

**CORRELATION OF THE DISTRIBUTION CURVE WITH THE
DISPERSION CURVE OF CELLULOSE NITRATE**

by

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THIS THESIS IS AFFECTIONATELY DEDICATED TO MY PARENTS

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INTRODUCTION

INTRODUCTION

A polymer consists of large molecules of varying molecular sizes. The dimensions of the polymer are dependent upon the number of monomer units and these may vary from a few units to many depending upon the conditions for the polymer formation.

Cellulose nitrate, which has been proven to be of a straight chain molecular structure, is heterogeneous with respect to chain length and thus the amounts of the different chain lengths may vary from one sample to another. Research has shown that in the determination of the mechanical properties of cellulose derivatives, the chain length distribution is a very important factor.

The best method to date for determining this distribution is fractional precipitation, however several weeks are required to perform this determination and the time element is not desirable. Also the individual fractions obtained from fractional precipitation contain several chain lengths which are reported as an average value and introduce an appreciable error.

In an earlier work by Testerman and Scherer (17) an attempt was made to determine the chain length distribution from dielectric dispersion measurements. Their

results were later shown to be invalid by Testerman and Pauley (15), due to the presence of a copper cellulose nitrate complex that formed between the cellulose nitrate and the copper electrodes.

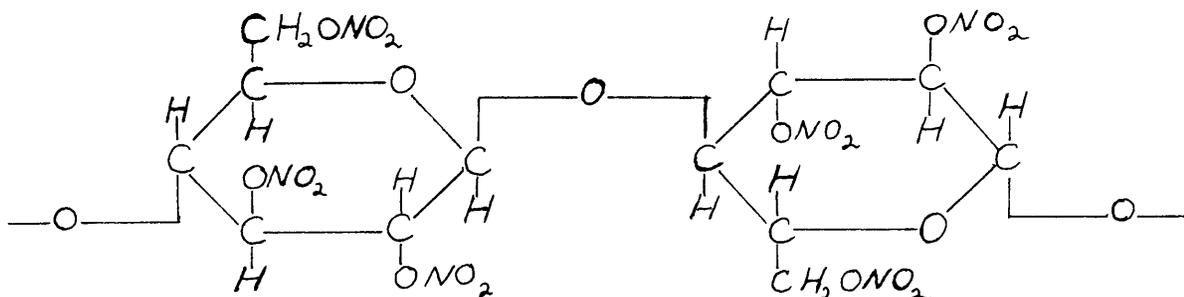
It is the purpose of the following research to attempt to determine the chain length distribution of cellulose nitrate from dielectric dispersion measurements using nickel electrodes. The dispersion curve will be compared to the distribution curve obtained from fractional precipitation to see if a relation between the two can be made.

LITERATURE REVIEW

LITERATURE REVIEW

Structure

The accepted structure of cellulose is that of a linear polymer consisting of anhydroglucose units linked together through the 1 and 4 carbon atoms with β -glucosidic linkages (13,14). In cellulose nitrate the hydroxyl groups on each unit are replaced by nitro groups with the maximum degree of substitution being three.



An examination of molecular models constructed with corrected atomic volumes and atomic distances reveals pronounced steric hindrance around the oxygen bridges, and thus a very limited amount of rotation and flexibility of the units relative to one another. The result of this restricted rotation is a relatively stiff chain which is characteristic of cellulose. The low molecular weight molecules tend to possess a fairly rigid, rod-shaped structure, while high molecular weight molecules assume

a coiled shape structure (2). The reason for this is that the small amount of rotation possible is magnified over a great distance.

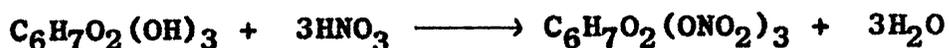
Preparation

Cellulose nitrate can be prepared by the action of nitric acid on cotton linters or wood pulp in the presence of a dehydrating agent. For each hydroxyl group that is esterified one molecule of water is liberated. The reaction is carried out at a temperature below 40°C to decrease the amount of degradation. However some degradation occurs through hydrolysis and oxidation in the acid medium. These degradation products must be removed by washing in order to stabilize the cellulose nitrate.

The usual dehydrating agents are strong mineral acids but under certain conditions acetic acid and acetic anhydride (22) are satisfactory. The most common dehydrating agent is sulfuric acid. The sulfuric acid serves a dual function in the preparation of cellulose nitrate. It not only removes water by forming a hydrate (4) but also acts as a swelling agent.

The degree of nitration is dependent upon the concentrations of nitric and sulfuric acids in relation to each other and to a lesser degree on the ratio of the acid mixture to cellulose. Lunge and Belice (8) showed

that the presence of a little water also exerts a great influence on the degree of nitration. The trinitrate, which is the completely substituted product, has a nitrogen content of 14.14% according to the reaction:



The preparation of the trinitrate has been difficult. Two reasons have been suggested to explain why this is so. The first is that an equilibrium exists in the esterification reaction and the second that the sulfuric acid also reacts to give a cellulose sulfate which is removed during the stabilization process.

Fractional Precipitation

Fractional precipitation of high polymers is based on the different solubilities of the many chain lengths in a polymer sample. It depends on the greater solubility of the low-molecular-weight species in a given solvent and also on the fact that the solvent power of the binary liquid mixture, composed of solvent and non-solvent, depends on the proportion of the two liquid constituents. The addition of a non-solvent to a polymer solution produces two phases at equilibrium when enough non-solvent is present to cause precipitation of the high-molecular-weight species. The more soluble (low-molecular-weight)

polymer will be in the upper phase while the lower phase (precipitated phase) is either a swollen gel or highly viscous liquid containing the high molecular weight species.

The two principal methods of precipitation are the following: (1) the addition of a precipitant under isothermal conditions and (2) the addition of the precipitant at one temperature and the precipitation at a lower temperature. It is possible to use a combination of these methods.

The choice of solvent and precipitant is very important in a fractionation. The relative solvent and precipitating powers can be determined by titrating a solution of the polymer in the solvent with the precipitant, using as the end point, the sudden appearance of turbidity. The larger the amount of precipitant required for each solvent in a series, the greater is the solvent power of that solvent. If a series of precipitants is used with a constant solvent, the precipitating power is less when a large amount of precipitant is required.

In the fractional precipitation method enough precipitant is added to cause separation into two phases but not enough to cause complete precipitation. The phases are then separated by decantation or centrifugation followed by decantation. Then more precipitant is added to the

supernatant liquid until two phases again appear and the process is repeated until all of the polymer is fractionated.

The other method, fractional precipitation by cooling, is based on the principle that the precipitation point of a polymer-solvent-precipitant solution is dependent upon the temperature. This method is somewhat analogous to fractional crystallization except that the precipitates are not crystalline. In the following work a combination of the two methods was used.

Viscosity

A solution of a polymer of high molecular weight has a viscosity considerably greater than that of the pure solvent, even when the concentration is relatively small. In 1930, Staudinger (21) suggested that the relative magnitude of this increase in viscosity could be quantitatively correlated with the molecular weight of the polymeric solute. This may be expressed by the following equation:

$$\eta_{sp}/c = K_m M$$

where η_{sp} is the specific viscosity, c is the concentration, M is the molecular weight, and K_m is a constant. Staudinger founded this empirical equation mainly on cryoscopic and end group determinations with low molecular weight polymers.

The uncertainty in extrapolating these results to high molecular weight polymers caused the method to be received with considerable doubt. The constant K_m was determined by obtaining the molecular weight of the polymer by the osmotic pressure method or ultracentrifuge method and determining the specific viscosity and substituting in Staudinger's equation.

Staudinger's viscosity rule has been criticized (1,6,11,12,19) on the basis of two assumptions that he made. One is that solutions of cellulose and cellulose derivatives contain these materials dispersed into single molecules. The other is that the chain molecules represent stretched-out rod-shaped units which retain their shape in solution. However the method is of practical value in determining a relative molecular weight.

Kraemer (7) in 1938 developed a more reliable method for calculating molecular weights from viscosity measurements. He expressed viscosities as intrinsic viscosities by extrapolating to zero concentration:

$$[\eta] = \left(\frac{\eta - \eta_0}{\eta_0 c} \right)_{c \rightarrow 0} = \left(\frac{\eta_{sp}}{c} \right)_{c \rightarrow 0}$$

Here η is the viscosity of the solution, η_0 the viscosity of the solvent, and c is the concentration in grams of solute per 100 milliliters of solution.

Further experimental work showed that this equation was of limited validity. Mark and Houwink proposed a more general empirical relationship:

$$[\eta] = K M^\alpha$$

Here K and α are constants for a given polymer, solvent and temperature (9,5).

Dielectric Dispersion

If two oppositely charged plates attract each other with a certain force, the effect of the material constituting the medium is measured by the dielectric constant (ϵ). The dielectric constant is determined by measuring the capacitance of a condenser (C) with the particular medium between the plates and then repeating with air (C_0).

$$\epsilon = \frac{C}{C_0}$$

Debye's interpretation of the dielectric constant is given by the equation which shows the relationship between the dipole moment and the dielectric constant (20):

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \alpha_0 + \frac{4\pi}{3} N \left(\frac{\mu^2}{3kT} \right)$$

μ is the permanent dipole moment, P is the molar polarization, N is Avogadro's number, M is the molecular weight, d is the density, k is the Boltzmann constant, T is the

absolute temperature, and α_0 is the molecular polarizability.

Dielectric dispersion occurs when the frequency is of such a magnitude that there is an observable lag in the attainment of equilibrium between the dielectric and the externally applied field. Drude (3) was the first to observe such dispersion in liquids.

In the absence of an externally applied field, the orientation of a polar molecule is unpredictable. If such molecules were placed in a low frequency field, then during each cycle the molecules will have time to align themselves with the field. During each reversal of the cycle, the molecules will revert gradually to the random orientation. The time required for the molecules to re-establish a random distribution is the relaxation time (τ). In such a case, the dielectric constant will be large.

If the frequency is increased, a point is reached where the orientation begins to lag behind the field reversals, the lag being greatest when the period of the frequency is of the same order as the relaxation time. This lag produces a decrease in molecular orientation, and the dielectric constant decreases. Thus at high frequencies the Debye equation does not hold and has been changed to:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left[\alpha_0 + \frac{u^2}{3KT} \left(\frac{1}{1+i\omega\tau} \right) \right]$$

where (τ) is the relaxation time and (ω) is equal to 2π times the frequency in cycles per second.

Literature on Dielectric Dispersion of Cellulose Nitrate

Scherer and Testerman (17) found that a solution of cellulose nitrate in acetone gives dielectric dispersion in two separate and distinct regions in the frequency range 100 to 500 KC. They were able to show that a relationship exists between the dielectric dispersion and the degree of polymerization. For different average degrees of polymerization, the dispersion regions were positioned in approximately the same frequency range, but changes in the degree of polymerization were accompanied by corresponding changes in the dispersion curves. They transformed their dispersion curves which were in excellent agreement with the distribution curves obtained by fractionation of the same sample.

Later, Testerman and Pauley (15) showed that the material they were measuring was not cellulose nitrate but a copper cellulose nitrate complex formed by a reaction of the cellulose nitrate with the copper electrodes.

EXPERIMENTAL

EXPERIMENTAL

Materials:

The cellulose nitrate was Lot 4182, Type RS 60-80 seconds, obtained from Hercules Powder Company, Parlin, New Jersey.

The acetone was chemically pure grade and was obtained from Commercial Solvents Corporation, Newark, New Jersey.

The ethyl acetate was chemically pure grade obtained from Commercial Solvents Corporation, Newark, New Jersey.

The n-butyl acetate was reagent grade obtained from Fisher Scientific Company, Washington, D. C. Its dielectric constant was 5.14 at 19°C.

Equipment:

The apparatus consisted of the following components:

1. variable oscillator
2. frequency counter
3. capacitance bridge
4. variable precision capacitor
5. null detector with unit power supply
6. two amplifiers
7. parallel resistance board
8. capacitance cell

The oscillator had a frequency range of 50 cycles to 5 megacycles and was manufactured by General Radio Company (type 700-A).

The frequency counter was manufactured by the Hewlett-Packard Company (type 524-A). It can be used to count frequencies from 10 cycles per second to 10 megacycles per second with an accuracy of 0.03%.

The capacitance bridge was manufactured by General Radio Company (type 722-D). It is an instrument of high stability and high precision of setting and has an accuracy of $\pm 2\%$.

The null detector was manufactured by General Radio Company (type 1212-A) and was designed primarily as a balance indicator in AC bridge measurements.

The amplifiers were manufactured by Hermon Hoshmer Scott, Inc. (type 140-A). The amplifiers were used to amplify the bridge signal.

The resistance board was built by W. C. Lawrence and had a range of 1 ohm to 11,111 ohms with an arrangement for increasing this range by connecting resistors to it in series.

The filters were used to eliminate any interference caused by oscillations in the bridge signal.

The capacitance cell was manufactured by J. C. Balsbaugh and consisted of concentric nickel cylinders. The cell was a 100 micromicrofarad cell (#II).

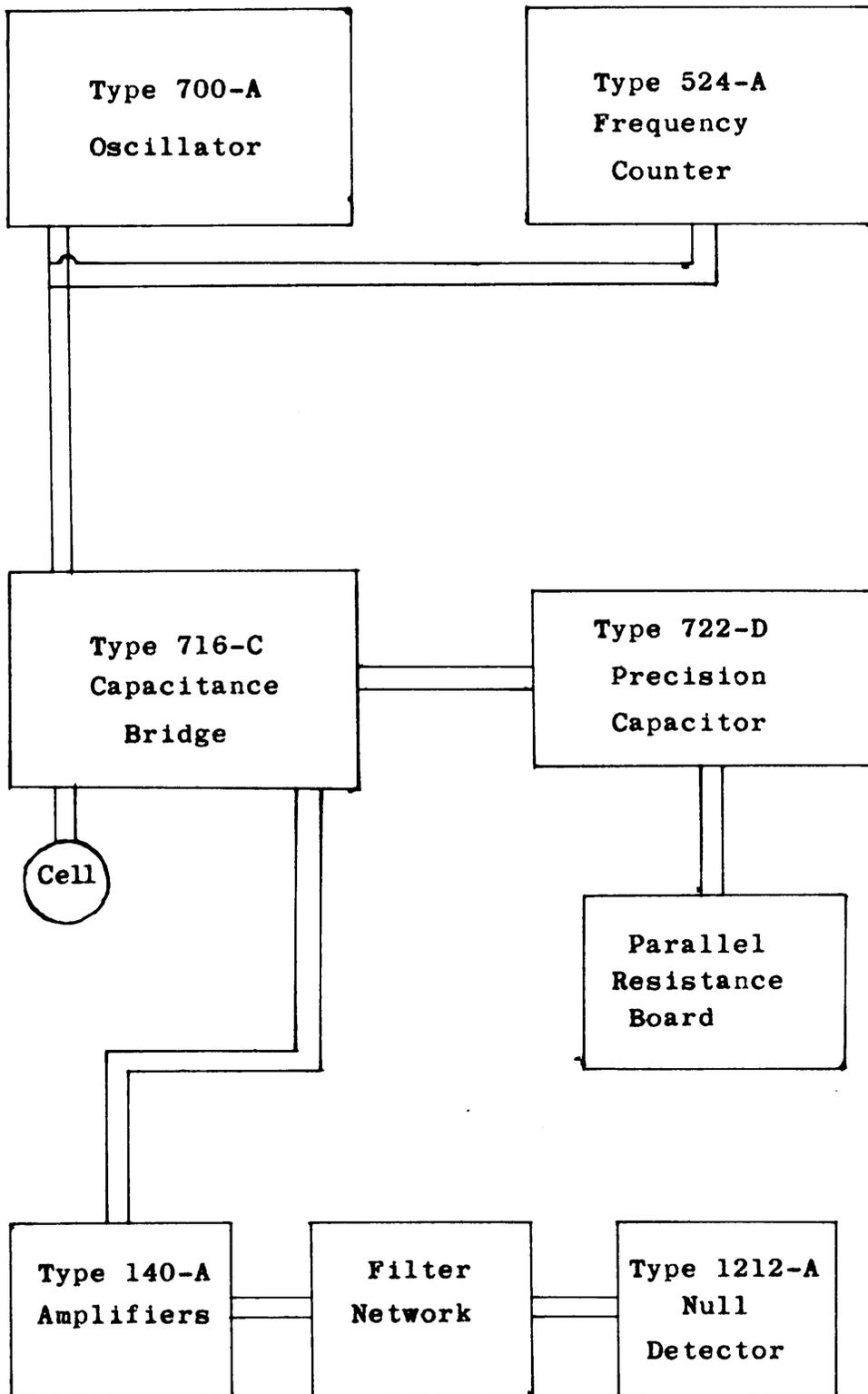
A block diagram of the apparatus appears in Figure 1.

Fractional Precipitation

The procedure for the fractional precipitation was based on unpublished work by Dr. Levi and the Master's Thesis of Rouse (16) of this department. A 200 gram sample of cellulose nitrate was dissolved in a mixture of acetone-ethyl acetate (81%:19%). After the cellulose nitrate had completely dissolved in the solvent mixture, a non-solvent mixture of acetone-water (40%:60%) was added with swirling until a slight cloudiness formed. The solution was then cooled to 15°C for two days. The supernatant liquid was decanted and the precipitate dried. The procedure was repeated after the supernatant liquid had returned to room temperature. Six fractions were obtained for a total of 192 grams. These six fractions were refractionated using the same procedure except this time only enough non-solvent was added to reach the point where precipitation would occur when the solution was cooled. This would provide for a finer separation. Fourteen fractions were obtained from the original six for a total weight of 104.6 grams.

Determination of Distribution Curve from Viscosity

The degree of polymerization was determined for each fraction from viscosity measurements in a Ubbelohde

**FIGURE 1**

Block Diagram of Apparatus

dilution viscometer. The viscosity was determined for several concentrations and the specific viscosities calculated using:

$$\frac{\eta - \eta_0}{\eta_0 c} = \frac{\eta_{sp}}{c}$$

where η is the measured viscosity at concentration c and η_0 is the viscosity of acetone.

The intrinsic viscosity was obtained by plotting η_{sp}/c against c and extrapolating to zero concentration.

From Staudinger's revised equation the degree of polymerization (P) was calculated. The constants K and α were obtained from the unpublished work of Dr. Levi.

$$[\eta] = K P^\alpha$$

The following is a sample calculation:

$$\begin{aligned} [\eta] &= 3.65 \\ K &= 7 \times 10^{-4} \\ \alpha &= 1.0 \end{aligned} \quad P = \frac{3.65}{7 \times 10^{-4}} = 522$$

The results of the viscosity measurements are tabulated in Table 1.

Table 2 shows the weights and the degree of polymerization for each fraction and the intrinsic viscosity and accumulative percent for the same fractions.

The integral distribution curve, (accumulative percent versus degree of polymerization) is plotted in Figure 2.

TABLE 1Viscosity and Degree of Polymerization for
Fractions Obtained from Fractional Precipitation

Fraction	Concentration (gm/100 ml)	η sp/C	$[\eta]$	DP
1a	.2502	5.84	3.65	534
	.2000	5.45		
	.1330	4.80		
	.1251	4.69		
	.0834	4.39		
1b	.2572	2.80	1.87	274
	.2106	2.70		
	.1716	2.47		
	.1404	2.46		
	.1286	2.34		
	.1053	2.32		
1c	.2460	2.06	1.51	221
	.1924	2.05		
	.1230	1.77		
	.0615	1.64		
	.0481	1.66		
1d	.2492	3.01	2.30	336
	.1953	2.83		
	.1246	2.64		
	.0830	2.54		
2a	.2488	3.66	2.70	386
	.1244	3.15		
	.0829	3.02		
2b	.2478	2.31	1.85	264
	.2416	2.26		
	.1239	2.07		
	.0826	2.01		
2c	.2460	1.65	1.38	202
	.1960	1.65		
	.1230	1.54		
	.0980	1.49		
	.0490	1.32		

TABLE 1

Viscosity and Degree of Polymerization for
Fractions Obtained from Fractional Precipitation

(Continued)

Fraction	Concentration (gm/100 ml)	η sp/C	[η]	DP
2d	.2548	2.04	1.49	218
	.1976	1.85		
	.1274	1.79		
	.0988	1.64		
	.0494	1.55		
3a	.2225	1.49	1.26	184
	.1780	1.47		
	.1112	1.41		
	.0741	1.36		
3b	.2547	1.16	1.00	146
	.2241	1.14		
	.1273	1.11		
	.1120	1.08		
4a	.2506	1.01	0.92	135
	.1253	0.97		
	.1196	1.00		
	.0835	0.94		
5a	.2474	1.33	1.20	175
	.1237	1.26		
	.0824	1.24		
5b	.2474	0.85	0.77	113
	.1237	0.79		
	.0824	0.77		
6a	.2488	0.85	0.75	110
	.1244	0.80		
	.0829	0.79		
	.0459	0.73		

TABLE 2

Final Results of Fractional Precipitation
and Viscosity Measurements

<u>Fraction</u>	<u>Weight</u>	<u>$[\eta]$</u>	<u>$1/[\eta]$</u>	<u>Acc. %</u>	<u>(100-Acc. %)</u>	<u>Dp</u>
1	11.5	3.65	.275	99.9	0.1	522
2	17.6	2.70	.370	88.9	11.1	386
3	7.0	2.30	.435	72.1	27.9	329
4	13.2	1.86	.537	65.4	34.6	265
5	15.6	1.50	.666	52.8	47.2	214
6	2.5	1.38	.725	37.7	62.3	197
7	24.2	1.23	.813	35.3	64.7	176
8	2.5	1.00	1.000	12.2	87.8	143
9	3.8	0.92	1.088	9.8	90.2	131
10	6.5	0.75	1.335	6.2	93.8	107

Integral Distribution Curve of Cellulose Nitrate

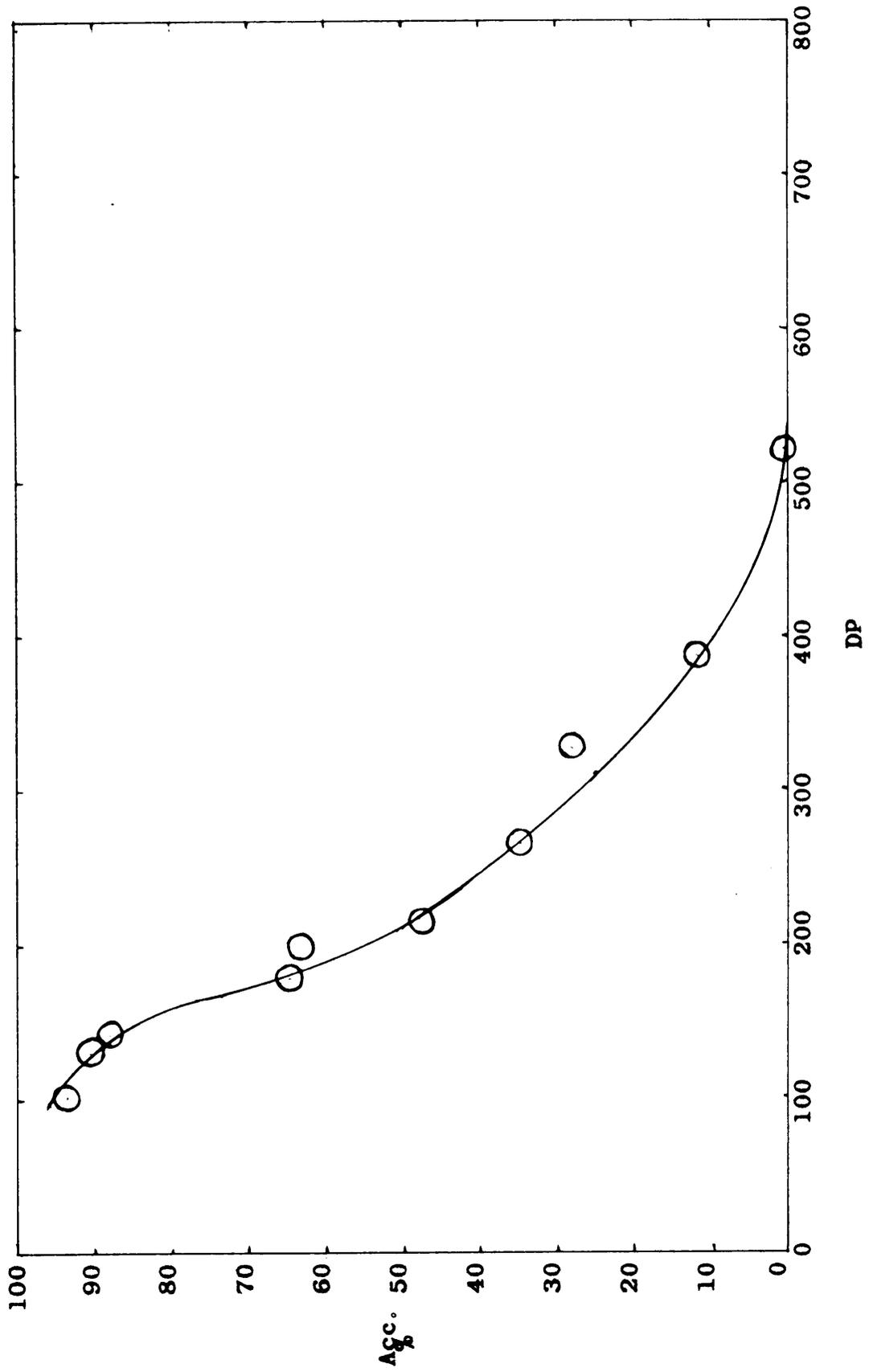


FIGURE 2

Dielectric Dispersion

Capacitance measurements were made over the frequency range 400 cycles to 400 KC using the parallel resistance method. n-Butyl acetate was used as the solvent. In the parallel resistance method, the cell containing the solution is placed in one arm of the bridge and a balancing capacitor and parallel resistance board in the other arm.

Two runs with a 0.5% solution of cellulose nitrate in n-butyl acetate were made over the above frequency range. The data obtained is given in Table 3. At the lower frequencies a small amount of polarization was observed. This polarization made it difficult to obtain C_0 . In order to find C_0 , the capacity C was plotted against $10^2/w^2$ and extrapolated to zero. The graph in Figure 3 shows how this is done, the data corresponds to the data for run 1 in Table 3.

In order to find the effect of concentration on the capacity, a 0.3% solution was used for three runs and the data is given in Table 4.

The dispersion may be obtained from the following identity:

$$D = \frac{C - C_{\infty}}{C_0 - C_{\infty}} = \frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}}$$

TABLE 3

Capacitance Measurements and % Dispersion
of Cellulose Nitrate in n-Butyl Acetate
Parallel Resistance Method

0.5% Solution 100 uuf. Cell

Frequency (cps)	Capacitance		Dispersion	
	Run 1	Run 2	Run 1	Run 2
700	599.5	599.0	100	100
800	599.3	598.9	96	98
900	599.2	598.7	95	94
1000	599.1	598.6	93	92
2000	598.4	597.9	80	79
3000	598.0	597.5	72	72
4000	597.7	597.2	67	66
6000	597.2	596.8	57	58
8000	596.8	596.5	50	53
10000	596.6	596.2	46	47
20000	595.8	595.5	31	34
30000	595.4	595.0	24	25
80000	594.8	594.4	13	13
160000	594.5	594.1	7	7
200000	594.3	593.9	4	4
300000	594.1	593.7	0	0
400000	594.1	593.7	0	0

Cellulose Nitrate in n-Butyl Acetate
Determination of C_0

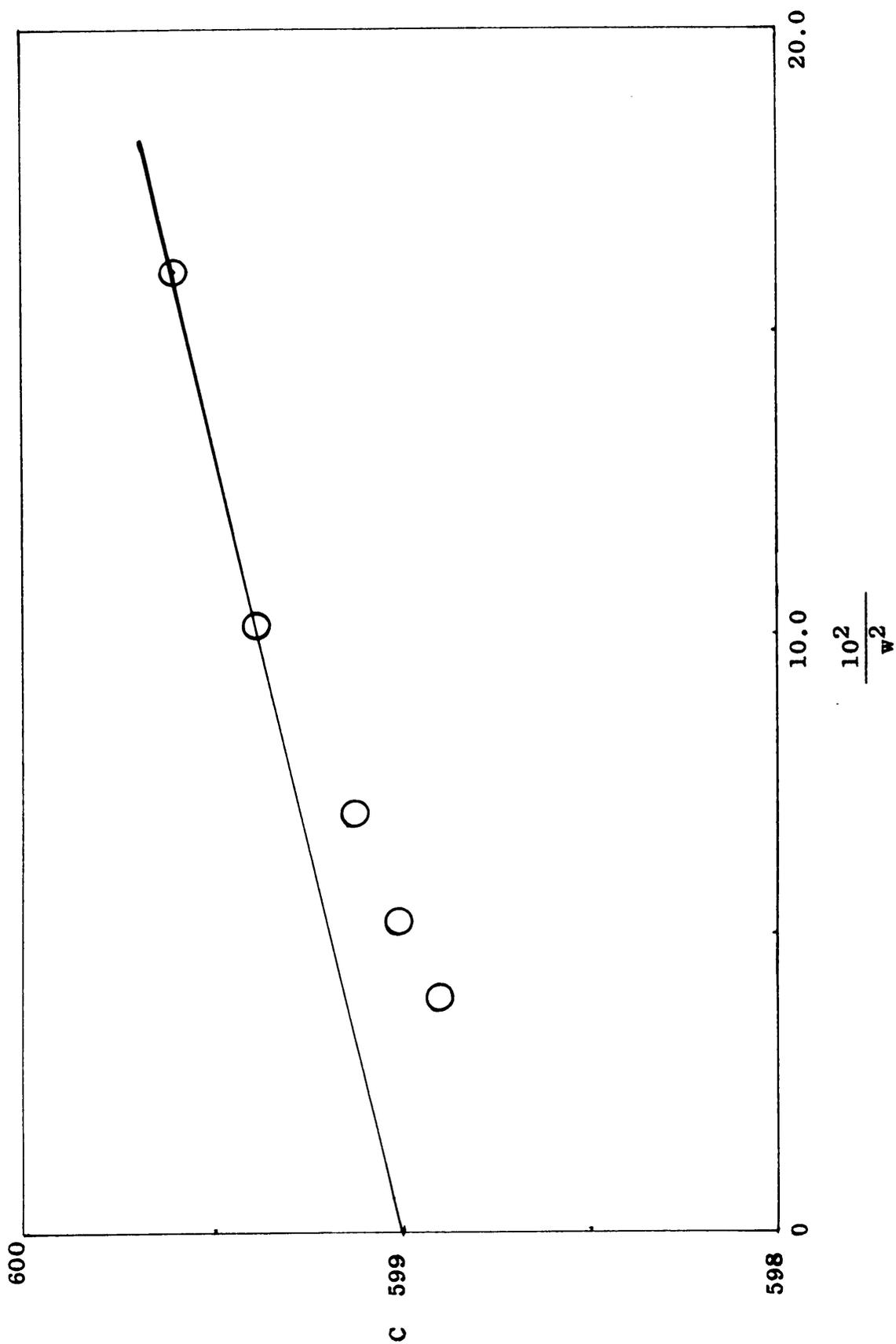


FIGURE 3

TABLE 4

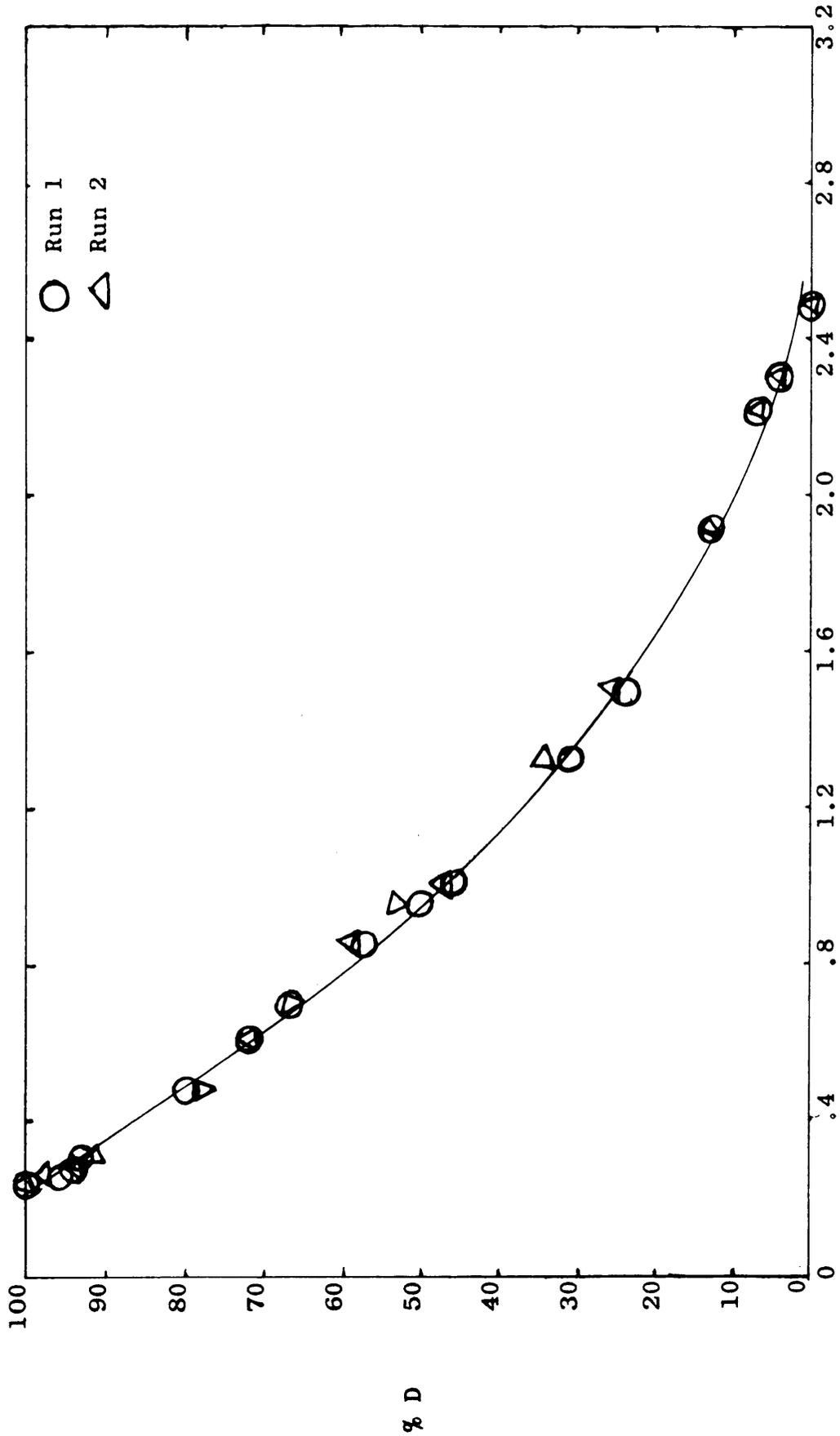
Capacitance Measurements and % Dispersion
of Cellulose Nitrate in n-Butyl Acetate
Parallel Resistance Method

0.3% Solution 100 uuf. Cell

Frequency (cps)	Capacitance		Dispersion	
	Run 1	Run 2	Run 1	Run 2
700	598.7	-----	100	---
800	598.6	600.2	98	100
900	598.4	600.0	95	97
1000	598.3	599.8	93	95
2000	597.5	598.9	78	80
3000	597.1	598.4	70	72
4000	596.7	598.0	63	66
6000	596.2	597.5	54	58
8000	595.9	597.1	48	52
10000	595.6	596.8	43	48
20000	594.8	595.9	28	34
30000	594.3	595.4	19	26
80000	593.8	594.9	9	18
160000	593.4	594.4	2	10
200000	593.3	594.2	0	7
300000	593.3	593.8	0	1
400000	593.3	593.7	0	0

The dispersions for the concentrations 0.5% and 0.3% are given in Tables 3 and 4 respectively. They are plotted on the graphs in Figures 4 and 5 respectively. The critical frequency, which is found at the point of 50% dispersion (18), was found to be about 8 KC for both concentrations. Thus the concentration may be said to have no appreciable effect on the dispersion.

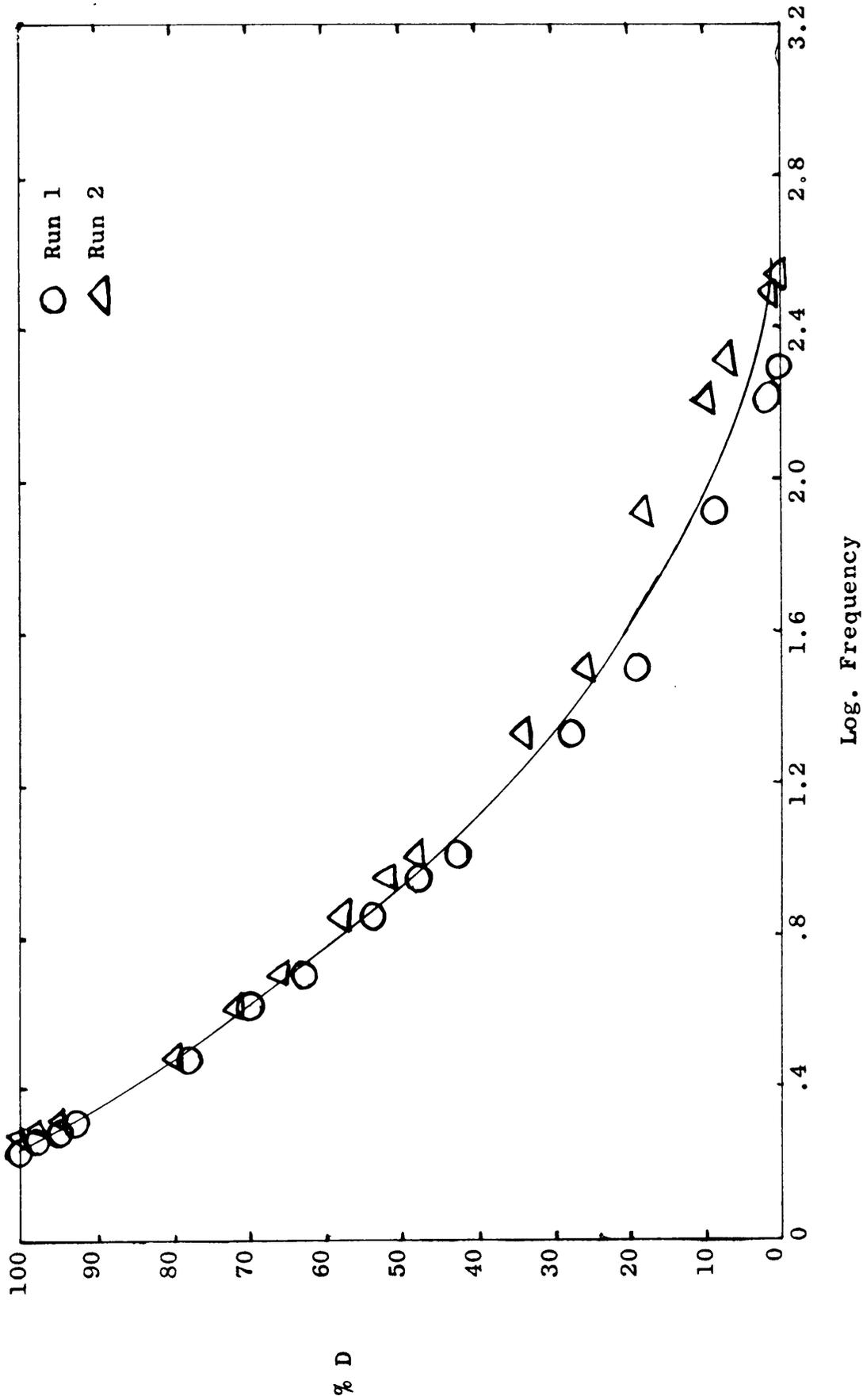
Cellulose Nitrate in n-Butyl Acetate
0.5% Solution



Log. Frequency

FIGURE 4

Cellulose Nitrate in n-Butyl Acetate
0.3% Solution



Log. Frequency

FIGURE 5

DISCUSSION

DISCUSSION

Discussion of Results

Since the values for the intrinsic viscosities are numerically similar to the logarithm of the frequency, they were used instead of the degree of polymerization to plot the distribution curve. The distribution and dispersion curves are compared in Figure 6 but the high DP material on the distribution curve appears at the opposite end of the graph from the high DP material on the dispersion curve. To correct for this the reciprocal of the intrinsic viscosity was used. Figure 7 shows a comparison of the two curves using the reciprocal of the intrinsic. The two curves parallel each other except for the lower part where the difference is not significant.

In order to convert the dispersion curve into the distribution curve, the following relationship was derived. The addition of the constant 0.32 to the log of the frequency at a specific % dispersion, shifts the point on or near the distribution curve. This new value of the log frequency may be converted to the intrinsic viscosity by the following relationship:

$$[\eta] = \frac{2}{\log \text{freq.} + 0.32}$$

Comparison of Distribution Curve and
Dispersion Curve of Cellulose Nitrate

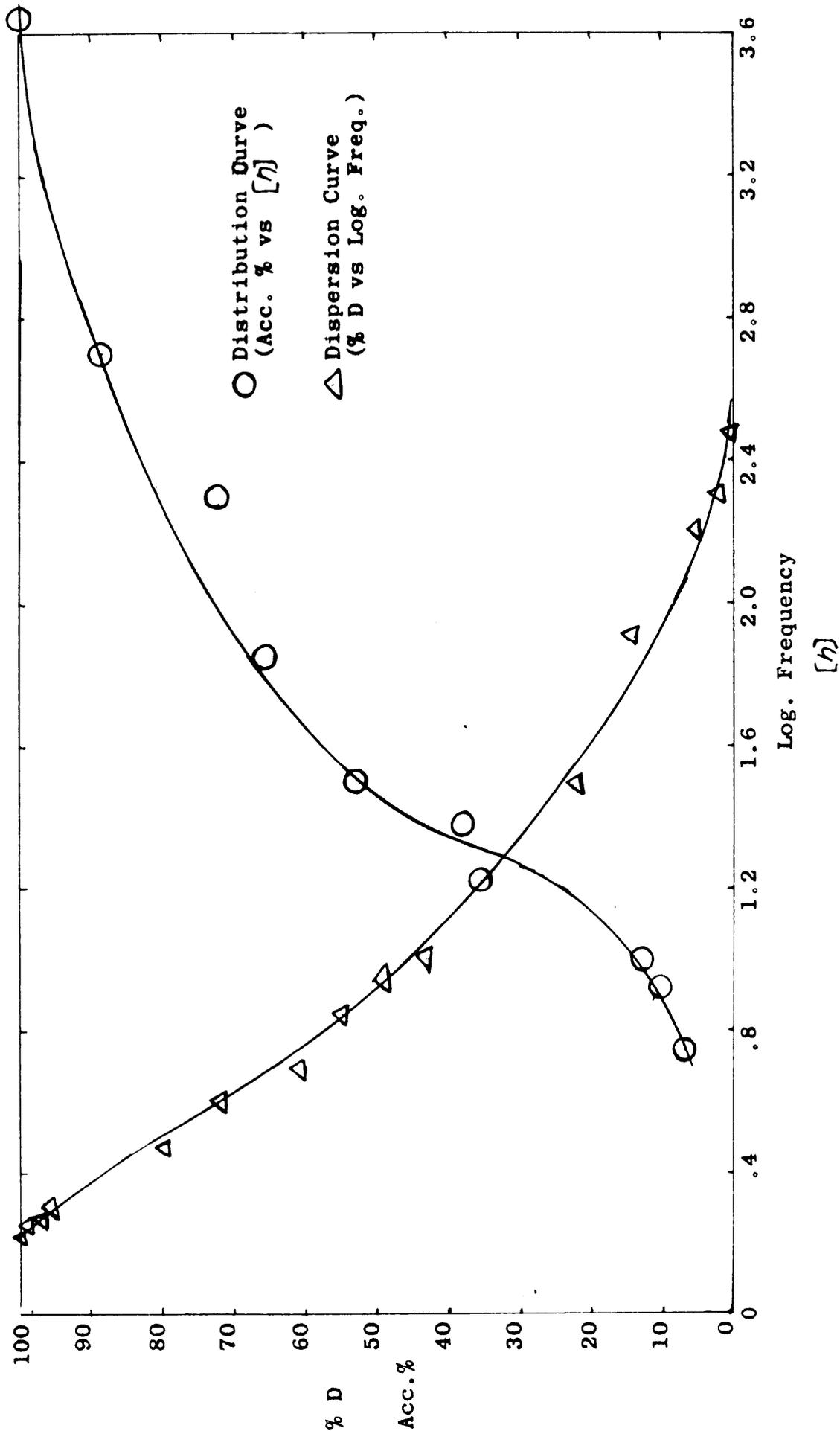
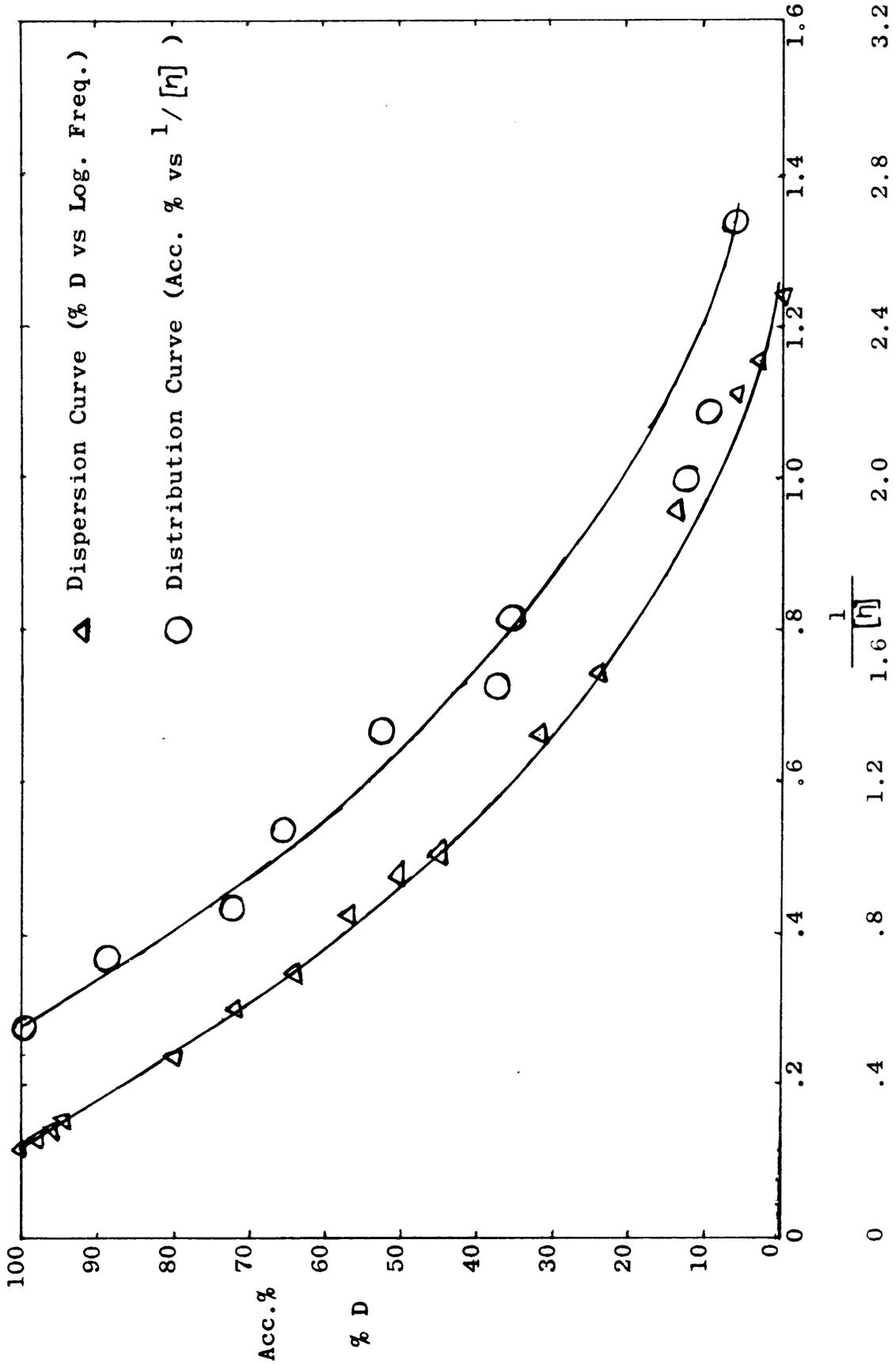


FIGURE 6

Comparison of Distribution Curve and
Dispersion Curve of Cellulose Nitrate



Log. Frequency
FIGURE 7

where 2 is used to convert the log frequency to the reciprocal of the intrinsic viscosity.

The values of DP obtained from fractional precipitation are only average values which are accurate to within $\pm 10\%$. If all the points on the dispersion curve were converted to the intrinsic viscosity they would fall within $\pm 10\%$ of the distribution curve. The dispersion and the distribution are dependent upon the contribution of the individual chains. Thus it is possible to determine the distribution curve of cellulose nitrate from dispersion measurements with reasonable accuracy over most of the distribution curve.

CONCLUSION

CONCLUSION

1. The dielectric dispersion curve of cellulose nitrate may be obtained over a low frequency range in n-butyl acetate. The parallel resistance method is used for the capacitance measurements in a nickel cell.
2. Comparison of the distribution curve and the dispersion curve shows a distinct similarity between the two curves.
3. A relationship of the log frequency to intrinsic viscosity has been derived and appears to be acceptable within $\pm 10\%$ of the values obtained from fractional precipitation. Thus the distribution curve of cellulose nitrate may be determined from the dielectric dispersion curve.

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ABSTRACT

The distribution and dispersion curves of cellulose nitrate were determined in an attempt to find a correlation between the two curves. The distribution curve was obtained by the fractional precipitation method and viscosity measurements. The dispersion curve was obtained by capacity measurements in n-butyl acetate over the frequency range 400 cycles to 400 kilocycles using the parallel resistance method.

A definite relationship of the distribution and dispersion curves does exist. An equation for converting the dispersion curve to the distribution curve was derived and was accurate over most of the distribution curve with a small error at the low degrees of polymerization.