chain lengths present, in spite of the average D1P. of 63.

Partial relaxation is probably the case for the 140 and 172 D.P. fractions. The former still had enough material which could keep up with the field to maintain the dielectric values high, while the latter gave evidence of proportionally greater relaxation, since the over-all values were low.

The discontinuity at the precipitation point seems to be an effect which does not depend on the chain length, but mainly on the concentration. The condition at precipitation is the immediate formation of a gel which gradually contracts to form a solid phase. The gel phase consists of bound solvent along with the solute. From a point just before precipitation to when the solid starts to separate we make the assumption that almost all the water added during this interval goes to the bound phase. This would account for a minimized change in the dielectric constant. After this period, the gel would start to contract, squeezing out the bound liquid. The freeing of the water would account for the sudden jump and then leveling off of the readings. It might be added that from this point on, the readings parallel the standard binary curve.

The lack of this effect when heptane is a precipitant can also be explained by this line of reasoning. Weakly polar heptane would not be attracted to the cellulose nitrate to any extent comparable with water. The heptane precipitation would be due to a straight-forward dilution of the acetone until the polarity of the mixture could no longer disperse the chains.

Starting with the basic assumption that water will be absorbed to some degree onto the particles in solution, a mathematical interpretation of some of the data may be attempted.

Since the fundamental theoretical work on dielectric constants made use of an additive function to combine two effect[49], it would seem reasonable that the total dielectric constant could be expressed as:

$$\epsilon = \epsilon_g + \epsilon_s$$

where:

ϵ = total dielectric constant (experimental value)

ϵ_g = dielectric constant of solvated gel phase

ϵ_s = dielectric constant of free liquid phase

The experimental data for acetone-water binary mixtures, gives an expression for the dielectric constant of the liquid phase as a function of y, the amount of water present in the free liquid phase:

$$\epsilon_s = .57y + 19.4$$

If x is the amount of water present in the solvated phase, the total water present is:

$$w = x + y$$

Since w is known quantity at all times it is possible to eliminate one unknown variable:

$$y = w - x$$

$$\epsilon_s = .57(w - x) + 19.4$$

Some assumption as to how the solvated phase value can be expressed in terms of the water added must now be made. Since the change in this phase is fundamentally a process of absorption, it would seem logical to use one of the known absorption equations. A theoretical equation based on the type developed by Langmuir[23] is therefore formulated:

$$x = \frac{k_1 W}{1 + k_2 W}$$

where k_1 and k_2 are constants defined for each absorption process.

It can now be assumed that ϵ_g has some value initially and increases with the water added:

$$\epsilon_g = \frac{k_1 W}{1 + k_2 W} + C$$

with the constant C being evaluated from the initial reading of the acetone solution.

The expression for the complete dielectric reading now becomes:

$$\epsilon = \frac{k_1 W}{1 + k_2 w} + C + .57w - .57 \frac{k_1 w}{1 + k_2 w} + 19.4$$

or:

$$\epsilon = .43 \frac{k_1 w}{1 + k_2 w} + C + .57w + 19.4$$

The validity of this equation as an adequate representation of the results can be tested by evaluating the constants for a particular run from two readings and then testing the resulting general equation for the complete run.

Using the data for the 75 D.P. run:

$$C = 21.2 - 19.4 = 1.8$$

For w = 4, = 26.4

$$26.4 = .43 \frac{(4)k}{1 + (4)k_2} + (4)\ .57 + 19.4 + 1.8$$

$$\frac{k_1}{1 + 4k_2} = 1.70$$

$$k_1 = 1.70 + 6.4\ k_2 \qquad (a)$$

For w = 10, = 33.1

$$33.1 = .43 \frac{(10)k_1}{1 + 10k_2} + (10).57 + 19.4 + 1.8$$

$$\frac{k_1}{1 + (10)k_2} = 1.44$$

$$k_1 = 1.44 + 14.4\ k_2 \qquad (b)$$

Solving (a) and (b) simultaneously:

$$k_1 = 1.93$$

$$k_2 = 0.034$$

This gives a general equation:

$$\epsilon = .43 \frac{1.93w}{1 + .034w} + .57w + 21.2$$

Values for the dielectric constant are calculated from this equation, and the results compared with the experimental readings are shown in Table V.

TABLE V

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES FOR 75 D.P. DATA

Water Added	ϵ(Calc.)	ϵ(Experimental)
0 gms.	21.20	21.20
2 "	23.88	23.90
4 "	(26.40)*	26.40
6 "	28.86	28.80
8 "	30.98	30.90
10 "	(33.10)*	33.10
12 "	35.10	35.00
14 "	37.04	36.60
16 "	38.90	38.50
17 "	39.80	39.20#
24 "	45.80	44.00
26 "	47.50	44.80

* Values used to determine constants.
# Precipitation point.

From Table V it can be seen that the constants will give good agreement with experimental data over almost all the range, and especially before precipitation where the readings are most accurate. The chosen expression seems to reasonably justify its use.

The next phase of the analysis is an attempt to evaluate, at least relatively, the quantity x; the water entering the solvated phase. To satisfy the general theory of a changing solvation film composition x must increase continuously until precipitation occurs and then either remain constant or decrease slightly.

A number of functions relating x to the experimental data were picked arbitrarily, but, in most cases, impossible values for x for one or more readings were found on calculation. However plausible results were obtained by using another variation of the basic absorption equation; keeping the same constants:

$$\epsilon = \frac{1.93x + 1.8}{1 + .034x} + .57w - .57x + 19.4$$

This makes the assumption that ϵ_g varies with x as x varies with the total water added. x is then calculated for each addition of water as in the following example:

For w = 2, = 23.9

$$23.9 = \frac{1.93x + 1.8}{1 + .034x} + 1.14 - .57x + 19.4$$

$$3.36 = \frac{1.93x + 1.8}{1 + .034x} - .57x$$

$$.0194x^2 - 1.25x + 1.56 = 0$$

$$x^2 - 64.4 + 80.4 = 0$$

$$x = \frac{64.4 - \sqrt{(64.4)^2 - 321.6}}{2}$$

$$x = 1.28$$

x values for the other readings are calculated and the results shown in Table VI.

These results show that the function used will give the desired variation to the x value.

Complete calculations using the general procedure outlined have been made for the 32 D.P. and 140 D.P. runs and the results are shown in Tables VII and VIII.

Since a value for the quantity of water solvated at any point during the titration is now available, it is possible to evaluate the solvation mole ratio of water to cellulose nitrate at the precipitation point. Using the monomer unit, or fundamental mole, 3.68 grams of solute is equivalent to

$$\frac{3.68}{252} = 0.015 \text{ moles}$$

The moles of solvated water are

$$\frac{10.15}{18} = 0.564 \text{ moles}$$

The mole ratio of water to cellulose nitrate is therefore:

$$\frac{0.564}{0.015} = \frac{37.6}{1}$$

This indicates a very high degree of solvation which might be ascribed to water being present in the form of associated polymolecules.

TABLE VI

CALCULATED VALUES FOR THE AMOUNT OF WATER SOLVATED FOR 75 D.P. RUN

Water Added	ϵ	(x) Gms. of Solvated Water
0	21.2	-
2	23.9	1.28
4	26.4	2.54
6	28.8	3.85
8	30.9	5.05
10	33.1	6.48
12	35.0	7.60
14	36.6	8.45
16	38.5	9.90
17	39.2*	10.15
24	44.0	12.05
26	44.8	11.20

* Precipitation point

TABLE VII

TABULATION OF CALCULATED RESULTS

FOR 32 D.P. RUN $K_1 = 1.65$, $K_2 = .05$

Water Added	ϵ	(x) Gms. of Solvated Water
0	20.6	-
2	23.1	1.50
4	25.1	2.65
6	26.9	3.75
8	28.7	5.05
10	30.4	6.50
12	32.0	8.15
14	33.4	9.52
16	35.0	-*
18#	36.2	-*

* Equation does not give real values for x at these points.

\# Precipitation point.

TABLE VIII

TABULATION OF CALCULATED RESULTS

FOR 140 D.P. RUN $K_1 = 8.1$, $K_2 = .25$

Water Added	ϵ	Gms. of Solvated Water
0	24.0	-
2	29.2	0.8
4	33.7	1.75
6	36.4	2.80
8	38.4	2.90
10	40.2	3.20
12	41.3	3.15
14*	42.7	3.30

* Precipitation point.

CONCLUSIONS

1. The polar nature of the solvated chains undergoes a marked change on the addition of water to a solution of cellulose nitrate in acetone. It therefore seems highly probable that a large portion of the water is bound by solvation to the cellulose nitrate.
2. At precipitation some of the water is released and returns to the free liquid phase.
3. The mechanism of precipitation with heptane seems to be different from that which occurs with water.
4. Dielectric relaxation, for the case of chain polymers in solution, is critically dependent on the length of the chains.

SUGGESTIONS FOR FUTURE WORK

1. The use of low D.P. fractions should be extended as far as possible, and the quality of the samples used should be controlled.
2. Heptane as a precipitant should be investigated thoroughly.
3. The use of other solvents and precipitants may yield essential correlating data and should increase the worth of the over-all investigation.
4. The study might also be extended to include other cellulose derivatives.
5. Some modification of the experimental procedure and apparatus, which would permit isolation and measurement of one of the phases in solution, would surely be valuable, and is worth special consideration.

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